



Mineralogical and geochemical features of the coarse saprolite developed on orthogneiss in the SW of Yaoundé, South Cameroon

P.-D. Ndjigui^{a,*}, M.F.B. Badinane^a, B. Nyeck^a, H.P.K. Nandjip^a, P. Bilong^b

^a Department of Earth Sciences, University of Yaoundé 1, P.O. Box 812, Yaoundé, Cameroon

^b Faculty of Science, University of Douala, P.O. Box 24157, Douala, Cameroon

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ABSTRACT

A petrological investigation was performed in the coarse saprolite on orthogneiss in Yaoundé (South Cameroon) using combined whole rock geochemical (XRF, ICP-MS) and mineralogical (XRD, SEM) techniques. The orthogneiss has high contents in SiO₂ (61.56 wt.%), Ba (916 ppm) and REE (209 ppm), moderate content in Al₂O₃ (14.34 wt.%) and negative Eu anomaly (Eu/Eu* = 0.68). The weathering leads to the formation of three main constituents in the coarse saprolite: (i) the loose materials (~85 vol.%) are basically clayey silty with relic structure. They are composed of kaolinite, quartz and goethite. The loose materials have high contents in SiO₂ (56–64.83 wt.%) and Al₂O₃ (21.48–23.96 wt.%), and moderate contents in V (163–236 ppm), Ba (95–340 ppm) and Zr (160–313 ppm). The REE content is low (~49–169 ppm) relative to the parent rock with LREE-enrichment (LREE/HREE ~ 7–17). Positive Ce anomaly (Ce/Ce* ~ 3.35) is observed in the white veins and slight positive Eu anomalies (Eu/Eu* ~ 1.2–1.4) are noted in all loose samples. The (La/Yb)_N ratios (~0.8–1.5) indicate high REE-fractionation. The mass balance calculation reveals the depletion of several elements except Al, Ti, Sc, Y, Th, Sb and Hf; (ii) the iron duricrust (~10 vol.%) is located at the bottom and the top of the horizon. The mineral assemblage is dominated by hematite and goethite. The upper iron duricrust has high contents in Fe₂O₃ (45.60 wt.%) and Cr (1641 ppm), moderate contents in V (459 ppm) and Zn (143 ppm), and low REE content (47 ppm) with low LREE/HREE ratio (4.28). The upper iron duricrust is more enriched in Fe₂O₃ (53.26 wt.%) than the lower one. Vanadium, Cr and Zr have high contents relative to other trace elements. The REE content is low (39 ppm) as well as the LREE/HREE ratio (2.94). The iron duricrust has negative Ce anomalies (Ce/Ce* ~ 0.66–0.69) and very low (La/Yb)_N ratios (0.1–0.3). Several elements reported in the iron duricrust are highly leached except Fe, Cr, Zn, Sc, V, Pb, Zr, Cu and Th; and (iii) the Mn-rich materials (<5 vol.%) are made up of birnessite, cryptomelane, and low quantities of quartz, kaolinite and goethite. The SEM investigation reveals that Ba and Pb are linked in Mn-bearing phases and Ce-oxides appear as fine-grained intergrowth between Mn-bearing phases. The Mn-bearing phases are enriched in MnO (33.86 wt.%), BaO (4.30 wt.%), Co (1716 ppm), Pb (1315 ppm) and Ce (5202 ppm). Positive Ce and Eu anomalies are observed (Ce/Ce* ~ 15.60 and Eu/Eu* ~ 2). The mass balance calculations indicate the strong accumulation of Mn, Ni, Co, Zn, Sc, Cu, Ba, Pb, Y, Ga, Zr and REE. The Mn-bearing phases might be derived from the accumulation of silicate residues and Mn within the parent rock.

The transition from the parent rock to the coarse saprolite is marked by high leaching of several elements.

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1. Introduction

Laterites are the main constituents of weathering mantles in the tropical zone (McFarlane, 1976). They are complex materials that derive from the weathering of various rock types (Kamgang Beyala and Ekodeck, 1991; Ndjigui et al., 2008; Etame et al., 2012). Laterites are characterized by large iron duricrust (Beauvais and Colin,

1993; Bitom et al., 2003; Beauvais, 2009). Several works have reported the determination and dating of geochemical fractionation in laterites using U–Th radioactive series (Boulad et al., 1977; Mathieu et al., 1995) or ²³⁸U–²³⁵U–²³⁰Th nuclides (Chabaux et al., 2003). Chabaux et al. (2003) highlighted the chemical mobility in the lateritic profile controlled by the iron-cap dismantling. The REE-geochemistry is a useful complementary tool to elucidate chemical variations in geological systems because of their coherent and predictable behaviour (Leybourne et al., 2000). This behaviour combined with their sensitivity to changes in pH, redox conditions and adsorption/desorption reactions, make the

* Corresponding author.

E-mail address: Indjigui@yahoo.fr (P.-D. Ndjigui).

rare-earth elements particularly useful as pedogenetic tracers in external geodynamic studies of the earth.

The geochemical characterization has for long been focused on the distribution of major and five or six trace elements in the whole fraction of each soil horizon along the lateritic profile in the Central African rainforest (Ndjigui et al., 1999; Bitom et al., 2003; Nguetnkam et al., 2006). Many works reported since the 1990s included the mineralogy and geochemistry of REE in laterites (Braun et al., 1993, 1998; Ndjigui et al., 2008, 2009; Kamgang Kabeyene Beyala et al., 2009). These works have shown that the redox conditions and the nature of the parent rock control the REE distribution in the weathering mantles. They also display an intense REE accumulation in laterites with strong Ce abundance. The lateritic profile is made up, from the bottom to top, of coarse saprolite, fine saprolite, nodular zone and loose clay horizon (Ndjigui et al., 2008). Each soil horizon is made up of numerous plates and patches with different petrophysical, mineralogical and geochemical characteristics. Previous works on the petrology of major constituents of horizon are very scarce. The Mn-oxide commonly observed is characterized by a fibrous growth texture. It contains Ba and, in few cases, K. This phase can be assigned to either hollandite ($\text{BaMn}_8\text{O}_{16}$) or cryptomelane ($\text{KMn}_8\text{O}_{16}$), which are both isostructural 2:2 tunnel manganates and can contain up to 16 wt.% Ba and 5 wt.% K, respectively, based on the formula (Loges et al., 2012). The behaviour of cerium is complex in the Mn-oxides; Ce has commonly positive anomaly (Koppi et al., 1996; Ohnuki et al., 2008) due to the stability of Ce^{4+} at the oxide surface (Ohta and Kawabe, 2001; Takahashi et al., 2000, 2007). The negative Ce anomaly is rarely observed (Loges et al., 2012). This is due to the strong complexation of Ce^{4+} by siderophores or organic molecules (Davranche et al., 2005, 2008; Loges et al., 2012). At the same time, experimental studies reveal the selective adsorption of REE on kaolinite (Laufer et al., 1984; Coppin et al., 2002). Larger amounts of cerium were adsorbed by natural kaolinite. Cerium may be adsorbed either as a monomeric species or as a polymeric hydroxyl cation (Laufer et al., 1984). In this study, we present detailed mineralogical and geochemical data of three major constituents (loose materials, iron duricrust and Mn-bearing phases) of a coarse saprolite on orthogneiss. The high Ba, Pb and Ce contents in the Mn-bearing phases enabled to determine their stable forms using the microchemistry of the Mn-bearing phases. The last step of this study is the mass balance evaluation of major and trace elements from three main constituents of the coarse saprolite.

2. Geographical and geological setting

The study site is located in the SW of Yaoundé ($11^\circ25'–11^\circ30' \text{E}$ and $3^\circ45'–3^\circ50' \text{N}$; Fig. 1). The climate is humid tropical with four seasons marked by a mean annual temperature of 24°C and an average annual rainfall of 1495 mm (Suchel, 1987). The vegetation corresponds to a transitional zone between rainforest and savannah (Letouzey, 1985). The morphology of the Yaoundé area ($\sim 750 \text{ m}$) is dominated by the smooth-rocky hills with large convex slopes relayed by large swampy valleys. The Yaoundé group constitutes a part of the Central African Mobile Zone (CAMZ) and is pan-African in age (Toteu et al., 2006). Micaschists, quartzites and gneiss occur and are intensively folded (Fig. 1B). The Yaoundé group is made up of two series: the Mbalmayo-Bengbis-Ayos and the Yaoundé series (Maurizot et al., 1986). Paragneiss and orthogneiss are predominant in the Yaoundé series (Fig. 1C). The weathering leads to hillside ferrallitic soils and the swampy hydromorphic soils. The whole swamp is overlain by a grey clayey sandy material with depth varying from 0.5 to 2 m. It is essentially composed of kaolinite and residual quartz, Ti-oxides and zircon grains (Braun et al., 2005).

3. Sampling and analytical techniques

3.1. Sampling techniques

The pit is situated at the hilltop. The weathering profile is 9 m thick and is made up, from the bottom to top, of a coarse saprolite, a fine saprolite, a lower nodular horizon, an iron duricrust horizon, an upper nodular horizon and a loose clayey horizon (Fig. 2). Eleven weathered samples from the coarse saprolite and two rock samples (fresh and slightly weathered) from the outcrop were collected for mineralogical and chemical analyses in the Geoscience Laboratories (Sudbury, Canada).

3.2. Analytical techniques

Thin sections of rocks were observed with an optical microscope (Euromex). Mineralogical analyses were performed on whole rock powders. Powders were prepared by crushing the samples using an agate mortar. Mineral assemblage of rocks and soils was determined using the Panalytical X'Pert Pro. The controlling software is X'Pert data collector, version 2.2 h. The analytical conditions are 40 kV and 45 mA. The scan range varies $5–85^\circ 2\theta$ and the step size is 0.01. The run time is 8 min and 30 s/scan. The scanning is continuous and the type of radiation is Co. The mineralogical composition is given in Table 1.

Samples were analyzed for major and trace (including lanthanides) elements. They were crushed in an agate mortar and then pulverized in a planetary ball mortar made up of 99.8% Al_2O_3 . After crushing, the loss on ignition (LOI) was determined. Firstly, the powders were oven-dried at 105°C under nitrogen in order to eliminate water; another sample fraction was heated at 1000°C under oxygen so as to remove the volatile components and oxidize iron. After the determination of the LOI, the major element composition was determined by X-ray Fluorescence (XRF) with a Panalytical Axios Advanced PW 4400 fluorescence spectrometer. The international reference materials (INTL-09-05401, 09-04868 and 09-04869) and internal laboratory standards (ISHT-09-04204, 09-03903 and 09-03904) were used. Comparisons of measured and reference values are available upon request. The precision of analysis is 5%. The detection limits and results of major elements are presented in Table 2. Another fraction of the powder was prepared for the trace elements analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) following the digestion using three acids (see e.g., Burnham and Schweyer, 2004; Ndjigui et al., 2008). The powders were then treated in an acid mixture (HCl and HClO_4) at 120°C in a closed container for 1 week, and then rinsed from their containers with dilute HNO_3 and dried. The residues were dissolved in an acid mixture (HCl and HClO_4) and oven-dried for a second time before they were then dissolved in an acid mixture (HNO_3 , HCl and HF) at 100°C . The dissolved samples were analyzed in a Perkin Elmer Elan 9000 ICP-MS instrument. The instrumental precision of almost all elements was 5% (2σ) for either all or five of the six compiled solutions where the elements were above the limit of quantification. Where the concentrations approached this limit (e.g., for Zr, Ba, La and Pr in the trace-element poor basalt standard BIR-1, or Eu in the rhyolite standard RGM-1), the error varies between 5% and 8.5% (Burnham and Schweyer, 2004).

Density measurements were carried out in the Department of Earth Sciences of the University of Yaoundé 1 and the results are presented in Table 3. The bulk density (ρ_w) was obtained by the paraffin method. The grain densities (ρ_g) were obtained by the air picnometer method (two replicates). Porosity is calculated using the equation $\Phi = [1 - (\rho_w/\rho_g)] * 100$.

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