



## Behavior of redox-sensitive elements during weathering of granite in subtropical area using X-ray absorption fine structure spectroscopy



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### ABSTRACT

The variation in chemical compositions of regolith along a weathering profile developed on a granite substrate in Jiangxi province, in southern China, was investigated in this paper, with the aim to characterize the speciation of redox-sensitive elements and to evaluate their mobility and redistribution during chemical weathering. Mass balance calculations indicate titanium (Ti) is the most immobile element in this weathering profile. A new method, X-ray absorption fine structure (XAFS) spectroscopy, was used to determine the speciation of Fe and Mn along the profile. Fe K-edge X-ray absorption near edge structure (XANES) spectra show Fe in saprolite is stabilized mainly in the state of Fe(III), suggesting Fe is as immobile as conservative elements during granite weathering. Mn K-edge XANES spectra show Mn (III/IV) oxides are reduced to Mn(II) in surface soil, where soil organic matter (SOM) acts as an important reductant. Although Ce, Co and V were unable to be analysed by XAFS, their concentrations have significant correlations with that of Mn, indicating that the mobilization and redistribution of Ce, Co and V may also be governed by redox condition. All in all, the results suggest that redox process impacts significantly on the redistribution of Mn, Ce, Co and V along the profile. The successful application of XAFS in the study on migration of redox-sensitive elements during granite chemical weathering has provided valuable information for the understanding and evaluating the geochemical behavior of elements in the environment.

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### 1. Introduction

Chemical weathering shapes the Earth's surface, determines nutrient supply to ecosystems and regulates global and local chemical cycles. Although granitic rocks cover ~25% of the continental surface, and that for example chemical weathering of these rocks plays a crucial role in transporting material at the Earth's surface, and contributes to the regulation of global climate over geological timescales (Oliva et al., 2003), relatively few chemical weathering mechanisms, especially of redistribution of elements in different physical and chemical conditions, have been proposed for granitoid rocks.

Long-term chemical weathering has led to the dissolution of primary and some heavy minerals, resulting in supergene forma-

tion and accumulation of secondary and residual minerals in profiles. In general, chemical elements are divided into two groups, immobile and mobile, on the basis of their geochemical distribution during weathering. Mobile elements are derived mainly from easily weatherable minerals such as feldspars, micas and apatites, whereas immobile elements are concentrated in residual phases or strongly adsorbed by secondary minerals (Harriss and Adams, 1966). Elements that are immobile during weathering include Al, Fe, Sc, Zr, Nb, Hf, Th and REEs, while the mobile elements include Ca, Na, P, K, Si, Sr, Ba, Rb and Mg (Middelburg et al., 1988; Taylor and Eggleton, 2001).

Many studies were carried out to deal with the mobility of major and trace elements during weathering (Harriss and Adams, 1966; Nesbitt, 1979; Braun et al., 1993, 2012; Jin et al., 2010; Babechuk et al., 2014). However, the mobilization and redistribution of redox-sensitive elements during weathering have been far less studied (van der Weijden and van der Weijden, 1995; Ma et al., 2007; Berger and Frei, 2014). Obviously, the mobility of redox-sensitive elements is more complicated than other elements due to

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their geochemical behavior which is not only influenced by general factors (i.e. dissolution of primary minerals, formation of secondary phases, mass transfers, and co-precipitation and ionic exchanges between various minerals), but also by a specific factor – redox processes. The research of Middelburg et al. (1988) proved that redox condition has a remarkable influence on redox-sensitive elements. The mobility of redox-sensitive elements in natural environments depends on reactivity and solubility, which are closely correlated to the speciation of the elements (i.e. the element's oxidation state and its association to other phases). For instance, Fe is usually immobile or shows a slight increase in weathered parts (Harris and Adams, 1966; Middelburg et al., 1988), but many studies showed that the geochemistry of Fe during chemical weathering may be more complicated and dependent on the redox and drainage conditions of the profile (Driese, 2004; Jin et al., 2010; Brantley and Lebedeva, 2011). The change between the di- and trivalent redox state of Fe initiates a number of significant geochemical reactions. Moreover, the large difference in mobility between soluble Fe(II) and insoluble Fe(III) results in the segregation of Fe in the soil sequences (Segalen, 1971; Marshall, 1977). Thus, understanding the specific forms of redox-sensitive elements in the weathering profiles is required for an adequate assessment of the mobility, availability and migration of chemical elements in the environment.

Previous studies on the chemical speciation of redox-sensitive elements were performed for seasonally saturated soils (Flessa and Fischer, 1992; Fox and Doner, 2002; Weber et al., 2009), bioturbated sediments (Aller, 1994; Collins and Kinsela, 2010), and forest soils (Clark et al., 1998; Silver et al., 1999). Comparatively, less information is available concerning redox transformation of trace metals during weathering of granitic rocks (Middelburg et al., 1988; van der Weijden and van der Weijden, 1995). Despite the total contents of redox-sensitive elements investigated in literature (Middelburg et al., 1988; van der Weijden and van der Weijden, 1995; Ma et al., 2007; Babechuk et al., 2014), there are still gaps in the knowledge about the specific forms of redox-sensitive elements that occur in the granite weathering profiles. Studies suggested that the mobilization and distribution of redox-sensitive elements could be attributed to their changes in chemical speciation during chemical weathering (Middelburg et al., 1988; Ma et al., 2007; Braun et al., 2012). However, there has been little direct evidence that changes in the oxidation states of these elements in profile.

Past analytical methods for elemental speciation have mainly been restricted to wet-chemical methods, which are time-consuming and destructive, and the different element species obtained in each fraction are operationally defined (Tessier et al., 1979; Nirel and Morel, 1990; Mester et al., 1998). A promising alternative for element speciation in natural materials is recent development in X-ray absorption fine structure spectroscopy (XAFS). However, there are few studies using XAFS to identify Fe and Mn species in natural geochemical samples. To the best of our knowledge, only one study has applied the technique in granite samples (Itai et al., 2008). However, the study only focused on speciation of Fe and Mn in the incipient stage of granite weathering. It is not fully clear whether or not the speciation of Fe and Mn would change with the increase of the weathering intensity.

Using mass balance calculation, XAFS and correlation analysis, this paper focuses on the speciation of Fe, Mn, Ce, Co and V in a well-developed granite regolith to understand the chemical reactions governing their dynamics during soil–water interactions and to assess their mobility and redistribution in the environment.

## 2. Geological setting, weathering profile and sample collection

The weathering profile studied (JLN-S1) is located in the Longnan County, Jiangxi province, China (Fig. 1). It lies within the south-

east monsoonal zone in East Asia, with warm and humid climatic conditions. The mean annual temperature is about 18.9 °C, with a monthly mean maximum temperature of 27.7 °C in July, and a minimum 8.3 °C in January. The mean annual precipitation is about 1526.3 mm, and over 50% of precipitation occurs during April and July.

Tectonically, the region corresponds to the southern part of the South-Jiangxi post-Caledonian uplift of the South China fold belt. The parent rock is the early Yanshanian syenite-granite assemblage (Chen et al., 2005). The granite cropped out with hilly terrain, which was characterized by slope angles less than 25 degrees and covered by well-developed plants. The vegetation is a subtropical evergreen broadleaf forest. In these forest, important species are *Camellia oleifera*, *Cunninghamia lanceolata* (Lamb.) Hook, *Pinus massoniana* Lamb, *Dicranopteris dichotoma* (Thunb.) Bernh, *Loropetalum chinese* (R.Br) Oliver, and so on.

The JLN-S1 profile (~10 m thick) was sampled at an elevation of 225 m along the hillslope. The Longtoutan reservoir, with a high water level of 199.5 m, is located near the profile. For about 15 m gap between the water level of reservoir and the bottom of profile, the water level can hardly reach the profile. Fig. 2 shows the details of the sampling profile. Interruption is not observed in the transition from granite to topsoil; hence, we inferred that this profile has developed continuously since intrusion of the granite. The upper 200 cm is homogeneous fine red soil, and the sampling interval is about 10 cm (JLN-S1-1 to JLN-S1-19). The soil between 200 and 350 cm is still fine in grain size, and its color turns a little yellowish. Seven samples (JLN-S1-20 to JLN-S1-26) were collected in this section. The soil color turns grey below 350 cm with numerous unweathered peddles. The soil between 350 and 800 cm was sampled in 20 cm intervals (JLN-S1-27 to JLN-S1-48), and 50 cm intervals in the last 200 cm (JLN-S1-49 to JLN-S1-53). Selective samples available for analyses are listed in Table 1. Samples for bulk density measurement were collected using bulk density samplers from the profile above 200 cm.

Samples of weathering front (JLN-WF1, JLN-WF2) were collected at the very base of the profile, which commonly preserves the structure of the bedrock. Four parent material (JLN-R1, R2, R3, R4), inferred to be similar to the parent lithology, were collected nearby the profile. Major minerals in the four unweathered granite samples are quartz, plagioclase, K-feldspar, and biotite, and minor minerals include hornblende and chlorite.

Soil samples were air-dried and sieved to 2 mm. The samples <2 mm were analysed for pH and grain size composition. Bulk soils (<2 mm), saprolite and fresh granite were then ball-milled to 75 µm prior to the measurement for major, trace element and soil organic carbon (SOC).

## 3. Analytic methods

### 3.1. Bulk density

In the laboratory, field-wet samples were weighted, oven-dried at 105 °C to equilibrium (in practice, over a 24 h period), and then re-weighted to determine bulk density. By dividing the dry weight of the soil sampled within the bulk density sampler by the volume of the sampler (100 cm<sup>3</sup>), bulk density was calculated for depths sample.

### 3.2. Soil pH and grain size composition

Soil pH was measured in 1:2.5 soil/CO<sub>2</sub>-free pure water extract. The absolute grain size composition of the <2 mm fraction of air-dried soil sample was determined using a Mastersizer 2000 (Malvern, UK) laser diffractometer, following a pretreatment with

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