Effects of human activities on pedogenesis and iron dynamics in paddy soils developed on Quaternary red clays

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ABSTRACT

A paddy soil chronosequence consisting of four profiles derived from Quaternary red clay (QRC) in Southern China with cultivation history from 0 to 300 years was studied to understand the underlying mechanisms and processes controlling the centennial scale Fe evolution during anthropedogenesis. We evaluated the chronosequencial changes in depth distribution of Fe oxides and Fe isotopic compositions. Results showed that paddy soil development on QRC over a centennial time scale caused increasing profile differentiation of Fe oxides and measurable Fe isotope fractionation. Total Fe and oxide bound Fe as well as the maximum Fe illuviation depth decreased as paddy soils age, leading to significant differences in morphological properties between paddy and non-paddy soils with the same parent material. Selective extractions showed that the weakly-bound, oxide-bound and silicate bound Fe corresponded to 4–18%, 49–81%, and 11–40% of the total Fe, respectively, and these proportions varied with both time and depth due to the redox-related Fe transformation and redistribution. δ^{56}Fe values in the studied paddy soil chronosequence ranged from 0.05‰ to 0.26‰ and exhibited a strong negative correlation with the logarithm of total Fe concentrations, suggesting mass-dependent Fe isotope fractionation occurred as a result of the preferential removal of lighter Fe isotopes during Fe leaching loss under the predominant reducing conditions. However, the Fe isotopic ratio of a specific paddy soil horizon was a result of a complex interaction of different processes, which were summarized and interpreted in our proposed conceptual model of Fe evolution in terraced paddy soils. Further investigations of Fe isotope signatures in the soil-plant-water system with a combination of laboratory simulation and prediction of Fe isotope fractionation under different pedogenic processes are needed to evaluate the relative contribution of multiple processes to Fe isotope fractionation during anthropedogenesis of paddy soils.

1. Introduction

Quaternary red clay (QRC) formed by chemical weathering under wet tropical and subtropical conditions is widely distributed in Southern China (Li, 1983) as well as in other countries around the world (Muggler et al., 2001). It is characterized by the red color, strong acidity, clayey structure, and high degree of weathering (Li, 1983; Muggler et al., 2001) due to the coincidence of high temperature and heavy rainfall. As a result, QRC shows substantial leaching of mobile elements (e.g., Ca, Mg, Na, and K), relative enrichment of Fe and Al, and a dominant clay mineral composition of kaolinite (Gong, 1985; He et al., 2008; Hu et al., 2010; Hong et al., 2014). Soils developed on QRC consist of a variety of different Fe phases, such as primary silicate minerals, pedogenic clay minerals, Fe (oxyhydr)oxides with different degrees of crystallinity, as well as in organic complexes. Previous studies have shown that Fe (oxyhydr)oxides undergo significant changes in species, amounts, and stability during the course of soil development, which are caused by chemical weathering, redox reactions, and the
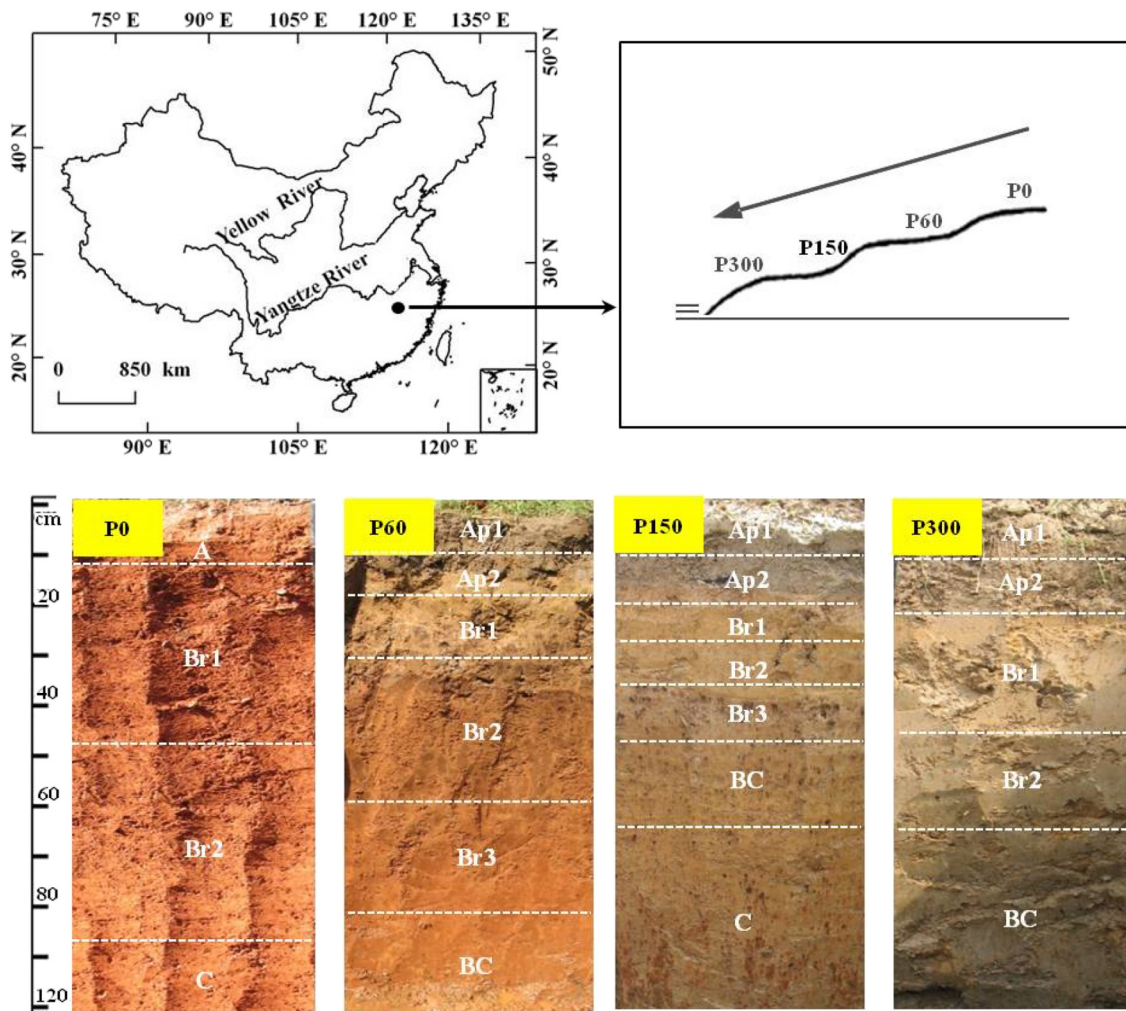

Fig. 1. Location of the study area and sampling sites, and representative soil profiles (P0, P60, P150, and P300) with 0, 60, 150, and 300 years of rice cultivation history.

lattice replacement of other metals with Fe in Fe-bearing minerals (van Breemen and Buurman, 2004; Vodyanitskii, 2010). The ratio of dithionite-citrate-bicarbonate extractable Fe to total Fe generally increases while the ratio of oxalate extractable Fe to total Fe decreases with increasing pedogenic age as indicated by the selective chemical extractions (Torrent et al., 1980; Aniku and Singer, 1990). In addition, the crystallinity of Fe (oxyhydr)oxides and the amount of Al that substitutes Fe in goethite often increase with increasing soil development (Cornell and Schwertmann, 2003). Therefore, the pedogenic Fe mobilization, translocation, and redistribution as well as the associated Fe mineral transformation are key processes in soil formation that influence the morphological and physico-chemical properties of soils (van Breemen and Buurman, 2004; Vodyanitskii, 2010).

The natural pedogenic controls on Fe evolution may be superseded by human activities (Dudal, 2005) that alter the rate and trajectory of net Fe dynamics either directly (e.g., by mineral and/or organic fertilizer additions) or indirectly (e.g., by alternate flooding and draining in rice paddies). For instance, paddy soils originating from QRC are widely distributed in Southern China, and are highly modified by anthropogenic management during paddy cultivation (Huang et al., 2015). The periodic artificial flooding and draining as well as groundwater fluctuations during paddy soil evolution result in significant changes in soil moisture regime and redox conditions with both time and depth, leading to coupled reduction-oxidation and eluviation-illuviation processes of Fe and formation of diagnostic horizons and features in paddy soil profiles (Gong, 1983, 1986; Zhang and Gong, 1993, 2003). The

redox changes of Fe in paddy soils are accompanied by the mobilization and translocation of Fe within soil profiles and transport of Fe as well as other redox sensitive elements to water bodies (Li, 1992; Kyuma, 2004). Despite the extensive researches during the past several decades on biogeochemical Fe cycling in paddy soils, the investigations have been limited to inferences from chemical extraction (e.g., Zhang and Gong, 2003), magnetic measurement (e.g., Han and Zhang, 2013; Chen et al., 2015) and mineralogical analysis (e.g., Han et al., 2015). The recent development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has drawn growing interests in the study of stable Fe isotopes, and this new tool has been widely used to trace the geochemical and biological cycling of Fe under both natural and experimental conditions (Dauphas et al., 2017).

Fe possesses four stable isotopes, ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe, with natural abundance percentage of 5.84%, 91.75%, 2.12%, and 0.29%, respectively. The isotopic composition of Fe is usually reported as $\delta^{56}Fe$, which is the deviation in parts per mil of the $^{56}Fe/^{54}Fe$ ratio relative to the IRMM-014 reference standard. $\delta^{57}Fe$ is also reported in literature, which is approximately equal to 1.5-fold of $\delta^{56}Fe$ (i.e. $\delta^{57}Fe \approx 1.5 \times \delta^{56}Fe$) due to the observed mass-dependent fractionation (Dauphas and Rouxel, 2006). It has been well established that Fe isotopes can be fractionated by kinetic and/or equilibrium effects during both biological and abiological processes (Kappler et al., 2010; Anbar, 2004; Johnson et al., 2004; Matthews et al., 2001; Anbar et al., 2000; Beard et al., 1999). Laboratory studies have shown that both ligand-promoted (Wiederhold et al., 2006; Brantley et al., 2004; Brantley et al.,