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Correlations between soil geochemical properties and Fe(III) reduction suggest microbial reducibility of iron in different soils from Southern China

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ABSTRACT

Fe(II) species are a group of active compounds during the soil geochemical processes. Various iron compounds show the different reducibility, solubility and extractability in soil, leading to the greatly different contribution of the iron compounds to Fe(II) concentrations. Therefore, it is very important to study the correlation of the total reducibility of iron and the soil geochemical properties in different soils for evaluating the activities of geochemical reactions. In this study, the Fe(III) reducibilities were investigated in 23 iron-rich soils with the different geochemical properties from Southern China. The results showed that the microbial reducibilities of Fe(III) in different soils with the same iron-reducing bacteria of *Shewanella decolorationis* S12 varied greatly. The soils derived from the same parent material had the similar microbial iron reduction rates. Furthermore, the soil Fe(III) reducibilities did not correlate well with any of the iron species in the soils except for Fe_2O_3. However, the soil weathering degree was found to be the most important factor in the microbial reducibilities of soil iron. All the weathering indices of studied soils were linearly correlated with Fe(III) reduction rate constants. The results illustrated the unique importance of soil geochemical properties on soil Fe(III) reduction susceptibilities and helped define the soil types to exhibit similar degrees of Fe(III) reduction under controlled lab conditions. In conclusion, the geochemical property of soil weathering degree was conducive to identify the iron reducibility and could become a powerful tool for characterizing the iron reducibilities in soils.

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1. Introduction

Soil Fe(II) species, mostly produced from iron minerals through microbial iron reduction, are highly active in soil geochemical processes and impact greatly on many prevailing soil reactions. For example, nitrate is easy to be reduced to ammonium with Fe(II) under the microbial actions of nitrate-dependent iron(II) oxidizers, providing more nitrogen fertilizer for plant growth (Klueglein and Kappler, 2013). Fe(II) species, especially those adsorbed or structured on/in soil minerals, have been widely recognized as the active reducer for the reductive degradation of soil pollutants (Li et al., 2008a; Neumann et al., 2008). Fe(II) are also reported as the good activators for acting other soil reagents, such as sulfur species, to produce highly reactive free radicals with high oxidative potential (Liu et al., 2012). In addition, soil Fe(II) species can be mass transported from the continents into the oceans to fertilize the ocean with Fe(II) and enhance the productivity of ocean ecosystems (Denman, 2008; Sarmiento et al., 2010). Therefore, microbial Fe(III) reduction is the key step in the iron cycle and produced Fe(II) species in soils are critical for stimulating the soil geochemical reactions (Agrawal et al., 2009; Hansel et al., 2004; Li et al., 2008b).

Since Fe(II) species are important for the prevailing reactions in soils, they should be considered when applied in pertinent soil tillage and management activities on the target soils (Inda et al., 2013). For example, nitrogen fertilizers are relatively sufficient and they are not the main supplemented fertilizer during the farming processes in the soils with high contents of Fe(II) species (Tang et al., 1990). Furthermore, the soils with high contents of Fe(II) species can result in quick degradation of organochlorine pesticides (Chen et al., 2013), which are considered for the production of “green food”. In addition, the soil pollutants of polycyclic aromatic hydrocarbons are degraded more quickly in the soils with relatively lower contents of Fe(II) species (Karthikeyan and Bhandari, 2001). As a result, it is very important to determine the different reducibilities of iron in a target soil for agricultural activities.

Many previous works have tried to explore the soil factors that affect the reducibilities of soil iron. The pool of reducible Fe(III) in soil comprises various iron compounds with different degrees of reducibility (Van Bodegom et al., 2003). Amorphous Fe(III) oxides, such as ferrihydrite, are partly reducible and are presumably the dominant components of reducible Fe(III) (Lovley, 1991), whereas crystalline Fe(III) oxides, such as magnetite and goethite, are much less reducible (Blodau and Gatzek, 2006; Lovley and Phillips, 1988). Structural Fe(III) in clay minerals such as smectite can also be reduced to Fe(II) by bacteria activities (Kostka et al., 1996; Stucki and Kostka, 2006). In addition, Fe(III) reduction in soils is a multi-factor process (Van Bodegom et al., 2003). Soil mineral types, microbiological and chemical factors had important effects on the microbial Fe(III) reduction processes (Blodau and Gatzek, 2006; Favre et al., 2002; Roden and Zachara, 1996; Sánchez-Alcalá et al., 2011). However, most previous geochemical studies solely focused on the soil Fe(III) reduction processes. The different reducibilities between different types of soils with various geochemical properties have been scarcely investigated. Therefore, it's important to elucidate the key soil geochemical factors influencing the reducibilities of iron in soils.

The soil geochemical properties are important parameters of soil development during geological periods. Many basic soil properties, such as mineral composition, molecular water content, and particle size distribution, are related to the soil weathering degree (Rahardjo et al., 2004). In addition, weathering of rocks and minerals results in soil formation and is proposed to act as the integrated geochemical property of soils (Clayton et al., 1979; Norra et al., 2008). Weathering in tropical and sub-tropical areas determines the secondary minerals and thus has a crucial effect on the chemical composition of the soil in these areas. For example, the amount of Fe(III) and H_2O^+ (structural water) increases with increasing intensity of weathering because of the oxidation of clay minerals in soils of higher weathering degree (Guan et al., 2001). Higher degrees of weathering reportedly induce higher soil cation exchange capacities (CECs) and base saturation (Abayneh et al., 2006), and similar degrees of weathering can result in similar pH_0 values even though the soil was developed from different parent materials (Anda et al., 2008). Considering that the extent of weathering is closely associated with soil properties, which in turn are important factors in Fe(III) reduction, the degree of soil weathering is likely to have an important relationship with the iron reducibilities of soil Fe(III).

Therefore, the gap between iron reducibilities and soil geochemical properties is filled in the present study. The same single kind of microbial iron-reducing bacterium, *Shewanella decolorationis* S12 (Xu et al., 2007), was used as a mediator of dissimilatory iron-reducing bacteria (DIRB) to study the reducibilities of soil iron after the studied soils being sterilized in the experiments (Davis, 1976). The impact of soil geochemical properties, including chemical properties, parent materials, and weathering degree on the iron reducibilities are investigated in detail in a vast array of iron-rich soils throughout Southern China in subtropical area. Our aim is to statistically disclose the key geochemical factors determining the iron reducibilities in different soils, and provide this information to scientists, site managers, and regulators for improved decision-making strategies regarding the activities of soil geochemical processes with the key factor of Fe(II) content in the soils.

2. Materials and methods

2.1. Soil sampling

Twenty-three soil samples were all collected from the A horizon (0–15 cm, the leached layer) in Southern China (between 20° and 28° latitude) (Fig. 1). These soils of 23 samples were developed from seven parent materials, including 3 from granite, 3 from basalt, 3 from limestone, 2 from sedimentary rocks, 4 from sandshale, 3 from alluvial deposits, and 5 from Quaternary Period red earths (Table 1). To concentrate on natural soil geochemical processes, anthropic soil samples such as paddy soil, which have suffered strong human disturbance during soil formation, were omitted in the present study. The soils were air dried and gently crushed before screening through a 2 mm sieve, and then stored at 4 °C prior to analysis and experimentation. The crystalline structures of the secondary minerals in soils were characterized by X-ray diffraction techniques (XRD) using a Rigaku D/Max-III A diffractometer at room temperature and operated at 40 kV and 30 mA with Cu Kα radiation ($\lambda = 1.5406$ nm), and the obtained diffraction patterns were shown in Fig. A1 in the Supporting Information (SI). Qualitative phase identification was executed by matching powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2, Release 2008).