



# Geochemistry of trace and rare earth elements during weathering of black shale profiles in Northeast Chongqing, Southwestern China: Their mobilization, redistribution, and fractionation



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## ARTICLE INFO

### Article history:

Received 23 December 2014

Received in revised form 17 June 2015

Accepted 16 July 2015

Editorial handling - A. Deutsch

### Keywords:

Black shale

Trace and rare earth elements

Chemical weathering

Mobilization

Redistribution

REE fractionation

## ABSTRACT

In this study, the mobilization, redistribution, and fractionation of trace and rare earth elements (REE) during chemical weathering in mid-ridge (A), near mountaintop (B), and valley (C) profiles (weak, weak to moderate, and moderate to intense chemical weathering stage, respectively), are characterized. Among the trace elements, U and V were depleted in the regolith in all three profiles, Sr, Nb, Ta, Zr, and Hf displayed slight gains or losses, and Th, Rb, Cs, and Sc remained immobile. Mn, Ba, Zn, Cu, and Cr were enriched at the regolith in profiles A and B, but depleted in profile C. Mn, Pb, and Co were also depleted in the saprock and fractured shale zones in profiles A and B and enriched in profile C. REEs were enriched in the regolith and depleted at the saprock zone in profiles A and B and depleted along profile C. Mobility of trace and REEs increased with increasing weathering intensity. Normalized REE patterns based on the parent shale revealed light REE (LREE) enrichment, middle REE (MREE), and heavy REE (HREE) depletion patterns. LREEs were less mobile compared with MREEs and HREEs, and this differentiation increased with increasing weathering degree. Positive Ce anomalies were higher in profile C than in profiles A and B. The Ce fractionated from other REE showed that Ce changed from trivalent to tetravalent (as CeO<sub>2</sub>) under oxidizing conditions. Minimal REE fractionation was observed in the saprock zone in profiles A and B. In contrast, more intense weathering in profile C resulted in preferential retention of LREE (especially Ce), leading to considerable LREE/MREE and LREE/HREE fractionation. (La/Yb)<sub>N</sub> and (La/Sm)<sub>N</sub> ratios displayed maximum values in the saprock zone within low pH values. Findings demonstrate that acidic solutions can mobilize REEs and result in leaching of REEs out of the highly acidic portions of the saprock material and transport downward into fractured shale. The overall behavior of elements in the three profiles suggests that solution pH, as well as the presence of primary and secondary minerals, play important roles in the mobilization and redistribution of trace elements and REEs during black shale chemical weathering.

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## 1. Introduction

Chemical and mechanical weathering leads to the disaggregation of rocks and minerals and the formation of regolith and saprock systems (Aubert et al., 2001). Weathering processes also control the mobilization, redistribution, and fractionation of trace elements and rare earth elements (REEs, La to Lu) in various natural settings.

The behavior of trace elements and REEs during chemical weathering has been investigated previously in several protoliths (Nesbitt, 1979; Middelburg et al., 1988; Braun et al., 1993, 2005; van der Weijden and van der Weijden, 1995; Nesbitt and Markovics, 1997; Aiuppa et al., 2000; Panahi et al., 2000; Ji et al., 2004; Brantley et al., 2007; Ma et al., 2007; Ndjigui et al., 2008; Beyala et al., 2009; Feng, 2010, 2011; Gong et al., 2011; Sanematsu et al., 2013; Nguetnkam et al., 2014), including weathering profiles from black shales (Peng et al., 2004; Tuttle et al., 2009; Ma et al., 2011a,b; Jin and Brantley, 2011; Yu et al., 2012). Trace elements and REEs in weathered material can be easily mobilized out of the regolith zone and retained in secondary minerals or colloids in weathering profiles as weathering proceeds (e.g., Sholkovitz, 1992, 1995; Faimon, 2003; Patino et al.,

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2003). Results from prior studies suggest that heavy REEs (HREE) are preferentially transported in solution, while light REEs (LREE) are easily absorbed by oxides/hydroxides or colloids within solid phases. In addition, Ce and Eu anomalies have been found in several weathering profiles within parent bedrocks. These observations provide a record of changes in redox conditions during geological processes (e.g., Brookins, 1989; Ji et al., 2004; Ma et al., 2011b). However, the geochemical behavior of trace elements and REEs during chemical weathering processes cannot easily be generalized due to variations in physico-chemical factors and location-specific weathering environments (Sharma and Rajamani, 2000).

Black shale is a very fine-grained sedimentary rock typically rich in sulfide minerals and organic matter, which contains trace elements (e.g., V, U, Cu, Zn, Mn, Ba, and Pb) (Jaffe et al., 2002; Lipinski et al., 2003; Piper and Calvert, 2009; Anjum et al., 2010). As a result of its sulfide and organic matter content, black shale is especially susceptible to chemical weathering processes, and thus serves to accelerate the decomposition of primary minerals and mobilize trace elements and REEs (Jin et al., 2010; Peng et al., 2007, 2014). Several field and laboratory studies have evaluated the mobility of trace elements in black shale during exposure to acidic groundwater (Lee et al., 1998; Tuttle et al., 2009; Yu et al., 2012) and reported on REE mobility and fractionation (Ma et al., 2011a; Peng et al., 2014). Although these investigations have contributed to the understanding of trace and REEs mobility, the geochemical behavior and factors controlling the mobility of these elements during chemical weathering processes require further investigation.

In this paper, we report on the behavior of select trace elements and REEs in three weathering profiles: mid-ridge (A), near mountaintop (B), and valley floor (C). The study area encompasses the Lower Cambrian black shale in northeastern Chongqing Province, Southwestern China. In this small catchment, profiles A, B, and C are characterized as weak, weak to moderate, and moderate to intense in terms of weathering intensity, respectively (Wu et al., 2015). We compared the composition of weathered products with parent shale in order to develop a better understanding of the geochemistry of trace elements and REEs in black shale profiles at different weathering intensities. The specific objectives of this study were to (i) understand the mobilization and redistribution of trace elements and REEs in weathering profiles during weak to intense chemical weathering; (ii) assess the elemental mobility and REE fractionation under different weathering intensities; (iii) determine inter-element relationships among major elements, trace elements, REEs, and pH in the three profiles; and (iv) identify which factors control the mobility and fractionation of trace elements and REE in black shale weathering profiles.

## 2. Geographical and geological setting

The study site is an excavated exposure near Chengkou County, northeastern Chongqing Province, China. This site crosses the two first-level tectonic division units of the Qinling orogenic belt and Yangtze Platform (Fig. 1a; Zeng et al., 2012). The Renhe River flows within the catchment from southeast to northwest, eventually joining the Yangtze River through the Han River. Chengkou County has a subtropical climate controlled by East Asian monsoons. The average annual temperature is approximately 13.8 °C and the mean annual precipitation is 1261.4 mm. The V-shaped catchment is characterized by an average local relief of 500 m, and an elevation ranging from 750 m at the riverside to 1250 m at the ridge-top.

The sample site is comprised of a fresh road cut on profiles A, B, and C and surface soil (SS) near the town of Chengkou County (N31°57'–31°58', E 108°37'–108°39'; Li et al., 2014; Ling et al., 2014). These profiles are covered by Shuijingtuo Formation black shale, Lower Cambrian. The strikes measured on the bedrock at pro-

files A, B, and C are N53°E, N73°E, and N57°E, and the dips are 60°SE, 78°SE, and 73°SE, respectively (Fig. 1b). The profiles were divided into four zones from surface to bedrock: regolith, saprock, fractured shale, and parent shale (protolith). Wu et al. (2015) reported that profiles A, B, and C possessed a chemical index of alteration (CIA) which ranged from 53.4 to 63.9, 52.4 to 70.8, and 70.6 to 88.7, which indicate weak, weak to moderate, and moderate to intense weathering stages, respectively. Minerals at the site include quartz, muscovite, albite, calcite, dolomite, illite, gypsum, smectite, organic matter, and sulfide (mainly as pyrite) with minor apatite, goethite, kaolinite, and jarosite.

## 3. Methods

### 3.1. Analysis techniques

#### 3.1.1. Trace and REE analyses

Samples were collected from each zone for the three profiles, and the sample numbers with corresponding zones and depths are shown in Table 1. After collection, the samples were dried at 65 °C and any plant roots seen in the top 1.5 m in profiles were removed. The samples were ground into 200 mesh (< 75 μm) grains using an agate mortar and pestle prior to laboratory analysis. The processed samples were baked at 700 °C to remove residual organic matter and then digested in a mixed acid solution of HNO<sub>3</sub> + HF in a platinum crucible for trace element and REE analysis. Trace and REEs concentrations were determined using a PerkinElmer Elan 6000 inductively coupled plasma-mass spectrometer (ICP-MS) with elemental detection limits of about 10 ppb for solid samples. The trace and REE concentrations were determined using Rh as an internal during ICP-MS analysis. Analytical precision for trace and REEs was greater than 5% (Liu et al., 1996). Experiments were conducted at the Key Laboratory of Geochronology and Geochemistry, Chinese Academy of Sciences. The analytical results are presented in Tables 1 and 2. Several United States Geological Survey (USGS), Geological Survey of Canada (GSC) and Chinese soils, such as BHVO-2, W-2, GSS-5, GSS-7, SY-4 and GXR-6 (soils) were repeatedly analyzed alongside samples to monitor the quality of ICP-MS measurements, and results were generally within ±10% of the certified values.

#### 3.1.2. pH and SEM-EDS analyses

In order to measure the pH of shale samples, 25 g of deionized water was initially equilibrated with 10 g rock powder in a 50 mL capped Teflon beaker for 20 min. The pH values of the slurry were measured using a calibrated HACH HQ30d acidity meter (USA) with precision better than 0.05. The measurement was repeated on three separate shale samples (Table 2). The handpicked samples were impregnated by vacuum and coated with gold for optical analysis. Scanning electron microscopy (SEM) was used to visualize textures and qualitative energy dispersive spectroscopy (EDS) analysis was performed on select mineral grains to determine phases present. SEM measurements were performed with an Ultra 55 (Car Zeiss Jena) and EDS analysis was conducted using an Oxford IE450X-Max80 at Southwest University of Science and Technology. The SEM was operated at 15 kV with a working distance of 10 mm to provide optimum resolution and minimize charging and sample damage.

### 3.2. Calculation methodologies

#### 3.2.1. Elemental mobility evaluation method during weathering

To assess the elemental mobility in the weathering profile, concentration (C) of an inert (or conservative) element (i) is commonly compared with the relative loss or gain of a more mobile element (j) by calculating the mass transfer coefficient  $\tau_{ij}$  (e.g., Brimhall and Dietrich, 1987; Brimhall et al., 1991; Anderson et al., 2002;

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