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Why was iron lost without significant isotope fractionation during the lateritic process in tropical environments?

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ABSTRACT

To investigate the formation of laterites and Fe cycling during tropical weathering, this study presents Fe isotope and major trace-element compositions of a laterite profile obtained from an equatorial rainforest, Southern Philippines. The lateritic profile is 7 m deep from top soil to less-weathered peridotites. X-ray diffraction analyses reveal that the major Fe-bearing minerals are hematite and goethite. The profile shows a large variation in Fe_2O_3 concentrations (32.1–73.3 wt%) and dramatic Fe loss based on $\tau_{Ti,Fe}$ factors ($\tau_{Ti,Fe} \approx -50\%$ to -90%) calculated from the open-system mass fraction transport function. Notably, δ^{56}Fe depicts a small range from −0.03‰ in the peridotite to +0.10‰ in the extremely weathered saprolites.

The small Fe isotopic fractionation and significant Fe loss provide important insights into Fe cycling during extreme weathering of peridotites in a tropical climate. Variations in Fe content and δ^{56}Fe can be modeled by a Rayleigh distillation process with apparently small fractionation factors of ^{56}Fe/^{54}Fe between the saprolite and fluid ($10^3\ln\alpha_{saprolite\text{–}fluid}$) of 0.01 to 0.20, much smaller than those experimentally determined for reductive dissolution of goethite ($10^3\ln\alpha_{goethite\text{-}Fe(II)} \approx 1.2$; Icopini et al., 2004) and hematite ($10^3\ln\alpha_{hematite\text{-}Fe(II)} \approx 1.3$; Beard et al., 2003). These observations suggest that Fe should have experienced a complete and *in situ* oxidation prior to Fe migration and Fe was probably transferred in the form of colloidal substances. Fe transport over the history of the laterite formation and evolution may not have had a discernible effect on the Fe isotopic composition of the ecosystem.

1. Introduction

Laterites are oxidized Fe-rich soils covering one third of the continents and are drained by half of the continental rivers. They represent a key role in continental evolution, element cycling from the solid earth to the ocean, and development of terrestrial life (Tardy, 1997). It is therefore necessary to understand how they evolve in response to natural and anthropogenic processes. Iron is the fourth most abundant element in the continental crust and is also extremely abundant in laterites, as shown in their characteristic red color due to the large amount of Fe^{3+}. Because Fe isotopes can be fractionated due to redox reaction during weathering and soil formation (Chapman et al., 2009; Fantle and DePaolo, 2004), Fe isotopic composition of soils can provide a useful tool to investigate laterite formation.

Understanding the behavior of Fe isotopes is important to evaluate transport of Fe during laterite formation and the impact on ecosystems. Previous studies on soils indicate that δ^{56}Fe of bulk soils show a large range from −0.62‰ to +0.72‰ (Emmanuel et al., 2005; Fantle and DePaolo, 2004; Fekiacova et al., 2013; Poitrasson et al., 2008; Thompson et al., 2007; Wiederhold et al., 2007a, 2007b). These pioneering studies have documented that notable Fe isotopic variation can occur due to reductive loss of Fe during weathering and soil formation (e.g., Bullen et al., 2001; Johnson et al., 2004; Wiederhold et al., 2006; Yesavage et al., 2012). Ligand-promoted dissolution, proton-promoted dissolution, or reductive Fe dissolution, have been proposed as the key process to control the Fe isotopic composition variation in soils (Emmanuel et al., 2005; Fantle and DePaolo, 2004; Liermann et al., 2011; Wiederhold et al., 2006, 2007a). Yesavage et al. (2012) suggested that the notable Fe isotopic fractionation in soils results from different dissolution and precipitation mechanisms. They invoked two models to explain the iron isotopic variations: (i) the fractionation occurs during dissolution process such as ligand-controlled dissolution or dissimilatory iron reduction, both of which preferentially enrich light iron isotopes in solution; (ii) the isotopic fractionation occurs during precipitation process rather than dissolution (Yesavage et al., 2012), which can be explained using a fractionation factor between the retained Fe precipitate and the mobile particles of 0.9987 (Skulan et al., 2002). There were later iron isotope studies on tropical or subtropical laterite profiles (Liu et al., 2014; Poitrasson et al., 2008). Liu et al. (2014) concerned laterites formed from basalt in southern China, while Poitrasson et al. (2008) studied laterites formed from

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granodiorites in Cameroon. Regardless of the different origin of laterites, they both demonstrate limited δ^{56}Fe variations (<0.15‰) of the whole profile with notable Fe loss during laterite formation. Given that redox transport of Fe could significantly fractionate Fe isotopes, it is not clear why Fe isotope fractionation is dramatically different in soils developed under different climates. There is also a lack of understanding for the coupling of limited iron isotope fractionation with dramatic iron loss. To better understand the Fe isotope variations and Fe loss in laterite forming, we conduct a comprehensive Fe isotope study for the laterites forming from weathering of peridotites under tropical climate.

The lateritic profile in this study is from Surigao, South Philippines. Because the climate is of an equatorial type with a mean annual rainfall of ≈3000 mm and a mean annual temperature of 27 °C, chemical weathering is significantly intensified and the laterite samples in this region have undergone extensive weathering. Therefore, laterites in Surigao, South Philippines, provide a good opportunity to study iron isotope fractionation and decipher iron cycling during extreme weathering processes. This is helpful for understanding how Fe is lost from the bedrocks to soil and water and how laterite forms via weathering of peridotites in tropical weather.

In this study, we report the Fe isotopic compositions, major- and trace-element contents of a typical lateritic profile developed from weathering of peridotites in Surigao, South Philippines. The purpose of this study is to understand the different response of Fe isotopes to weathering conditions and to investigate the cycling of Fe in the near-surface environment. We attribute the Fe lost with small Fe isotope variations in the laterite to a complete and in situ oxidation in the profile to the highly oxidized nature of the Surigao followed by migration, probably in the form of colloid substances, during laterite formation under the tropical climate.

2. Geology background and sample description

The laterite in this study formed in a humid, tropical climate due to weathering of peridotites (Fig. 1). Peridotites are a common ultramafic igneous rock containing <45 wt% silica. They are very important because they are the dominant rock of the upper Earth's mantle. The mineral compositions of peridotites are mainly olivine, clinopyroxene, orthopyroxene, and Al-bearing phases that change with increasing depth from plagioclase (<30 km) to spinel (30–70 km) and then to garnet (>70 km). The major Fe-bearing minerals are olivine ($(Mg, Fe)_2SiO_4$) and pyroxene ($(Ca, Na, Fe^{II},Mg)(Cr, Al, Fe^{III}, Mg, Mn, Ti, V)Si_2O_6$). Olivine is essentially free of Fe^{3+} compared with the other mineral phases in peridotites (i.e., pyroxenes), while both ferrous and ferric irons can exist in garnet, spinel, and pyroxene.

The weathering profile is located in Pili Country, Surigao, the capital city of Surigao del Norte Province and 30 km west of Mainit Lake. This region has a mean annual temperature of 27 °C. The highest maximum monthly temperature is 32–33 °C during August to September, and lowest maximum monthly temperature is 22–24 °C during January and February. Annual precipitation in Surigao is ≈3000 mm and most of the precipitation occurs from November to March. Integrated geological and mineralogical studies of the Surigao area can be found in Braxton et al. (2009).

The studied profile consists of peridotites at the bottom to extremely weathered laterites toward the surface (Fig. 2). The topsoil in the upper 50 cm was not sampled to avoid the disruption of vegetation activities onto iron isotopes. Beneath the topsoil, a set of gravel layers has developed. Four samples (Pili-1 to Pili-4) were collected at intervals of around 40 cm from the gravel layer. The gravels are hematite-rich nodules and the X-ray diffraction (XRD) results reveal that this layer

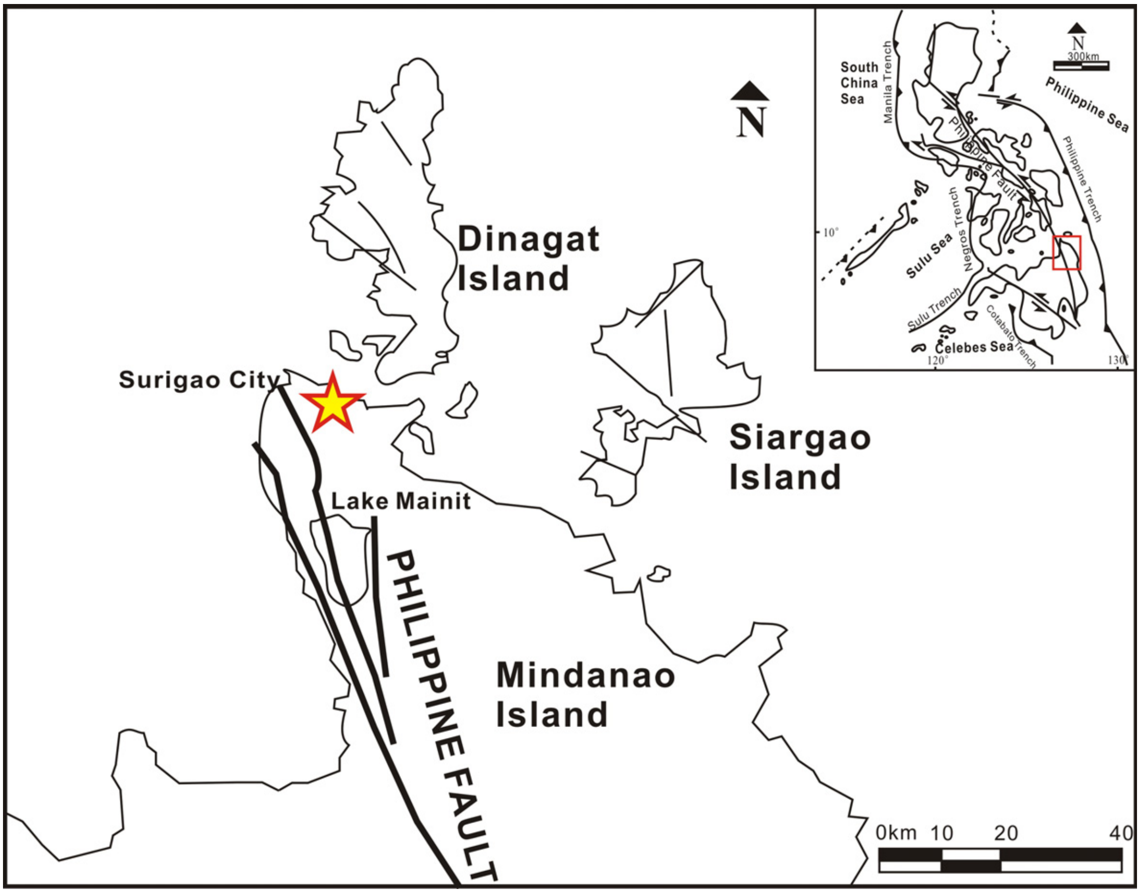

Fig. 1. A simplified geological map for South Philippines with sample location. Star represents sample locality.