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## Origin and evolution of Ngaye River alluvial sediments, Northern Cameroon: Geochemical constraints

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## Accepted Manuscript

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

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

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34 **Abstract**

35 A petrological investigation was performed in the coarse saprolite on orthogneiss in  
36 Yaoundé (South Cameroon) using combined whole rock geochemical (XRF, ICP-MS) and  
37 mineralogical (XRD, SEM) techniques. The orthogneiss has high contents in SiO<sub>2</sub> (61.56  
38 wt.%), Ba (916 ppm) and REE (209 ppm), moderate content in Al<sub>2</sub>O<sub>3</sub> (14.34 wt.%) and  
39 negative Eu anomaly (Eu/Eu\* = 0.68). The weathering leads to the formation of three main  
40 constituents in the coarse saprolite: (i) the loose materials (~85vol.%) are basically clayey  
41 silty with relic structure. They are composed of kaolinite, quartz and goethite. The loose  
42 materials have high contents in SiO<sub>2</sub> (56 to 64.83 wt.%) and Al<sub>2</sub>O<sub>3</sub> (21.48 to 23.96 wt.%), and  
43 moderate contents in V (163 to 236 ppm), Ba (95 to 340 ppm) and Zr (160 to 313 ppm). The  
44 REE content is low (~ 49 to 169 ppm) relative to the parent rock with LREE-enrichment  
45 (LREE/HREE ~ 7 to 17). Positive Ce anomaly (Ce/Ce\* ~ 3.35) is observed in the white veins  
46 and slight positive Eu anomalies (Eu/Eu\* ~ 1.2 to 1.4) are noted in all loose samples. The  
47 (La/Yb)<sub>N</sub> ratios (~ 0.8 to 1.5) indicate high REE-fractionation. The mass balance calculation  
48 reveals the depletion of several elements except Al, Ti, Sc, Y, Th, Sb and Hf; (ii) the iron  
49 duricrust (~10vol.%) is located at the bottom and the top of the horizon. The mineral  
50 assemblage is dominated by hematite and goethite. The upper iron duricrust has high contents  
51 in Fe<sub>2</sub>O<sub>3</sub> (45.60 wt.%) and Cr (1641 ppm), moderate contents in V (459 ppm) and Zn (143  
52 ppm), and low REE content (47 ppm) with low LREE/HREE ratio (4.28). The upper iron  
53 duricrust is more enriched in Fe<sub>2</sub>O<sub>3</sub> (53.26 wt.%) than the lower one. Vanadium, Cr and Zr  
54 have high contents relative to other trace elements. The REE content is low (39 ppm) as well  
55 as the LREE/HREE ratio (2.94). The iron duricrust has negative Ce anomalies (Ce/Ce\* ~ 0.66  
56 to 0.69) and very low (La/Yb)<sub>N</sub> ratios (0.1 to 0.3). Several elements reported in the iron  
57 duricrust are highly leached except Fe, Cr, Zn, Sc, V, Pb, Zr, Cu and Th; and (iii) the Mn-rich  
58 materials (<5vol.%) are made up of birnessite, cryptomelane, and low quantities of quartz,

59 kaolinite and goethite. The SEM investigation reveals that Ba and Pb are linked in Mn-  
60 bearing phases and Ce-oxides appear as fine-grained intergrowth between Mn-bearing phases.  
61 The Mn-bearing phases are enriched in MnO (33.86 wt.%), BaO (4.30 wt.%), Co (1716 ppm),  
62 Pb (1315 ppm) and Ce (5202 ppm). Positive Ce and Eu anomalies are observed ( $Ce/Ce^* \sim$   
63 15.60 and  $Eu/Eu^* \sim 2$ ). The mass balance calculations indicate the strong accumulation of Mn,  
64 Ni, Co, Zn, Sc, Cu, Ba, Pb, Y, Ga, Zr and REE. The Mn-bearing phases might be derived  
65 from the accumulation of silicate residues and Mn within the parent rock.

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

68

69 **Keywords:** Yaoundé; Orthogneiss; Coarse saprolite; Mineralogy; Geochemistry; Mass  
70 balance

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84 **1. Introduction**

85 Laterites are the main constituents of weathering mantles in the tropical zone (Mc  
86 Farlane, 1976). They are complex materials that derive from the weathering of various rock  
87 types (Kamgang Beyala and Ekodeck, 1991; Ndjigui et al., 2008; Etame et al., 2012).  
88 Laterites are characterized by large iron duricrust (Beauvais and Colin, 1993; Bitom et al.,  
89 2003; Beauvais, 2009). Several works have reported the determination and dating of  
90 geochemical fractionation in laterites using U-Th radioactive series (Boulad et al., 1977;  
91 Mathieu et al., 1995) or  $^{238}\text{U}$ - $^{235}\text{U}$ - $^{230}\text{Th}$  nuclides (Chabaux et al., 2003). Chabaux and co-  
92 workers (2003) highlighted the chemical mobility in the lateritic profile controlled by the  
93 iron-cap dismantling. The REE-geochemistry is a useful complementary tool to elucidate  
94 chemical variations in geological systems because of their coherent and predictable behaviour  
95 (Leybourne et al., 2000). This behaviour combined with their sensitivity to changes in pH,  
96 redox conditions and adsorption/desorption reactions, make the rare-earth elements  
97 particularly useful as pedogenetic tracers in external geodynamic studies of the earth.

98 The geochemical characterization has for long been focused on the distribution of  
99 major and five or six trace elements in the whole fraction of each soil horizon along the  
100 lateritic profile in the Central African rainforest (Ndjigui et al., 1998; Bitom et al., 2003;  
101 Nguetnkam et al., 2006). Many works reported since the 90s included the mineralogy and  
102 geochemistry of REE in laterites (Braun et al., 1993, 1998; Ndjigui et al., 2008, 2009;  
103 Kamgang Kabeyene Beyala et al., 2009). These works have shown that the redox conditions  
104 and the nature of the parent rock control the REE distribution in the weathering mantles. They  
105 also display an intense REE accumulation in laterites with strong Ce abundance. The lateritic  
106 profile is made up, from the bottom to top, of coarse saprolite, fine saprolite, nodular zone and  
107 loose clay horizon (Ndjigui et al., 2008). Each soil horizon is made up of numerous plates and  
108 patches with different petrophysical, mineralogical and geochemical characteristics. Previous

109 works on the petrology of major constituents of horizon are very scarce. The Mn-oxide  
110 commonly observed is characterized by a fibrous growth texture. It contains Ba and, in few  
111 cases, K. This phase can be assigned to either hollandite ( $\text{BaMn}_8\text{O}_{16}$ ) or cryptomelane  
112 ( $\text{KMn}_8\text{O}_{16}$ ), which are both isostructural 2:2 tunnel manganates and can contain up to 16 wt.%  
113 Ba and 5 wt.% K, respectively, based on the formula (Loges et al., 2012). The behaviour of  
114 cerium is complex in the Mn-oxides; Ce has commonly positive anomaly (Koppi et al., 1996;  
115 Ohnuki et al., 2008) due to the stability of  $\text{Ce}^{4+}$  at the oxide surface (Ohta and Kawabe, 2001;  
116 Takahashi et al., 2000, 2007). The negative Ce anomaly is rarely observed (Loges et al.,  
117 2012). This is due to the strong complexation of  $\text{Ce}^{4+}$  by siderophores or organic molecules  
118 (Davranche et al., 2005, 2008; Loges et al., 2012). At the same time, experimental studies  
119 reveal the selective adsorption of REE on kaolinite (Laufer et al., 1984; Coppin et al., 2002).  
120 Larger amounts of cerium were adsorbed by natural kaolinite. Cerium may be adsorbed either  
121 as a monomeric species or as a polymeric hydroxyl cation (Laufer et al., 1984). In this study,  
122 we present detailed mineralogical and geochemical data of three major constituents (loose  
123 materials, iron duricrust and Mn-bearing phases) of a coarse saprolite on orthogneiss. The  
124 high Ba, Pb and Ce contents in the Mn-bearing phases enabled to determine their stable forms  
125 using the microchemistry of the Mn-bearing phases. The last step of this study is the mass  
126 balance evaluation of major and trace elements from three main constituents of the coarse  
127 saprolite.

128

## 129 **2. Geographical and geological setting**

130 The study site is located in the SW of Yaoundé ( $11^{\circ}25'$ - $11^{\circ}30'$ E and  $3^{\circ}45'$ - $3^{\circ}50'$ N;  
131 Fig. 1). The climate is humid tropical with four seasons marked by a mean annual temperature  
132 of  $24^{\circ}\text{C}$  and an average annual rainfall of 1495 mm (Suchel, 1987). The vegetation  
133 corresponds to a transitional zone between rainforest and savannah (Letouzey, 1985). The

134 morphology of the Yaoundé area (~750 m) is dominated by the smooth-rocky hills with large  
135 convex slopes relayed by large swampy valleys. The Yaoundé group constitutes a part of the  
136 Central African Mobile Zone (CAMZ) and is pan-African in age (Toteu et al., 2006).  
137 Micaschists, quartzites and gneiss occur and are intensively folded (Fig. 1B). The Yaoundé  
138 group is made up of two series: the Mbalmayo-Bengbis-Ayos and the Yaoundé series  
139 (Maurizot et al., 1986). Paragneiss and orthogneiss are predominant in the Yaoundé series  
140 (Fig. 1C). The weathering leads to hillside ferrallitic soils and the swampy hydromorphic  
141 soils. The whole swamp is overlain by a grey clayey sandy material with depth varying from  
142 0.5 to 2 m. It is essentially composed of kaolinite and residual quartz, Ti-oxides and zircon  
143 grains (Braun et al., 2005).

144

### 145 **3. Sampling and analytical techniques**

#### 146 **3.1. Sampling techniques**

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

153

#### 154 **3.2. Analytical techniques**

155 Thin sections of rocks were observed with an optical microscope (Euromex).  
156 Mineralogical analyses were performed on whole rock powders. Powders were prepared by  
157 crushing the samples using an agate mortar. Mineral assemblage of rocks and soils was  
158 determined using the Panalytical X'Pert Pro. The controlling software is X'Pert data collector,



159 version 2.2h. The analytical conditions are 40 kV and 45 mA. The scan range varies 5 to 85  
160 degrees 2 theta and the step size is 0.01. The run time is 8 minutes and 30 seconds/scan. The  
161 scanning is continuous and the type of radiation is Co. The mineralogical composition is  
162 given in Table 1.

163 Samples were analyzed for major and trace (including lanthanides) elements. They  
164 were crushed in an agate mortar and then pulverized in a planetary ball mortar made up of  
165 99.8% Al<sub>2</sub>O<sub>3</sub>. After crushing, the loss on ignition (LOI) was determined. Firstly, the powders  
166 were oven-dried at 105°C under nitrogen in order to eliminate water; another sample fraction  
167 was heated at 1000°C under oxygen so as to remove the volatile components and oxidize iron.  
168 After the determination of the LOI, the major element composition was determined by X-Ray  
169 Fluorescence (XRF) with a Panalytical Axios Advanced PW 4400 fluorescence spectrometer.  
170 The international reference materials (INTL-09-05401, 09-04868 and 09-04869) and internal  
171 laboratory standards (ISHT-09-04204, 09-03903 and 09-03904) were used. Comparisons of  
172 measured and reference values are available upon request. The precision of analysis is 5 %.  
173 The detection limits and results of major elements are presented in Table 2. Another fraction  
174 of the powder was prepared for the trace elements analysis by Inductively Coupled Plasma-  
175 Mass Spectrometry (ICP-MS) following the digestion using three acids (see e.g., Burnham  
176 and Schweyer, 2004; Ndjigui et al., 2008). The powders were then treated in an acid mixture  
177 (HCl and HClO<sub>4</sub>) at 120°C in a closed container for one week, and then rinsed from their  
178 containers with dilute HNO<sub>3</sub> and dried. The residues were dissolved in an acid mixture (HCl  
179 and HClO<sub>4</sub>) and oven-dried for a second time before they were then dissolved in an acid  
180 mixture (HNO<sub>3</sub>, HCl and HF) at 100°C. The dissolved samples were analyzed in a Perkin  
181 Elmer Elan 9000 ICP-MS instrument. The instrumental precision of almost all elements was  
182 5% (2σ) for either all or five of the six compiled solutions where the elements were above the  
183 limit of quantification. Where the concentrations approached this limit (e.g., for Zr, Ba, La

184 and Pr in the trace-element poor basalt standard BIR-1, or Eu in the rhyolite standard RGM-  
185 1), the error varies between 5 and 8.5% (Burnham and Schweyer, 2004).

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

190 Scanning Electron Microscope (SEM) analysis were carried out at the Geoscience  
191 Laboratories using the BSE detector and ED X-ray spectrometer to (i) search for various Mn,  
192 Ba, Pb and Ce mineral species due to their high abundances in Mn-bearing phases; and (ii)  
193 provide qualitative X-ray data and BSE images of the individual phases. The sample was  
194 prepared in three steps: (i) mineral grains and representative pieces of the sample were hand-  
195 picked; (ii) several grains were mounted in epoxy plug, polished and carbon coated prior to  
196 analysis by SEM; and (iii) several grains were crushed with an agate mortar and pestle, and a  
197 smear mount created for XRD analysis. SEM used is a Zeiss EVO 50 and the operating  
198 conditions were 20 kV acceleration voltage/1 nA beam current.

199

## 200 **4. Results**

### 201 **4.1. Petrology of orthogneiss**

202 The orthogneiss is dark, microbedded and has an augen structure. The rock, with  
203 heterogranular grano-lepidoblastic texture, is essentially made up of quartz, biotite, green  
204 hornblende, garnet, orthoclase, and accessory microcline, opaque minerals and zircon. The  
205 XRD spectra reveal the presence of micas (Table 1). The fresh rock is characterized by high  
206 SiO<sub>2</sub>, and moderate Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, K<sub>2</sub>O and Na<sub>2</sub>O contents (Table 2). The slightly  
207 weathered sample is characterized by an increase in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>  
208 contents (Table 2). The bulk density is 2; it is a less porous rock (27.6%, Table 3). The trace

209 element contents are variable (Table 4). In the fresh rock, elements whose concentrations are  
210 more than 100 ppm include Cr, Zn, V, Ba, Zr, Rb and Sr (Table 4). The second category,  
211 made up of elements with low concentrations (20 to 90 ppm), include Ni, Cu, Y, Co, Li and  
212 Ga. The third category is made up of those whose concentrations are below 19 ppm (Table 4).  
213 The chondrite-normalized (McDonough and Sun, 1995) multi-element patterns reveal that  
214 orthogneiss and their weathered products are depleted in Co, Ni and Cr contrary to several  
215 trace elements (Fig. 3). The total REE content is 209 ppm (Table 4). The elements whose  
216 concentrations are high (>40 ppm) include La (43.04 ppm), Ce (87.02 ppm) and Nd (40.79  
217 ppm) (Table 5). The orthogneiss is more enriched in LREE (LREE/HREE ~ 10). The  
218 chondrite-normalized REE spectra reveal: (i) strong LREE-enrichment; (ii) slight HREE-  
219 enrichment; and (iii) moderate negative Eu anomaly ( $\text{Eu}/\text{Eu}^* = 0.68$ ) (Fig. 4). The  $(\text{La}/\text{Yb})_N$   
220 ratios are very high (13.19).

221

## 222 **4.2. Petrology of the coarse saprolite**

### 223 *4.2.1. Morphology, mineralogy and distribution of major elements*

224 The coarse saprolite is 2.50 m thick (Fig. 2), with a microbedded structure inherited  
225 from the parent rock. It is mainly violet red, silty and interspersed with plates of variable  
226 colour and texture.

227 The bottom is made up of a brown material and white veins. The brown material (~80  
228 vol.%) is organized in horizontal, mm-sized, red, grey yellow or white layers. The mineral  
229 assemblage is comprised of kaolinite, quartz, goethite, anatase and accessory hematite (Table  
230 1). This material shows high contents in  $\text{Al}_2\text{O}_3$  (22.48 wt.%) and  $\text{TiO}_2$  (1.36 wt.%) relative to  
231 the orthogneiss (Table 2). The  $\text{Fe}_2\text{O}_3$ , MnO, MgO, CaO,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  contents decrease  
232 strongly from the parent rock to the brown material (Table 2). The white veins occur inside  
233 the brown material. They are cm-thick, sandy clayey and oriented parallel to the brown

234 material. Kaolinite and quartz are the dominated minerals (Table 1). Slight increase of  
235 contents in  $\text{SiO}_2$  (64.83 wt.%),  $\text{Al}_2\text{O}_3$  (22.76 wt.%) and  $\text{TiO}_2$  (1.46 wt.%) is observed relative  
236 to the orthogneiss (Table 2).

237 The whole fraction of the bottom shows a similar mineralogy and geochemistry like  
238 the brown material (Tables 1-2).

239 The upper part is mainly yellowish brown, clayey silty and microbedded. The whole  
240 fraction has practically the same mineralogy and geochemistry like the brown material  
241 (Tables 1-2). It embeds numerous plates like dark red iron duricrust, black plates, yellowish  
242 brown plates and dusky red iron duricrust.

243 The dark red iron duricrust is fusiform (2 to 3 m long and 0.5 m wide), and includes  
244 piled up concentric and cm-layers. It is surrounded by the yellowish brown plate (Fig. 2). The  
245 mineral assemblage is made up of hematite, goethite, and few amounts of kaolinite, quartz  
246 and anatase (Table 1). The  $\text{Fe}_2\text{O}_3$  content is 53.26 wt.% and those of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are 26.7  
247 and 10.04 wt.%, respectively.

248 The black phases (~5vol.%) form cm- to dm-sized lobe-shape. They are porous and  
249 very hardened materials. They are made up of birnessite, cryptomelane, with accessory  
250 quartz, kaolinite and goethite (Table 1). The X-ray diffraction data of selected grains confirms  
251 the presence of the birnessite and cryptomelane groups (Fig. 5). The Mn-bearing phases are  
252 very enriched in Mn (33.86 wt.%), and depleted in  $\text{SiO}_2$  (27.97 wt.%) and  $\text{Al}_2\text{O}_3$  (12.16  
253 wt.%). The  $\text{Fe}_2\text{O}_3$  content is quite high (10.08 wt.%) as well as those of other major elements  
254 (Table 2).

255 The yellowish brown plates are disseminated with variable shapes and sizes. They are  
256 composed of kaolinite, quartz, goethite and few amounts of rutile and anatase (Table 1). The  
257 chemical composition is very close to the uppermost part whole fraction one (Table 2).

258 The upper boundary of the coarse saprolite is also marked by the presence of dusky  
259 red iron duricrust. It is made up of flattened and lobular, interconnected and millimetric  
260 plates. The X-ray diffraction data show that hematite and goethite are dominantly associated  
261 with few amounts of quartz, kaolinite and anatase (Table 1). The dusky red iron duricrust  
262 have high content in  $\text{Fe}_2\text{O}_3$  (45.60 wt.%) and moderate contents in  $\text{SiO}_2$  (30.79 wt.%) and  
263  $\text{Al}_2\text{O}_3$  (11.90 wt.%).

264 The bulk density values range between 0.9 and 2.53 (Table 3). The high values are  
265 measured in the lower iron duricrust (2.53) and in the Mn-bearing phases (2.36). The upper  
266 iron duricrust is less dense (1.66). The loose materials have low density (0.93-1.42) and  
267 moderate porosity (35-50%).

268

#### 269 4.2.2. Distribution of trace elements

270 Trace element behaviour was subdivided into five groups according to the periodic  
271 table of elements:

272 a) - alkaline (Li, Rb, Cs) and alkali-earth (Be, Sr, Ba) contents are very low in the  
273 loose samples and iron duricrust compared with the parent rock (Table 4). Lithium, Rb, Sr  
274 and Ba contents are high in Mn-bearing phases (Table 4);

275 b) - scandium, V, Cr, Co, Ni and Cu contents are low, except Cr (1641 ppm) and V  
276 (459 ppm) in the upper iron duricrust and Co (1716 ppm) in the Mn-bearing phases (Table 4).  
277 Other elements also show high contents in Mn-bearing phases (Table 4);

278 c) - yttrium, Nb, Mo, Hf and W show low concentrations except Zr (Table 4). The Zr  
279 contents vary from 83 to 316 ppm; the lowest content occurs in the upper iron duricrust and  
280 the highest one is observed in the white veins. Other trace elements of this series have high  
281 contents in the Mn-bearing phases (Table 4);

282 d) - other metals (Ga, Zn, Cd, In, Sn, Sb, Tl and Pb) show a similar behaviour like  
283 those of the previous groups (Table 4). Elements which show high contents include Pb (1315  
284 ppm) and Zn (242 ppm) in the Mn-bearing phases;

285 e) - thorium contents range between 5 and 42 ppm. The upper iron duricrust and white  
286 veins have highest Th contents, 42.50 and 32.66 ppm, respectively. The lowest Th contents  
287 are measured in the Mn-bearing phases (5.8 ppm). A slight increase of uranium contents is  
288 observed from the parent rock (1.52 ppm) to the weathered samples (ranging from 1.75 to  
289 3.76 ppm) (Table 4).

290

#### 291 4.2.3. Correlations

292 The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$  ratios show that Si and Fe are most abundant than Al  
293 and K (Table 2). The Th/U and Th/Co ratios show that orthogneiss and their weathered  
294 products are more enriched in Th than U and Co (Table 4). The parent rock-normalized multi-  
295 element patterns show strong negative Rb anomalies (Fig. 6). The Harker diagrams show that  
296  $\text{SiO}_2$  has positive correlations with  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , Y and U (Fig. 7). However,  
297 correlations of  $\text{SiO}_2$  with  $\text{Fe}_2\text{O}_3$ , Zr, Cr and V are negative.  $\text{K}_2\text{O}$ , Rb and Th have no  
298 significant correlations with  $\text{SiO}_2$  (Fig. 7). The binary diagrams show that  $\text{Fe}_2\text{O}_3$  has a similar  
299 trend with ferromagnesian trace elements (Fig. 8). Figure 9 shows (i) strong positive  
300 correlations of Zr with Hf, Nb and U; (ii) negative correlations of Zr with Y and Mo; and (iii)  
301 any correlation between Zr and Th.

302

#### 303 4.2.4. Behaviour of rare-earth elements

304 The total REE content varies between 39 and 5633 ppm (Table 5). The high value is  
305 measured in the Mn-phases. The REE content is higher than 100 ppm in two samples and  
306 varies from 49 to 96 ppm in several loose samples (Table 5). Both iron duricrust samples have

307 very low REE content, ranging from 39 to 47 ppm. All the weathered samples highlight  
308 LREE-enrichment (LREE/HREE  $\sim$  3 to 86). LREE have strong positive correlations with  
309 HREE (Fig. 10).

310 Overall, the high concentrated REE include La, Ce, Pr, Nd, Sm, Gd and Dy (Table 5).

311 The binary diagrams reveal that Zr and Pb have strong positive correlations with Ce  
312 (Fig. 11A-B). Cerium reveals positive correlation with LREE and REE (Fig. 11C-D). The Ce  
313 content influences the behaviour of the bulk LREE and REE. The sum of three lanthanide (La,  
314 Ce and Nd) contents is moderate to high, ranging from 30 to 5408 ppm. Lanthanum, cerium  
315 and neodymium are the most abundant REE. The binary diagram (La+Ce+Nd) vs. REE shows  
316 strong positive correlation of three LREE (La, Ce and Nd) with REE (Fig. 11E). Europium  
317 shows a moderate positive correlation with Sr (Fig. 11F).

318 The parent rock-normalized patterns reveal (Fig. 12A; Table 5): (i) similar behaviour  
319 of REE except in the Mn-bearing phases; (ii) slight LREE-depletion; (iii) strong positive Ce  
320 and Eu anomalies in Mn-bearing phases ( $Ce/Ce^* = 15.57$  and  $Eu/Eu^* = 2.01$ ); (iv) positive Ce  
321 anomaly in white veins ( $Ce/Ce^* = 3.35$ ); and (v) moderate negative Ce ( $Ce/Ce^* \sim 0.66$  to  $0.86$ )  
322 and weak positive Eu anomalies ( $Eu/Eu^* \sim 1.18$  to  $1.40$ ) in the loose materials and in the iron  
323 duricrust. The chondrite-normalized (McDonough and Sun, 1995) patterns reveal the similar  
324 trend like the parent rock-normalized spectra (Fig. 12 B). The  $(La/Yb)_N$  ratios range between  
325 0.12 and 1.63 (Table 5).

326

#### 327 4.2.5. SEM analysis of Mn-phases

328 The SEM analysis is initiated to understand the distribution of several elements with  
329 high concentrations like Mn, Pb, Ba and Ce inside the Mn-rich materials. Under SEM, the  
330 Mn-rich material has concentric structure (Figs. 13-14). Barium is detected in all Mn-bearing  
331 phases that were analyzed from numerous pieces of the sample. Kaolinite is also detected in

332 the Mn-bearing phases with Al/Si ratio  $\sim 1$  (Fig. 13). In addition, the atomic ratio of Ba/K is  
 333 always  $>1$  suggesting that the cryptomelane component could be termed "hollandite". The  
 334 "typical" birnessite type composition using the SEM is not identified; the birnessite structure  
 335 in this case also contains significant Ba, where the ratio of Ba/K also exceeds 1. Cyclical  
 336 growth patterns are evident in the sample (Fig. 13). The SEM investigation also reveals a  
 337 much less abundant Pb bearing Mn-phase, perhaps the corandite member of the cryptomelane  
 338 group. Ce-oxide phase is also relatively common in this sample. In some cases, it forms a rim  
 339 around the sample or is contained between the apparent growth rings (Fig. 14). There appears  
 340 to be a fine grained intergrowth between the Mn-bearing phase and an aluminosilicate mineral  
 341 with a stoichiometry that is consistent with kaolinite (Figs. 14-15).

342

#### 343 **4.3. Mass balance calculation**

344 The mass balance calculation is a method that enables one to confirm the mobility of  
 345 chemical elements during weathering. This is done by the estimation of losses or gains of  
 346 matter expressed either in per cent or  $\text{kg/m}^3$  of the weathered parent material. The method  
 347 currently used takes into account the concentrations, the bulk density and the volume  
 348 (Brimhall and Dietrich, 1987; Colin and Ambrosi, 1993; Mungall and Martin, 1994;  
 349 Beauvais, 1999; Cornu et al, 1999; Moroni et al., 2001; Tollari et al., 2008). This method  
 350 enables one to estimate the quantity of each element which is depleted or accumulated (Colin  
 351 et al., 1993). This approach can be summarized by the following equations:

352 The first equation is that of Millot and Bonifas (1955), improved by Brimhall and  
 353 Dietrich (1987):

$$354 \quad K_{jm} = \left\{ \left( \frac{C_{jw} \times \rho_w}{C_{jp} \times \rho_p} \right) - 1 \right\} \times 100 \quad (1)$$



355 where  $K_{jm}$  is the enrichment or depletion factor,  $C_{jw}$  is the concentration of the element  
 356  $j$  in the weathered material  $w$ ,  $C_{jp}$  is the concentration of the element  $j$  in the fresh rock  $p$ ,  $\rho_{jw}$   
 357 is the bulk density of the weathered material  $w$ , and  $\rho_{jp}$  is the bulk density of the parent rock  $p$ .

358 The total mass  $m_{jw}$  of each chemical element is obtained through the application of the  
 359 following equation by Colin et al. (1993):

$$360 \quad m_{jw} = C_{jp} \rho_p V_p K_{jm} \quad (2)$$

361 where  $m_{jw}$  is in kg,  $C_{jp}$  is the concentration of the element  $j$  in the parent rock in  
 362 mg/kg,  $\rho_p$  is the bulk density of the parent rock in  $10^3 \text{ kg/m}^3$ ,  $V_p$  is the volume of the parent  
 363 rock in  $\text{m}^3$  ( $V_p = 1 \text{ m}^3$ ),  $K_{jm}$  is the enrichment or depletion factor of the element  $j$  in the  
 364 weathered material  $w$ .

365 Equation #2 gives the mass  $m$  (in kg or g) of each element that is transferred per unit  
 366 volume of the parent rock during the weathering.

367 The application of the previous equations leads to results presented in Tables 6, 7, 8, 9,  
 368 10 and 11. The mass balance calculations reveal a clear disparity in the behaviour of elements  
 369 in the coarse saprolite.

370

#### 371 *4.3.1. Relative element mobility*

372 The relative mobility of major elements enables one to classify them into four  
 373 categories (Table 7): (i) the strongly depleted elements (depletion rate > 90%) such as Mn,  
 374 alkaline and alkali-earths, and P; (ii) the second category is made up of moderately leached  
 375 elements (leaching rate ~ 50%) such as Fe and Si; (iii) the third category is made up of  
 376 weakly leached elements such as Al and Ti; and (iv) the fourth category is that of moderately  
 377 leached elements to strongly accumulated elements in several materials notably Fe in the iron  
 378 duricrust, Mn in the Mn-bearing phases and Ti in some loose samples from the top of the  
 379 coarse saprolite.

380 Trace elements display a high mobility compared to the major elements. The notable  
381 accumulation is found within Mn-bearing phases with more than ten elements (Table 8).  
382 Three or four trace elements are accumulated in most samples from the upper part of the  
383 coarse saprolite. In all, trace elements are leached from this horizon (Table 8).

384 The behaviour of REE is very close to that of trace elements. Lanthanides are strongly  
385 depleted (rate > 60%) except in the Mn-bearing phases (Table 9).

386

#### 387 4.3.2. Mass balance calculation

388 The weathering of 1 m<sup>3</sup> of orthogneiss into coarse saprolite indicates: (i) strong  
389 depletion of an important quantity of Si (400 to 726 kg); (ii) low accumulation of Al in the  
390 whole fraction from the upper part (17.85 kg), in the yellowish brown plates (24.45 and 14.05  
391 kg); (iii) more pronounced depletion of Fe than Al (Table 9). However, Fe is strongly  
392 accumulated in the Mn-bearing phases (95.98 kg), in the iron duricrust from the bottom (1205  
393 kg) and from the top (615.05 kg); (iv) high Mn accumulation in the Mn-bearing phases  
394 (796.48 kg) and leaching of Mn in several samples (Table 9); (v) strong depletion of alkaline  
395 and alkali-earth elements (Table 9); (vi) moderate Ti and P depletion; (vii) accumulation of Ti  
396 in the upper whole fraction (1.31 kg), in the lower iron duricrust (1.44 kg), and in loose  
397 materials (Table 9); (viii) relative accumulation of Pb, Zr, Th, Hf, Sc, V and U in several  
398 loose samples (Table 10); (ix) relative accumulation of Zn, Sc, V, Pb, Th, U, Cr, Zn, Cu and  
399 Zr in the iron duricrust (Table 10); (xi) accumulation of Ba, Co, Pb, Ni, Zn, Sc, Cu, V, Y, Ga,  
400 U, Zr, Sb, Hf, Cd, Mo and Tl in the Mn-bearing phases (Table 10); (xii) high REE-enrichment  
401 in the Mn-bearing phases particularly Ce (Table 11); and (xiii) high REE-depletion in almost  
402 all the weathered samples (Table 11).

403

404

## 405 **5. Discussion**

### 406 **5.1. Petrology of orthogneiss**

407 The mineralogy and geochemistry indicate that orthogneiss are derived from plutonic  
408 rocks. These plutonic rocks might be heterogeneous and characterized by a very variable  
409 chemistry. The increase of porosity from the fresh rock to the slightly weathered one might be  
410 the result of the dissolution of primary minerals. In the slightly weathered rock, the slight  
411 increase in  $K_2O$  is due to adsorption and the increase in  $Al_2O_3$  is due to the silicate  
412 dissolution. The total moderate REE content might be due to the low proportion of primary  
413 REE-bearing minerals (allanite, monazite, xenotime and apatite) in the gneissic formations of  
414 South Cameroon (Braun et al., 1998). The negative Eu anomaly could be due to the partial  
415 dissolution of feldspars (Gromet and Silver, 1983; Panahi et al., 2000).

416

### 417 **5.2. Petrology of the coarse saprolite**

#### 418 *5.2.1. Morphology, mineralogy and distribution of major elements*

419 The presence of several phases in the coarse saprolite reveals that the high degree of  
420 weathering favours the thinning out of the large microbedded layers observed at the bottom.  
421 The mineralogical composition reveals two mineral phases: (i) the first one is composed of  
422 kaolinite, goethite, quartz, gibbsite, hematite and anatase. Kaolinite, goethite and gibbsite are  
423 characteristic of the well-drained environments in the rainforest region (Nguetnkam et al.,  
424 2006). The high quartz proportion is related to acid nature of the parent rock, as well as its  
425 slow dissolution during weathering. Goethite might be related to the high porosity that  
426 seemingly facilitates the stagnation of water in cavities. It has already been strongly  
427 documented that goethite is the main Fe-hydroxide that crystallizes in the saprolite zone  
428 (Tardy, 1993; Delvigne, 1998). Hematite results from the dehydration of goethite (Tardy,  
429 1993); and (ii) the second mineral phase is mainly manganiferous. It is characteristic of Mn-

430 rich materials which might derive directly from the accumulation of silicate residues and Mn  
431 within the parent rock (Bourgauth and Rabenhorst, 2011). The presence of the concentric  
432 structures could result from successive centripetal reorganizations (Beauvais and Nahon,  
433 1985).

434 The high SiO<sub>2</sub> contents might be related to the low degree of quartz dissolution  
435 (predominant mineral in these samples) in the rainforest zone (Nandjip, 2010). The sharp drop  
436 in the concentrations of alkaline and alkali-earth elements might be linked to a rapid  
437 dissolution of carrier minerals. The increase in aluminium contents might be correlated with  
438 an intense weathering and formation of kaolinite. High Mn contents have been noted in the  
439 lower horizons of Ni-laterites in New Caledonia (Golightly, 1979; Llorca and Monchoux,  
440 1991; Traoré, 2005). The positive correlations of SiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Y and U  
441 confirm that Si and Al are the main constituents of silicate residues. At the same time, Ti, P,  
442 Y and U might be associated with the relic minerals. The negative correlation between SiO<sub>2</sub>  
443 and Fe<sub>2</sub>O<sub>3</sub> is due to the weathering of ferromagnesian primary minerals (e.g., biotite, green  
444 hornblende) and the formation of goethite and hematite.

445

#### 446 5.2.2. Trace elements

447 The behaviour of trace elements is also dependent on the nature of weathered phases.  
448 The Mn-phases are characterized by their high contents in more than ten trace elements  
449 including Ni, Co, Zn, Cu, Ba, Pb, Y, Li, Cd, Mo and Tl. These highly concentrated elements  
450 might have been adsorbed by precipitation in the interlayer spaces of Mn-oxides (Brindley  
451 and Brown, 1980; Mishra et al., 2007). The high Cd contents are related to its fixation by  
452 adsorption on kaolinite (Vasconcelos et al., 2008). The highest Cr contents observed in the  
453 upper iron duricrust result from relative Cr accumulation as mineral species that were not  
454 identified by X-ray diffraction or from their incorporation in the lattice of goethite (Singh et

455 al., 2002). The negative Nb anomalies confirm the high mobilization of Nb during  
456 weathering. The correlation between  $\text{Fe}_2\text{O}_3$  and ferromagnesian trace elements reveals that  
457 ferromagnesian trace elements could be fixed by adsorption on goethite. Both positive  
458 correlations (Zr vs. Hf, Nb vs. U) show that Zr, Hf, Nb and U could be hosted by the same  
459 minerals such as zircon. The flat signature between Zr and Th shows that zircon is not  
460 probably the main Th-bearer.

461

### 462 5.2.3. Rare-earth elements

463 The low REE content in the loose materials and iron duricrust are characteristic of the  
464 weathered materials developed on acidic parent rock (Kamgang Kabeyene Beyala et al.,  
465 2009). This might be due to the rapid dissolution of REE-bearers (Braun et al., 1998).  
466 Meanwhile, the LREE-enrichment is inherited from the parent rock; this could be also due to  
467 the formation of secondary LREE-bearers such as rhabdophane ( $\text{LREEPO}_4 \cdot n\text{H}_2\text{O}$ ) (Braun et  
468 al., 1998). Braun and co-workers (1998) have reported that xenotime is the major HREE-  
469 bearer in gneiss; the low HREE content in the coarse saprolite is controlled by the dissolution  
470 of xenotime. The REE content in the Mn-bearing phases is very high (5632 ppm) as compared  
471 to those of the parent rock (209 ppm) and other weathered samples ( $\Sigma\text{REE}$  is 39-169 ppm).  
472 The formation and distribution of secondary minerals have an effect on the REE distribution  
473 (Harlavan et al., 2009). The positive correlation of HREE with LREE confirms the coherent  
474 behaviour of REE in the coarse saprolite. The positive correlation of the sum of three  
475 lanthanide (La, Ce and Nd) contents with the total REE content confirms the prevalence of  
476 La, Ce and Nd inside REE. The high Ce content (5202 ppm) in the Mn-bearing phases is due  
477 to the stronger sorption of  $\text{Ce}^{4+}$  or to the probable Ce precipitation as cerianite ( $\text{CeO}_2$ ) onto  
478 Mn-hydroxides (Huang and Wang, 2004; Laveuf and Cornu, 2010; this study). The strong  
479 positive Ce anomaly results from the lower mobility of  $\text{Ce}^{4+}$  than  $\text{REE}^{3+}$  (Yoshida et al., 2004;

480 Tanaka et al., 2010). This positive Ce anomaly is commonly observed in manganese oxides  
481 (Koppi et al., 1996; Ohnuki et al., 2008; Feng, 2010). Also, positive Ce anomaly in the  
482 kaolinitic white veins indicates that Ce might have been retained by adsorption into the  
483 intracellular crystals of kaolinite (Coppin et al., 2002; Vasconcelos et al., 2008). Laufer and  
484 co-workers (1984) have shown that Ce (IV) forms several hydroxyl complexes such as  
485  $[\text{Ce}(\text{OH})]^{3+}$  and  $[\text{Ce}(\text{OH})_2]^{2+}$ . The number of hydroxyls which are coordinated to Ce depends  
486 on the pH and the age of the solution (Laufer et al., 1984). The negative Ce anomalies in  
487 several samples show that cerium exists in trivalent form as other REE<sup>3+</sup> (Marsh, 1990;  
488 Leybourne et al., 2000; Ndjigui et al., 2009). The positive Eu anomalies might be due to either  
489 the dissolution of feldspars or to other supergene mechanism. Europium might partially  
490 substitute  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  in feldspars (Gromet and Silver, 1983; Panahi et al., 2000). The  
491 proportion of relic primary minerals (e.g.: feldspars, zircon) and secondary minerals (e.g.:  
492 kaolinite, goethite) control the major and trace element distribution (Dequency et al., 2006).

493

#### 494 5.2.4. Mass balance calculation

495 The high leaching of major elements might be related to the primary mineral  
496 weathering. The dissolution of feldspars in alkaline granites of NW Spain leads to  
497 considerable losses in Si, Na, Ca, K, Rb, Cs, Ba, U and P (Galán et al., 2007). The  
498 accumulation of Al, Ti and Fe is reported in the saprolite developed on granodioritic gneiss of  
499 Southern India (Tripathi and Rajamani, 2007) or on serpentinite in the South-East Cameroon  
500 (Ndjigui et al., 2008; Lambiv Dzemua et al., 2011). The Al accumulation might be due to the  
501 fact that aluminium is included within kaolinite. Those of Fe in the iron duricrust suggest an  
502 autochthonous origin by leaching of the uppermost ferruginous horizon (Dequency et al.,  
503 2002). The mobility of trace elements is intimately related to the weathering. The high REE-  
504 depletion might be linked to the dissolution of REE-bearers (Boulangé and Colin, 1994).

## 505 **6. Conclusion**

506 This study enables us to understand the mobilization and redistribution of major and  
507 trace elements inside the variegated coarse saprolite represented by three main constituents:

508 1) - loose materials have simple mineral assemblage (quartz, kaolinite and goethite) and  
509 slight positive Eu anomalies. However, strong positive Ce anomaly is observed in the  
510 kaolinitic white veins;

511 2) - iron duricrust is hematitic and goethitic with negative Ce and positive Eu  
512 anomalies;

513 3) - Mn-bearing phases are dominated by birnessite and cryptomelane groups. They  
514 show: (i) higher Mn and trace element contents than other weathered samples; (ii) high REE  
515 abundance; and (iii) strong positive Ce and Eu anomalies. Ce-oxides appear as fine grained in  
516 the Mn-bearing phases.

517 Weathering helps in accumulation of Al and Ti in the loose samples and numerous  
518 elements (Fe, Mn, Cr, Ni, Co, Zn, Sc, Cu, V, Ba, Pb, Y, Ga, Zr, Th and Tl) in the iron  
519 duricrust and Mn-bearing phases. This study shows that the nature and the proportion of  
520 weathered phases have a prominent influence on the horizon mineralogical and geochemical  
521 budget.

522

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529

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- 726

727

**Figure captions**

728 Fig. 1. Location and geological map of Yaoundé. A. Location of Yaoundé; B. Geological map  
729 of the SW Cameroon (modified after Maurizot et al., 1986); C. Geological map of the  
730 Yaoundé (modified after Owona et al. 2003).

731

732 Fig. 2. Macroscopic organization of the weathering profile.

733

734 Fig. 3. Chondrite-normalized (McDonough and Sun, 1995) multi-element patterns for  
735 orthogneiss and main constituents of the coarse saprolite (for acronyms, see Table 4).

736

737 Fig. 4. Chondrite-normalized (McDonough and Sun, 1995) rare-earth element patterns for  
738 orthogneiss.

739

740 Fig. 5. X-ray diffraction spectra for Mn-bearing phase of several grains from the black plates,  
741 indicating good peaks for birnessite and cryptomelane groups, as well as quartz.

742

743 Fig. 6. Parent rock-normalized multi-element patterns for the coarse saprolite (for acronyms,  
744 see Table 4).

745

746 Fig. 7. Harker diagrams of selected major and trace elements.

747

748 Fig. 8. Scattergrams of  $\text{Fe}_2\text{O}_3$  with selected ferromagnesian trace elements: A.  $\text{Fe}_2\text{O}_3$  vs. Cr;  
749 B.  $\text{Fe}_2\text{O}_3$  vs. Ni; C.  $\text{Fe}_2\text{O}_3$  vs. Co; D.  $\text{Fe}_2\text{O}_3$  vs. V.

750



751 Fig. 9. Scattergrams of Zr with selected trace elements: A. Zirconium vs. vanadium; B.  
752 Zirconium vs. hafnium; C. Zirconium vs. niobium; D. Zirconium vs. molybdenum; E.  
753 Zirconium vs. thorium; F. Zirconium vs. uranium.

754

755 Fig. 10. Scattergram of light rare-earth elements (LREE) with heavy rare-earth elements  
756 (HREE).

757

758 Fig. 11. Scattergrams of selected rare-earth elements with Zr, Pb and rare-earth elements: A.  
759 Cerium vs. zirconium; B. Cerium vs. lead; C. Cerium vs. light rare-earth elements; D. Sum of  
760 Total rare-earth element (REE) content vs. cerium; E. Three lanthanide (Ce, La and Nd)  
761 content vs. total rare-earth element (REE) content; F. Strontium vs. europium.

762

763 Fig. 12. A. Parent rock-normalized rare-earth element patterns for the coarse saprolite. B.  
764 Chondrite-normalized (McDonough and Sun, 1995) rare-earth element patterns for the coarse  
765 saprolite (for acronyms, see Table 5).

766

767 Fig. 13. BSE image of a grain displaying cyclic growth patterns in sample. The EDS spectra  
768 are shown for the Mn-bearing phase (bright contrast) and the aluminosilicate phase (dark-grey  
769 contrast). Several Ce-oxides grains (very bright contrast, each approximately 1 to 10 microns  
770 in diameter) appear marginal to the sample as indicated.

771

772 Fig. 14. BSE image of the Mn-bearing phase with a blow-out picture of Ce-oxide marginal to  
773 the sample (lower left) and a blow-out picture of the Mn-bearing phase intergrowth with the  
774 aluminosilicate phase (upper right).

775

776 Fig. 15. BSE image displaying the intergrowth of the Mn-bearing phase with the  
777 aluminosilicate phase.

778

779

780 Positive Eu-anomalies in all weathered samples.

781 Negative Ce-anomalies in the loose and iron duricrust samples, and positive one in the  
782 kaolinitic white veins.

783 High Mn, Co, Ba, Zr, Pb and Ce contents in the Mn-bearing phases. Strong positive  
784 Ce-anomaly is observed.

785 Strong depletion of several elements in the loose and iron duricrust samples.

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ACCEPTED MANUSCRIPT

Table 1  
Mineralogical composition of the parent rock and the main constituents of the coarse saprolite.

	Parent rock		Coarse saprolite										
	Fresh rock	Slightly weathered rock	Bottom			Top							
			Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Black phases	Yellowish brown plates		Dusky red iron duricrust		
Depth (m)				+ 0.10	+ 0.40	-	+1.70	+1.7 0	(a)	(b)	(c)	(d)	+2.50
Ref. code	CE 01	CE 02	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
Micas	++	++	-	-	-	-	-	-	-	-	-	-	-
Plagioclase	++	++	-	-	-	-	-	-	-	-	-	-	-
Green hornblende	+	+	-	-	-	-	-	-	-	-	-	-	-
Garnet	+	+	-	-	-	-	-	-	-	-	-	-	-
Orthose	+	+	-	-	-	-	-	-	-	-	-	-	-
Microcline	ε	ε	-	-	-	-	-	-	-	-	-	-	-
Epidote	ε	ε	-	-	-	-	-	-	-	-	-	-	-
Kaolinite	-	-	+++	+++	+++	+++	+	+	++	+++	+++	+++	+
Quartz	+++	+++	+++	+++	++	+++	+	++	+++	+++	+++	+++	++
Rutile	-	-	-	-	+	-	-	-	-	-	+	-	-
Goethite	-	-	+	+	+	++	+++	+	++	++	++	++	+++
Hematite	-	-	-	ε	ε	-	+++	-	-	-	-	-	+++
Cryptomelane	-	-	-	-	-	-	-	+++	-	-	-	-	-
Birnessite	-	-	-	-	-	-	-	+++	-	-	-	-	-
Anatase	-	-	+	-	+	-	+	-	+	+	-	-	+

+++ : very abundant; ++ : abundant; + : poorly represented; ε : trace; - : not identified.

Table 2

Major element composition of the parent rock and the main constituents of the coarse saprolite (% wt of oxides).

	d.l.	Parent rock		Coarse saprolite											
		Fresh material	Slightly weathered material	Bottom			Top					Yellowish brown plates			Dusky red iron duricrust
				Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	(a)	(b)	(c)	(d)		
Depth (m)	-	-	-	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50	
Ref. code	-	CE 01	CE 02	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05	
SiO <sub>2</sub>	0.01	61.56	61.84	61.80	61.25	64.83	58.03	26.70	27.97	56.10	57.01	59.05	60.30	30.79	
Al <sub>2</sub> O <sub>3</sub>	0.01	14.34	15.63	22.34	22.48	22.76	22.18	10.04	12.16	22.02	22.90	23.96	21.48	11.90	
Fe <sub>2</sub> O <sub>3</sub>	0.01	7.06	6.66	5.12	5.41	2.26	7.68	53.26	10.08	8.63	6.46	4.80	6.74	45.60	
MnO	0.01	0.13	0.11	0.01	0.01	0.01	0.01	0.01	33.86	0.01	0.01	0.01	0.01	0.01	
MgO	0.01	4.40	2.92	<dl	<dl	<dl	0.01	0.04	0.15	0.09	0.08	<dl	0.01	0.04	
CaO	0.01	4.71	3.64	0.03	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	
Na <sub>2</sub> O	0.01	2.72	2.58	<dl	<dl	<dl	0.02	<dl	0.11	0.02	0.02	<dl	0.02	<dl	
K <sub>2</sub> O	0.01	2.81	3.15	0.04	0.03	0.04	0.03	0.01	0.32	0.02	0.02	0.04	0.05	0.01	
TiO <sub>2</sub>	0.01	0.91	1.07	1.35	1.36	1.46	1.42	0.78	0.16	1.50	1.46	1.52	1.02	0.67	
P <sub>2</sub> O <sub>5</sub>	0.01	0.23	0.28	0.09	0.09	0.08	0.07	0.03	0.03	0.05	0.06	0.10	0.09	0.10	
LOI	0.05	0.43	1.64	9.37	9.38	9.23	9.97	8.93	12.41	10.45	10.64	10.17	9.60	10.24	
Total	-	99.30	99.52	100.15	100.03	100.69	99.44	99.82	97.28	98.91	98.68	99.67	97.28	99.38	
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	-	4.29	3.96	2.77	2.72	2.85	2.62	2.66	2.30	2.55	2.49	2.46	2.81	2.59	
Fe <sub>2</sub> O <sub>3</sub> /K <sub>2</sub> O	-	2.51	2.11	1.28	180.33	56.50	256.00	5326.00	31.50	431.50	323.00	120.00	134.80	4560.00	

d.l.: detection limits.

Note that the BaO content is 4.30 wt.% in the Mn-phases.

Ref. code: reference code.

Table 3  
Bulk density and porosity (in %) of the parent rock and the main constituents of the coarse saprolite.

	Parent rock		Coarse saprolite										
	Fresh rock	Slightly weathered rock	Bottom			Top							
			Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
									(a)	(b)	(c)	(d)	
Depth (m)	-	-	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50
Ref. code	CE 01	CE 02	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
Bulk density	2.01	2.06	1.28	0.93	1.10	1.38	2.53	2.36	1.42	1.32	1.14	1.29	1.66
Porosity	27.69	25.09	50.38	35.22	46.41	45.01	22.86	27.00	47.00	49.00	51.81	50.00	36.72

Table 4  
Trace element composition of the parent rock and the main constituents of the coarse saprolite (ppm).

	d.l.	Parent rock		Coarse saprolite										
		Fresh rock	Slightly weathered rock	Bottom			Top							
				Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
CE 01	CE 02	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	(a) CE 11	(b) CE 12	(c) CE 06	(d) CE 14	CE 05		
Cr	3.00	276.30	101.00	309.00	338.00	272.00	367.00	189.00	105.00	341.00	313.00	373.00	238.00	1641
Ni	1.60	84.50	30.30	21.00	20.20	16.30	25.90	33.00	79.80	25.10	24.50	26.60	21.10	18.20
Co	0.13	27.32	15.56	3.05	2.71	2.00	2.66	7.28	1716	2.79	2.20	2.27	3.44	5.37
Zn	7.00	105.00	110.00	40.00	38.00	37.00	54.00	155.00	242.00	62.00	51.00	53.00	53.00	143.00
Sc	1.10	17.60	15.10	23.80	25.10	25.50	26.50	33.80	28.00	28.80	27.00	24.40	24.70	48.80
Cu	1.40	38.30	12.50	18.80	21.30	20.60	37.10	22.90	333.90	43.90	31.40	23.90	34.80	82.10
V	0.80	134.90	123.40	212.10	196.70	190.60	236.80	282.40	126.30	246.80	217.40	233.70	163.20	459.00
Ba	0.80	916.00	871.90	319.60	323.40	311.70	181.70	18.60	51690	95.00	158.20	320.40	340.60	106.30
Pb	0.60	15.30	17.30	25.90	25.50	20.20	21.00	18.00	1315	17.10	22.50	27.30	28.80	25.10
Y	0.05	25.09	27.23	11.31	10.71	10.75	8.30	6.05	34.37	5.58	7.31	13.03	12.81	6.45
Ga	0.04	21.17	22.74	31.53	31.14	33.91	31.14	15.17	26.28	30.18	30.18	36.08	30.66	18.94
Th	0.02	10.72	11.67	15.80	13.76	32.66	15.55	10.53	5.80	11.68	12.91	18.13	14.65	42.50
U	0.01	1.52	1.79	2.20	2.19	2.61	2.65	2.65	1.75	2.81	2.57	2.24	1.90	3.76
Zr	6.00	132.00	224.00	260.00	224.00	316.00	241.00	147.00	129.00	293.00	275.00	199.00	160.00	83.00
Li	0.40	27.00	27.00	4.70	4.60	6.20	3.70	1.50	6.30	3.40	3.80	5.10	3.80	1.70
Sb	0.04	0.01	0.05	0.10	0.09	0.14	0.06	0.07	0.31	<dI	<dI	0.12	0.04	0.11
Nb	0.03	12.78	15.12	16.33	17.00	20.12	17.70	8.45	7.30	17.40	15.15	18.15	14.77	7.94
Hf	0.14	3.66	5.91	6.93	6.15	8.81	6.44	3.86	3.59	7.66	7.22	5.31	4.43	2.41
Be	0.04	1.89	1.93	2.51	2.43	2.82	2.22	1.16	1.37	2.28	2.45	2.66	2.47	1.47
Cd	0.01	0.14	0.13	0.02	0.02	0.01	0.03	0.05	26.51	0.01	0.02	0.01	0.03	0.03
Mo	0.08	4.05	0.64	1.67	1.81	1.94	1.99	0.96	7.91	1.55	1.40	1.94	2.45	4.17
Sn	0.16	3.23	3.22	4.27	4.31	4.82	4.15	2.45	2.77	3.58	4.37	5.71	3.77	1.40
Tl	0.01	0.52	0.60	0.01	0.08	0.01	0.02	0.01	34.04	0.01	0.01	0.03	0.09	<dI
W	0.05	0.72	0.34	0.44	0.35	0.54	0.51	0.22	0.27	0.59	0.59	0.50	0.27	0.28
Cs	0.01	3.77	4.20	0.15	0.12	0.12	0.25	0.04	0.07	0.12	0.12	0.35	0.17	0.06
Rb	0.23	114.46	134.75	1.79	1.30	1.56	1.97	0.36	1.43	1.00	1.03	2.98	1.75	0.60
Sr	0.60	382.20	336.80	49.20	48.80	45.01	31.20	4.80	13.60	19.80	28.40	54.60	57.50	20.20
Ta	0.02	0.76	0.91	0.93	1.03	1.07	1.02	0.52	0.46	1.03	0.83	1.09	0.86	0.50
Th/U	-	7.05	6.52	7.18	6.28	12.51	5.87	3.97	3.31	4.16	5.02	8.09	7.71	55.92
Th/Co	-	0.39	0.75	5.18	5.07	16.33	5.84	1.45	0.00	4.19	5.87	7.99	4.26	3.53

d.l.: detection limits.

Table 5

Rare-earth element composition of the parent rock and the main constituents of the coarse saprolite (ppm).

REE	d.l.	Parent rock		Coarse saprolite											
		Fresh rock	Slightly weathered rock	Bottom			Top				Yellowish brown plates				Dusky red iron duricrust
				Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	(a)	(b)	(c)	(d)		
		CE 01	CE 02	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05	
La	0.04	43.04	44.92	23.95	24.63	20.61	17.47	4.57	166.89	10.91	14.56	25.76	22.48	8.34	
Ce	0.12	87.02	86.86	35.92	33.31	117.58	27.00	9.15	5,202	17.15	21.77	39.54	33.40	12.62	
Pr	0.01	10.54	10.55	4.41	4.39	3.58	3.72	2.27	40.06	2.48	3.15	5.33	4.47	2.63	
Nd	0.06	40.79	41.32	16.79	16.86	13.58	14.20	9.40	123.75	9.61	12.66	20.81	17.42	10.87	
Sm	0.01	7.86	7.60	4.08	4.20	3.34	3.39	3.04	26.68	2.42	3.20	5.07	4.46	3.28	
Eu	0.03	1.56	1.56	1.08	1.11	0.90	0.88	0.70	9.092	0.64	0.88	1.30	1.25	0.80	
Gd	0.01	6.21	6.15	3.88	4.16	3.49	3.06	2.26	15.45	2.09	2.91	4.62	4.44	2.50	
Tb	0.002	0.88	0.89	0.56	0.61	0.53	0.44	0.45	3.21	0.32	0.43	0.67	0.64	0.43	
Dy	0.01	4.91	5.25	3.12	3.24	2.84	2.48	2.79	17.18	1.82	2.37	3.59	3.62	2.58	
Ho	0.003	0.91	0.98	0.51	0.52	0.49	0.41	0.49	3.08	0.30	0.37	0.61	0.61	0.44	
Er	0.01	2.50	2.66	1.20	1.21	1.17	1.00	1.48	9.45	0.74	0.90	1.47	1.42	1.24	
Tm	0.002	0.35	0.37	0.14	0.14	0.14	0.13	0.25	1.63	0.10	0.12	0.18	0.17	0.20	
Yb	0.01	2.22	2.29	0.80	0.78	0.83	0.86	1.95	12.40	0.70	0.74	1.05	0.96	1.42	
Lu	0.002	0.32	0.33	0.10	0.09	0.11	0.11	0.26	1.75	0.09	0.09	0.13	0.12	0.19	
ΣREE	-	209.10	211.73	96.56	95.24	169.17	75.16	39.06	5632.61	49.38	64.15	110.13	95.45	47.53	
ΣLREE	-	190.81	192.81	86.23	84.51	159.59	66.66	29.14	5568.48	43.22	56.22	97.81	83.48	38.53	
ΣHREE	-	18.29	18.92	10.34	10.73	9.59	8.50	9.92	64.13	6.16	7.92	12.32	11.10	8.99	
a.	-	10.44	10.19	8.34	7.87	16.65	7.84	2.94	86.83	7.01	7.09	7.94	6.97	4.28	
Ce/Ce* (1)	-	0.99	0.97	-	-	-	-	-	-	-	-	-	-	-	
Eu/Eu* (1)	-	0.68	0.69	-	-	-	-	-	-	-	-	-	-	-	
Ce/Ce* (2)	-	-	-	0.86	0.78	3.35	0.82	0.69	15.57	0.81	0.79	0.83	0.82	0.66	
Eu/Eu* (2)	-	-	-	1.22	1.19	1.18	1.23	1.20	2.01	1.40	1.30	1.20	1.25	1.25	
(La/Yb) <sub>N</sub>	-	13.19	13.35	1.51	1.63	1.29	1.05	0.12	0.69	0.80	1.02	1.26	1.21	0.30	

d.l.: detection limits.

a. = LREE/ HREE.

$$\text{Ce anomaly} = (\text{Ce}/\text{Ce}^*) (1) = (\text{Ce}_{\text{orthogneiss}}/\text{Ce}_{\text{chondrite}})/(\text{La}_{\text{orthogneiss}}/\text{La}_{\text{chondrite}})^{0.5} (\text{Pr}_{\text{orthogneiss}}/\text{Pr}_{\text{chondrite}})^{0.5}.$$

$$\text{Eu anomaly} = (\text{Eu}/\text{Eu}^*) (1) = (\text{Eu}_{\text{orthogneiss}}/\text{Eu}_{\text{chondrite}})/(\text{Sm}_{\text{orthogneiss}}/\text{Sm}_{\text{chondrite}})^{0.5} (\text{Gd}_{\text{orthogneiss}}/\text{Gd}_{\text{chondrite}})^{0.5}.$$

$$\text{Ce anomaly} = (\text{Ce}/\text{Ce}^*) (2) = (\text{Ce}_{\text{weathered sample}}/\text{Ce}_{\text{orthogneiss}})/(\text{La}_{\text{weathered sample}}/\text{La}_{\text{orthogneiss}})^{0.5} (\text{Pr}_{\text{weathered sample}}/\text{Pr}_{\text{orthogneiss}})^{0.5}.$$

$$\text{Eu anomaly} = (\text{Eu}/\text{Eu}^*) (2) = (\text{Eu}_{\text{weathered sample}}/\text{Eu}_{\text{orthogneiss}})/(\text{Sm}_{\text{weathered sample}}/\text{Sm}_{\text{orthogneiss}})^{0.5} (\text{Gd}_{\text{weathered sample}}/\text{Gd}_{\text{orthogneiss}})^{0.5}.$$

$$\text{For rock samples: } (\text{La}/\text{Yb})_N = (\text{La}_{\text{orthogneiss}}/\text{La}_{\text{chondrite}})/(\text{Yb}_{\text{orthogneiss}}/\text{Yb}_{\text{chondrite}}).$$

$$\text{For weathered samples: } (\text{La}/\text{Yb})_N = (\text{La}_{\text{weathered sample}}/\text{La}_{\text{orthogneiss}})/(\text{Yb}_{\text{weathered sample}}/\text{Yb}_{\text{orthogneiss}}).$$

Table 6  
Geochemical balance evaluation of major elements in the coarse saprolite by isovolumetric method (%).

	Coarse saprolite										
	Bottom			Top							
	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
							(a)	(b)	(c)	(d)	
Depth (m)	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50
Ref. code	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
Si	-36.07	-53.96	-42.37	-35.28	-45.28	-46.65	-35.62	-39.18	-45.60	-37.13	-58.69
Al	-0.79	-27.47	-13.14	<b>6.19</b>	-11.87	-0.44	<b>8.48</b>	<b>4.87</b>	-5.24	-3.87	-31.47
Fe	-53.82	-64.54	-82.48	-25.31	<b>849.56</b>	<b>67.64</b>	-13.64	-39.91	-61.44	-38.73	<b>433.42</b>
Mn	-95.10	-96.44	-95.79	-94.72	-90.32	<b>30482</b>	-94.57	-94.95	-95.64	-95.06	-93.65
Mg	-	-	-	-99.84	-98.86	-96.00	-98.55	-98.81	-	-99.85	-99.25
Ca	-99.59	-99.80	-99.77	-99.71	-99.47	-99.25	-99.70	-99.72	-99.76	-99.73	-99.65
Na	-	-	-	-99.50	-	-95.25	-99.48	-99.52	-	-99.53	-
K	-99.09	-99.51	-99.22	-99.27	-99.55	-86.63	-99.50	-99.53	-99.19	-98.86	-99.71
Ti	-5.53	-30.85	-12.20	<b>7.13</b>	<b>7.89</b>	-79.36	<b>16.45</b>	<b>5.36</b>	-5.26	-28.06	-39.19
P	-75.08	-81.89	-80.96	-79.10	-83.58	-84.69	-84.64	-82.87	-75.34	-74.89	-64.09
LOI	<b>1288</b>	<b>909</b>	<b>1075</b>	<b>1492</b>	<b>2541</b>	<b>3281</b>	<b>1617</b>	<b>1525</b>	<b>1241</b>	<b>1333</b>	<b>1867</b>



Table 7

Geochemical balance evaluation of trace elements in the coarse saprolite by isovolumetric method (%).

	Coarse saprolite										
	Bottom			Top							
	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
							(a)	(b)	(c)	(d)	
Depth (m)	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50
Ref. code	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
Cr	-28.78	-43.40	-46.13	-8.81	-13.90	-55.38	-12.81	-25.61	-23.43	-44.72	<b>390.50</b>
Ni	-84.17	-88.94	-89.44	-78.96	-50.84	<b>10.88</b>	-78.01	-80.96	-82.15	-83.97	-82.21
Co	-92.89	-95.41	-95.99	-93.32	-66.46	<b>7275</b>	-92.79	-94.71	-95.29	-91.92	-83.77
Zn	-75.74	-83.26	-80.72	-64.69	<b>85.81</b>	<b>170.61</b>	-58.28	-68.10	-71.37	-67.60	<b>12.48</b>
Sc	-13.89	-34.01	-20.71	<b>3.38</b>	<b>141.73</b>	<b>86.79</b>	<b>15.60</b>	<b>0.75</b>	-21.37	-9.93	<b>128.99</b>
Cu	-68.74	-74.27	-70.56	-33.49	-24.74	<b>923.61</b>	-19.02	-46.16	-64.61	-41.69	<b>77.03</b>
V	<b>0.13</b>	-32.53	-22.68	<b>20.52</b>	<b>163.50</b>	<b>9.93</b>	<b>29.25</b>	<b>5.83</b>	-1.74	-22.36	<b>181.00</b>
Ba	-77.78	-83.66	-81.38	-86.38	-97.44	<b>6526</b>	-92.67	-88.66	-80.16	-76.14	-90.42
Pb	<b>7.80</b>	-22.89	-27.75	-5.77	<b>48.08</b>	<b>9991</b>	-21.04	-3.42	<b>1.20</b>	<b>20.81</b>	<b>35.49</b>
Y	-71.29	-80.25	-76.55	-77.29	-69.65	<b>60.84</b>	-84.29	-80.87	-70.55	-67.23	-78.77
Ga	-5.15	-31.94	-12.34	<b>0.99</b>	-9.80	<b>45.75</b>	<b>0.71</b>	-6.38	-3.34	-7.05	-26.11
Th	-6.13	-40.60	<b>66.74</b>	-0.43	<b>23.62</b>	-36.47	-23.03	-20.90	-4.07	-12.31	<b>227.44</b>
U	-7.61	-33.21	-5.65	<b>20.23</b>	<b>120.09</b>	<b>35.47</b>	<b>31.17</b>	11.32	-16.07	-19.68	<b>105.02</b>
Zr	<b>25.43</b>	-21.48	<b>31.01</b>	<b>25.35</b>	<b>40.17</b>	<b>14.74</b>	<b>56.81</b>	<b>36.82</b>	-14.50	-22.21	-48.07
Li	-88.91	-92.12	-87.73	-90.59	-93.01	-72.60	-91.10	-90.76	-89.29	-90.97	-94.80
Sb	<b>961.36</b>	<b>594.03</b>	<b>1177</b>	<b>587</b>	<b>1368</b>	<b>5966</b>	-	-	<b>1034</b>	<b>327.86</b>	<b>1,414</b>
Nb	-18.66	-38.47	-13.89	-4.97	-16.75	-32.95	-3.83	-22.15	-19.49	-25.85	-48.69
Hf	<b>20.58</b>	-22.25	<b>31.73</b>	<b>20.81</b>	<b>32.75</b>	<b>15.17</b>	<b>47.86</b>	<b>29.55</b>	-17.71	-22.32	-45.62
Be	-15.43	-40.51	-18.34	-19.36	-22.75	-14.89	-14.78	-14.87	-20.18	-16.13	-35.77
Cd	-90.20	-95.15	-95.02	-86.08	-56.87	<b>21667</b>	-93.58	-93.11	-94.45	-86.54	-80.36
Mo	-73.74	-79.32	-73.79	-66.26	-70.16	<b>129.32</b>	-72.96	-77.30	-72.83	-61.18	-14.97
Sn	-15.81	-38.26	-18.33	-11.79	-4.53	<b>0.69</b>	-21.70	-11.15	<b>0.26</b>	-25.09	-64.20
Tl	-98.52	-99.37	-98.94	-97.35	-98.30	<b>7616</b>	-99.05	-99.37	-96.72	-89.34	-
W	-61.08	-77.51	-58.96	-51.37	-61.54	-55.97	-42.11	-46.19	-60.61	-75.93	-67.88
Cs	-97.45	-98.59	-98.21	-95.42	-98.73	-97.79	-97.71	-97.84	-94.68	-97.19	-98.73
Rb	-99.00	-99.47	-99.25	-98.82	-99.60	-98.53	-99.38	-99.41	-98.52	-99.02	-99.57
Sr	-91.80	-94.09	-93.56	-94.40	-98.42	-95.82	-96.34	-95.12	-91.90	-90.34	-95.64

Table 8

Geochemical balance evaluation of rare-earth elements in the coarse saprolite by isovolumetric method (%).

	Coarse saprolite										
	Bottom			Top							
	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
							(a)	(b)	(c)	(d)	
Depth (m)	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50
Ref. code	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
La	-64.56	-73.52	-73.79	-72.13	-86.64	<b>355.28</b>	-82.09	-77.78	-66.05	-66.48	-84.00
Ce	-73.71	-82.29	-26.05	-78.70	-86.76	<b>6919</b>	-86.08	-83.57	-74.23	-75.37	-88.02
Pr	-73.37	-80.73	-81.43	-75.81	-72.85	<b>346.26</b>	-83.37	-80.36	-71.35	-72.79	-79.43
Nd	-73.79	-80.99	-81.78	-76.10	-70.99	<b>256.21</b>	-83.36	-79.62	-71.06	-72.59	-77.99
Sm	-66.98	-75.26	-76.76	-70.36	-51.28	<b>298.58</b>	-78.22	-73.26	-63.39	-63.58	-65.56
Eu	-55.84	-67.00	-68.37	-61.07	-43.40	<b>584.75</b>	-70.91	-62.85	-52.63	-48.75	-57.73
Gd	-60.15	-69.02	-69.23	-66.10	-54.09	<b>192.26</b>	-76.26	-69.25	-57.73	-54.08	-66.74
Tb	-59.40	-68.30	-67.34	-65.63	-35.85	<b>326.70</b>	-74.40	-68.09	-57.16	-53.34	-59.41
Dy	-59.47	-69.49	-68.38	-65.37	-28.39	<b>310.93</b>	-73.75	-68.29	-58.56	-52.62	-56.61
Ho	-63.83	-73.31	-70.67	-68.90	-32.27	<b>299.72</b>	-76.97	-72.86	-61.71	-57.10	-59.66
Er	-69.33	-77.64	-74.77	-72.54	-25.69	<b>343.59</b>	-79.03	-76.44	-66.63	-63.44	-59.10
Tm	-74.16	-81.89	-77.64	-73.91	-9.37	<b>445.47</b>	-79.01	-78.23	-71.64	-69.56	-53.99
Yb	-76.91	-83.80	-79.63	-73.34	<b>10.60</b>	<b>556.56</b>	-77.76	-78.20	-73.11	-72.24	-47.03
Lu	-79.31	-86.72	-81.01	-75.53	<b>1.25</b>	<b>547.44</b>	-79.05	-80.53	-76.74	-76.11	-51.80

Table 9

Mass balance calculations of major elements in the coarse saprolite by isovolumetric method (kg/m<sup>3</sup>).

	Coarse saprolite										
	Bottom			Top							
	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
							(a)	(b)	(c)	(d)	
Depth (m)	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50
Ref. code	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
Si	-446.32	-667.73	-524.23	-436.54	-560.33	-577.26	-440.74	-484.82	-564.19	-459.49	-726.24
Al	-2.28	-79.17	-37.87	<b>17.85</b>	-34.22	-1.26	<b>24.45</b>	<b>14.05</b>	-15.09	-11.14	-90.69
Fe	-76.37	-91.59	-117.05	-35.92	<b>1205</b>	<b>95.98</b>	-19.36	-56.63	-	-54.96	<b>615.05</b>
Mn	-2.49	-2.52	-2.50	-2.48	-2.36	<b>796.48</b>	-2.47	-2.48	-2.50	-2.48	-2.45
Mg	-	-	-	-88.30	-87.43	-84.90	-87.16	-87.38	-88.44	-88.31	-87.78
Ca	-94.29	-94.49	-94.45	-94.40	-94.17	-93.96	-94.39	-94.41	-94.44	-94.41	-94.34
Na	-	-	-	-54.40	-	-52.08	-54.39	-54.41	-	-54.41	-
K	-55.97	-56.20	-56.04	-56.07	-56.23	-48.93	-56.20	-56.22	-56.03	-55.84	-56.32
Ti	-1.01	-5.64	-2.23	<b>1.31</b>	<b>1.44</b>	-14.52	<b>+3.01</b>	<b>+0.98</b>	-0.96	-5.13	-7.17
P	-3.47	-3.79	-3.74	-3.66	-3.86	-3.92	-3.91	-3.83	-3.48	-3.46	-2.96
LOI	<b>11.29</b>	<b>78.59</b>	<b>92.89</b>	<b>128.94</b>	<b>217.29</b>	<b>284.23</b>	<b>139.75</b>	<b>131.81</b>	<b>107.30</b>	<b>115.20</b>	<b>161.34</b>

Table 10

Mass balance calculations of trace elements in the coarse saprolite by isovolumetric method ( $\text{g/m}^3$ ).

	Coarse saprolite										
	Bottom			Top							
	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
							(a)	(b)	(c)	(d)	
Depth (m)	-	+0.10	+0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50
Ref. code	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05
Cr	-160	-241	-256	-49	-77	-308	-71	-142	-130	-248	<b>2 169</b>
Ni	-143	-151	-152	-134	-86	<b>18</b>	-134	-138	-140	-143	-140
Co	-51	-52	-53	-51	-36	<b>3995</b>	-51	-52	-52	-50	-46
Zn	-160	-176	-170	-137	<b>181</b>	<b>360</b>	-123	-144	-151	-143	<b>26</b>
Sc	-5	-12	-7	<b>1</b>	<b>50</b>	<b>31</b>	<b>6</b>	0	-8	-4	<b>46</b>
Cu	-53	-57	-54	-26	-19	<b>711</b>	-15	-36	-50	-32	<b>59</b>
V	0	-88	-61	<b>56</b>	<b>443</b>	<b>27</b>	<b>79</b>	<b>16</b>	-5	-61	<b>491</b>
Ba	-1432	-1540	-1498	-1590	-1794	<b>120147</b>	-1706	-1632	<b>1476</b>	-1402	-1665
Pb	<b>2</b>	-7	-9	-2	<b>15</b>	<b>3073</b>	-6	-1	0	<b>6</b>	<b>+11</b>
Y	-36	-40	-39	-39	-35	<b>31</b>	-43	-41	-36	-34	-40
Ga	-2	-14	-5	0	-4	<b>19</b>	0	-3	-1	-3	-11
Th	-1	-9	<b>14</b>	0	<b>5</b>	-8	-5	-5	-1	-3	<b>49</b>
U	0	-1	0	<b>1</b>	<b>4</b>	<b>1</b>	<b>1</b>	0	0	-1	<b>+3</b>
Zr	<b>67</b>	-57	<b>82</b>	<b>67</b>	<b>107</b>	<b>39</b>	<b>51</b>	<b>98</b>	-38	-59	-128
Li	-48	-50	-47	-49	-50	-39	-49	-49	-48	-49	-51
Nb	-5	-10	-4	-1	-4	-8	-1	-6	-5	-7	-13
Hf	<b>2</b>	-2	<b>2</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>4</b>	<b>2</b>	-1	-2	-3
Be	-1	-2	-1	-1	-1	-1	-1	-1	-1	-1	-1
Mo	-6	-6	-6	-5	-6	<b>11</b>	-6	-6	-6	-5	-1
Sn	-1	-2	-1	-1	0	0	-1	-1	0	-2	-4
Tl	-1	1	-1	-1	-1	<b>79</b>	-1	-1	-1	-1	-
W	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
Cs	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7
Rb	-228	-229	-228	-227	-229	-227	-229	-229	-227	-228	-229
Sr	-705	-723	-719	-725	-756	-736	-740	-731	-706	-694	-735

Table 11

Mass balance calculations of rare-earth elements in the coarse saprolite by isovolumetric method ( $\text{g/m}^3$ ).

	Coarse saprolite											
	Bottom			Top								
	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust		
							(a)	(b)	(c)	(d)		
Depth (m)	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40	+2.50	
Ref. code	CE 04	CE 07	CE 08	CE 10	CE 09	CE 13	CE 11	CE 12	CE 06	CE 14	CE 05	
La	-56	-64	-64	-62	-75	<b>307</b>	-71	-67	-57	-58	-73	
Ce	-129	-144	-46	-138	-52	<b>12102</b>	-151	-146	-130	-132	-154	
Pr	-16	-17	-16	-16	-15	<b>73</b>	-18	-17	-15	-15	-17	
Nd	-60	-66	-67	-62	-58	<b>210</b>	-68	-65	-58	-60	-64	
Sm	-11	-12	-12	-11	-8	<b>47</b>	-12	-12	-10	-10	-10	
Eu	-2	-2	-2	-2	-1	<b>18</b>	-2	-2	-2	-2	-2	
Gd	-8	-9	-9	-8	-7	<b>24</b>	-10	-9	-7	-7	-8	
Tb	-1	-1	-1	-1	-1	<b>6</b>	-1	-1	-1	-1	-1	
Dy	-6	-7	-7	-6	-3	<b>31</b>	-7	-7	-6	-5	-6	
Ho	-1	-1	-1	-1	-1	<b>5</b>	-1	-1	-1	-1	-1	
Er	-3	-4	-4	-4	-1	<b>17</b>	-4	-4	-3	-3	-3	
Tm	-1	-1	-1	-1	0	<b>3</b>	-1	-1	-1	0	0	
Yb	-3	-4	-4	-3	0	<b>25</b>	-3	-3	-3	-3	-2	
Lu	-1	-1	-1	0	0	<b>3</b>	-1	-1	0	0	0	

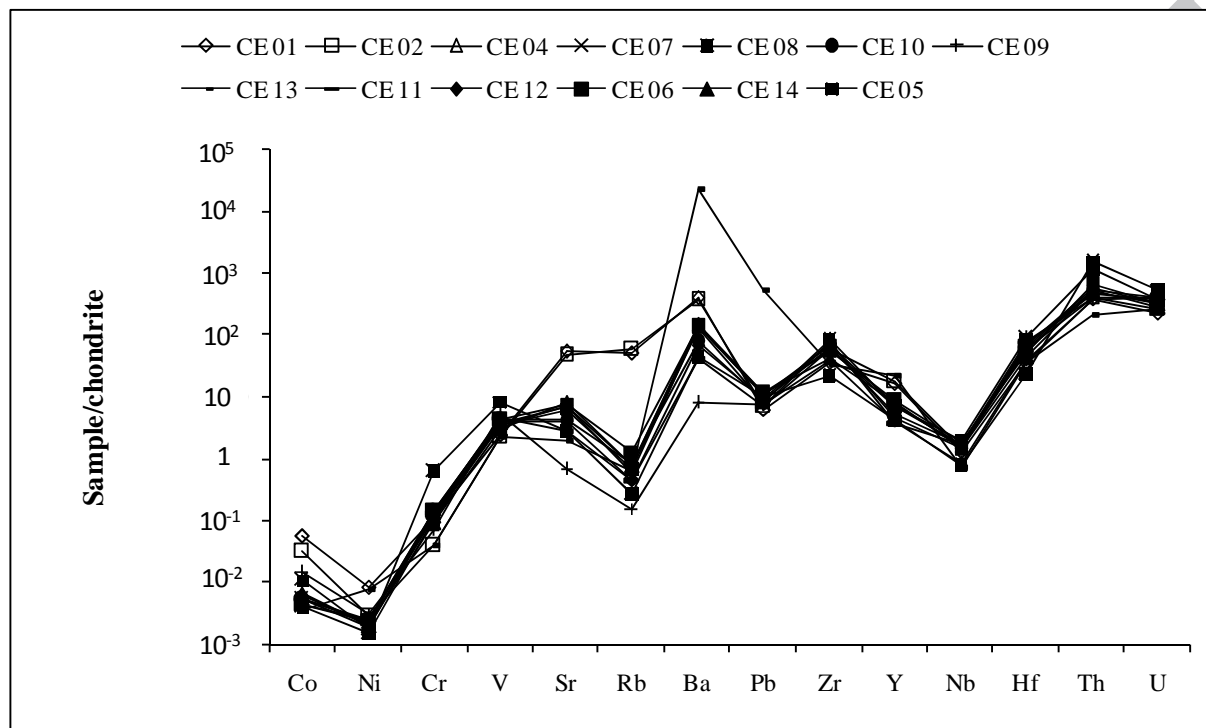


Figure 3

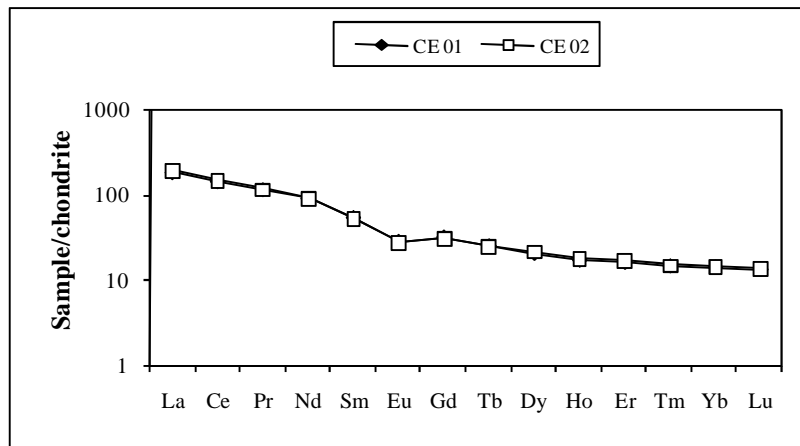


Figure 4

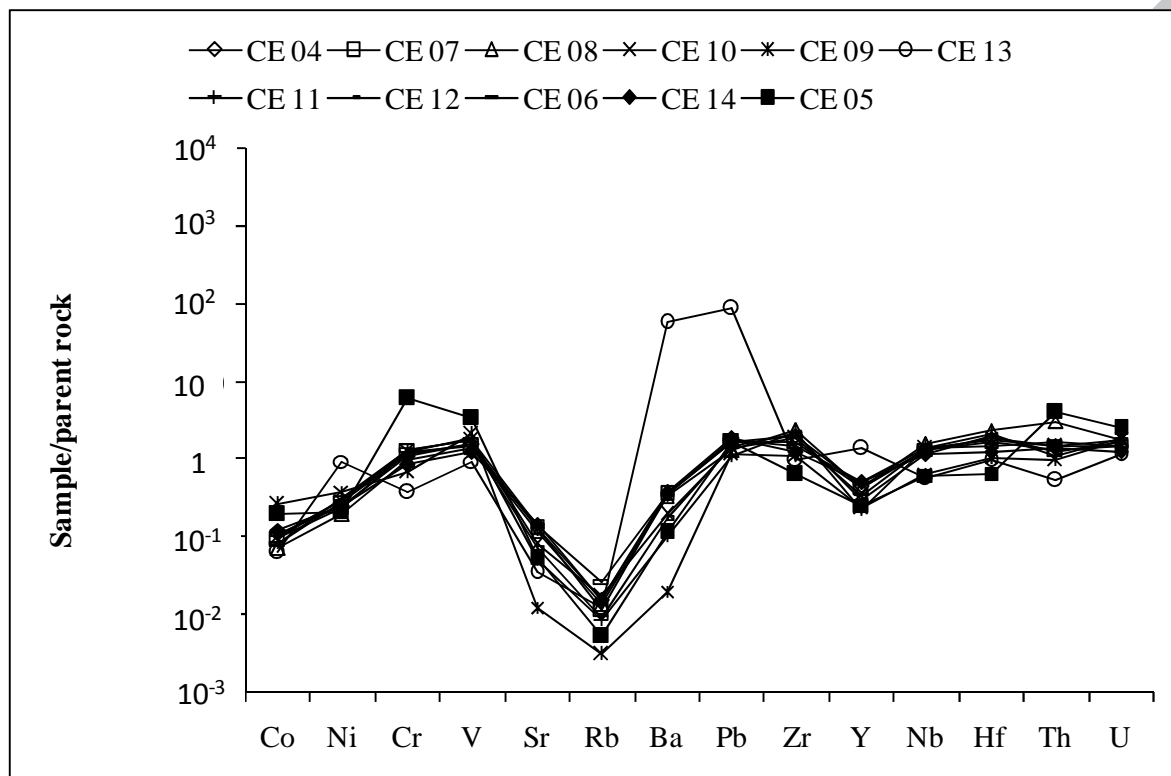


Figure 6



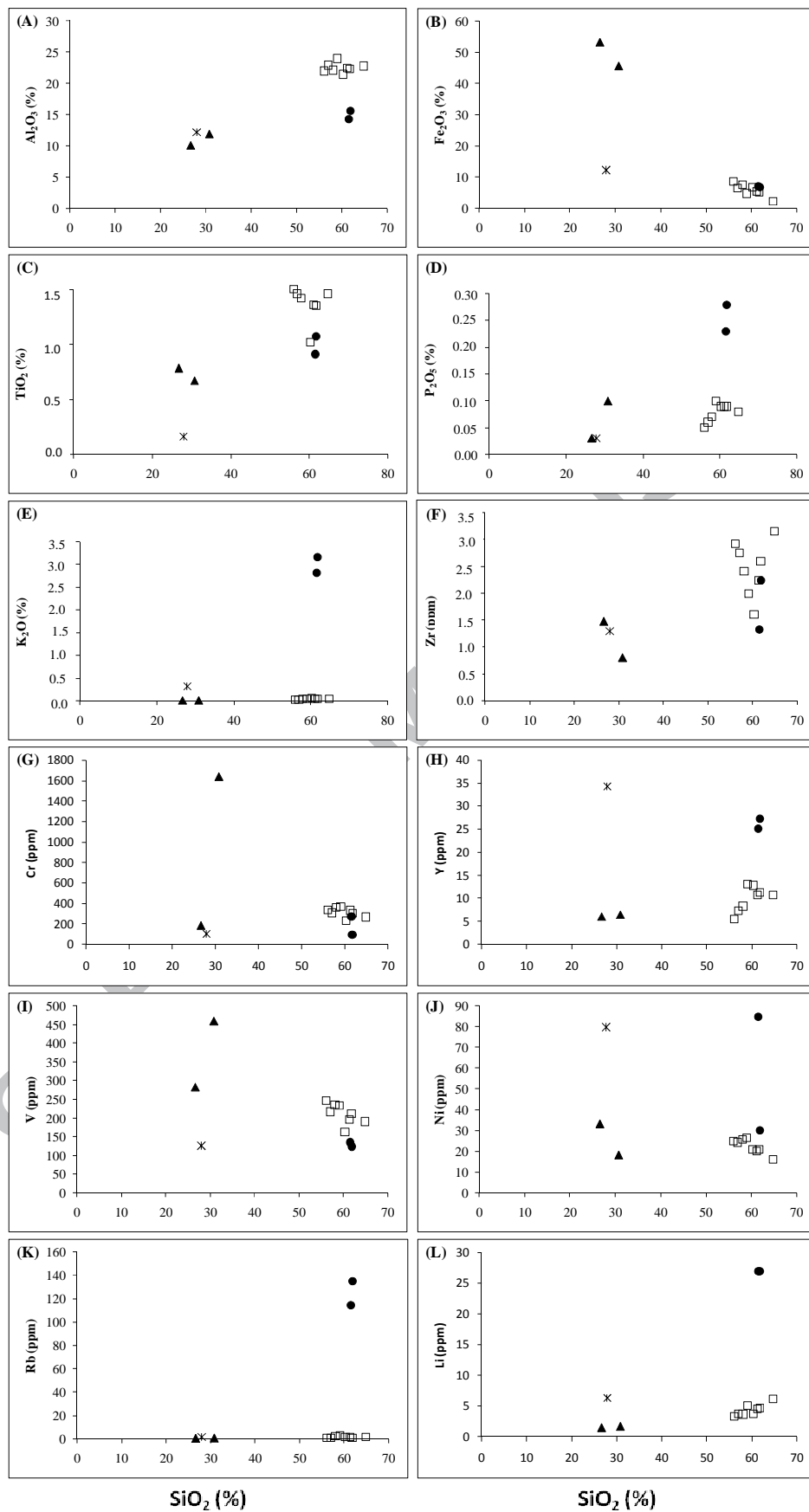


Figure 7

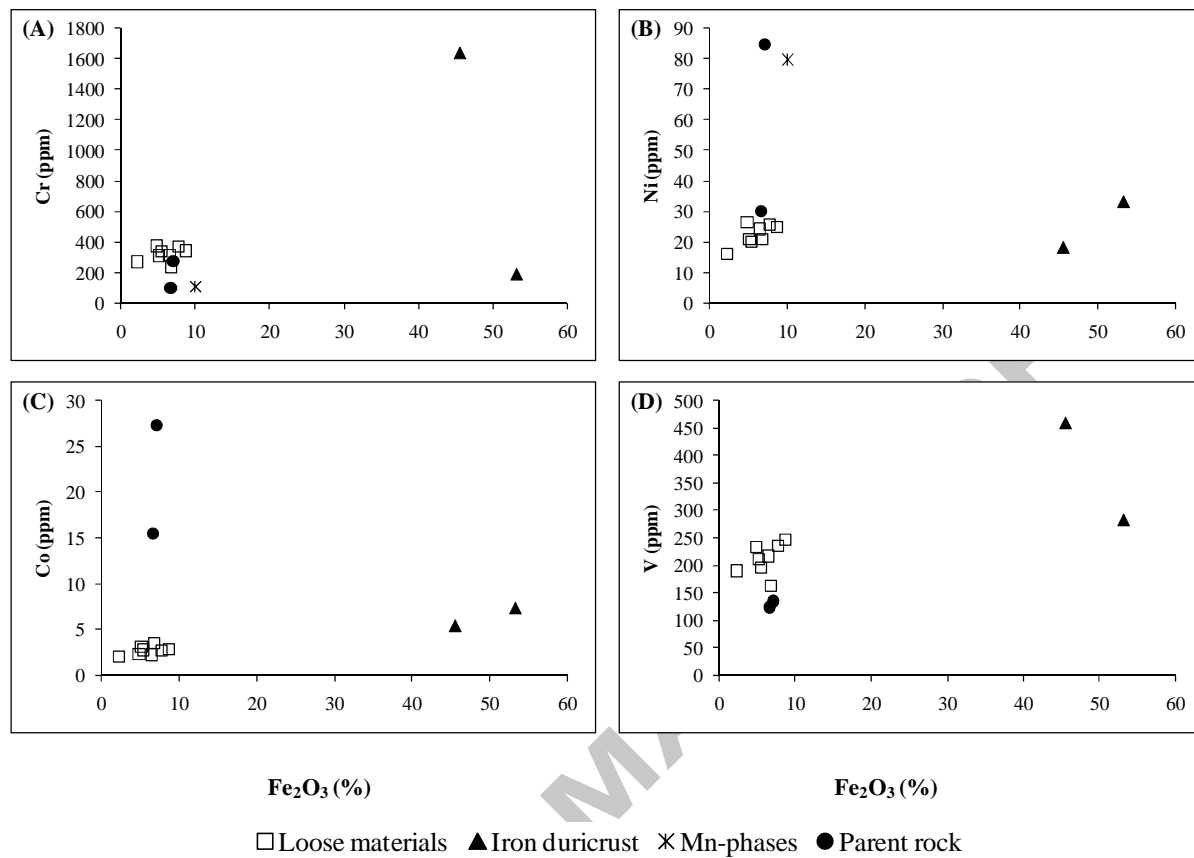


Figure 8

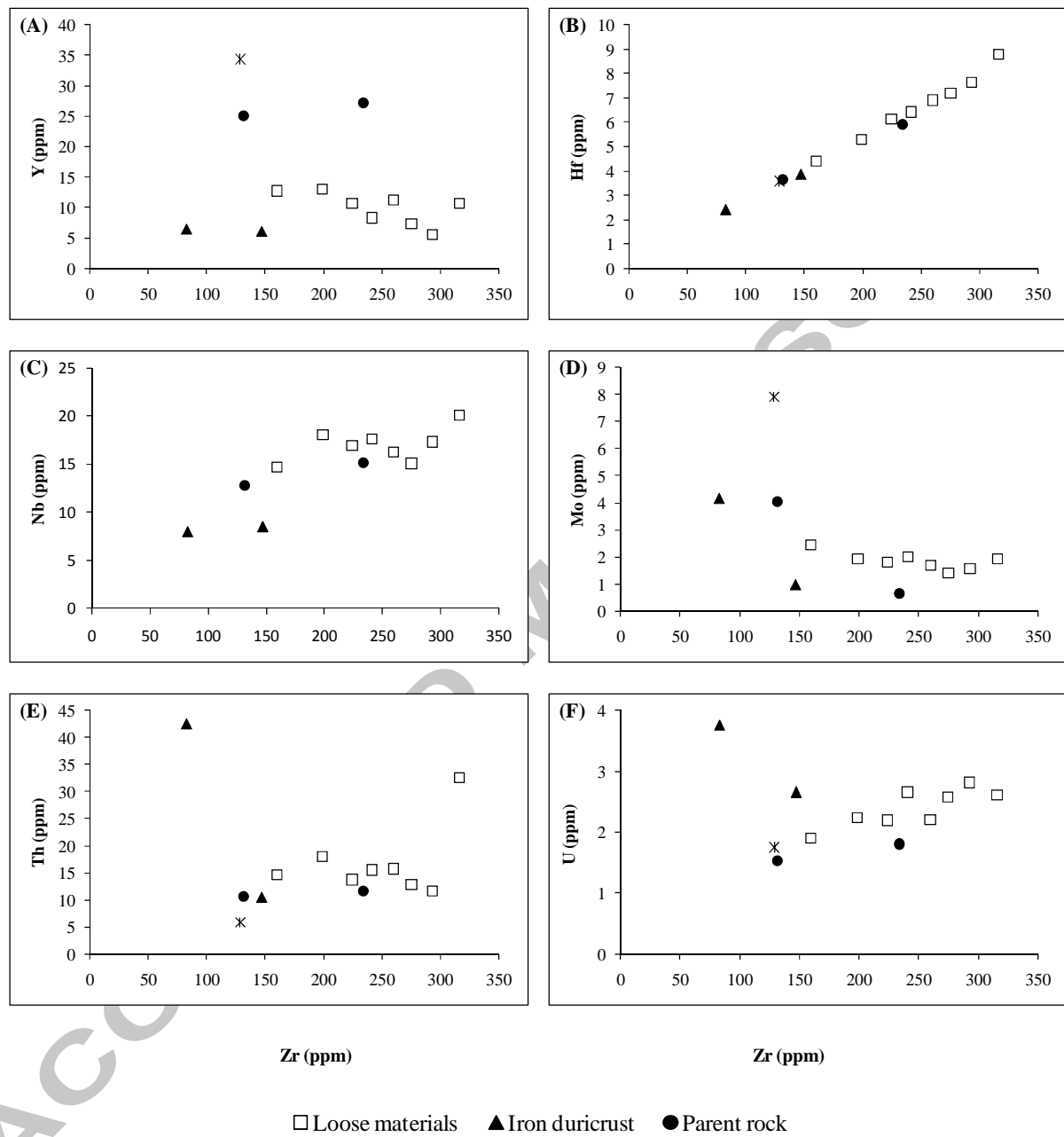
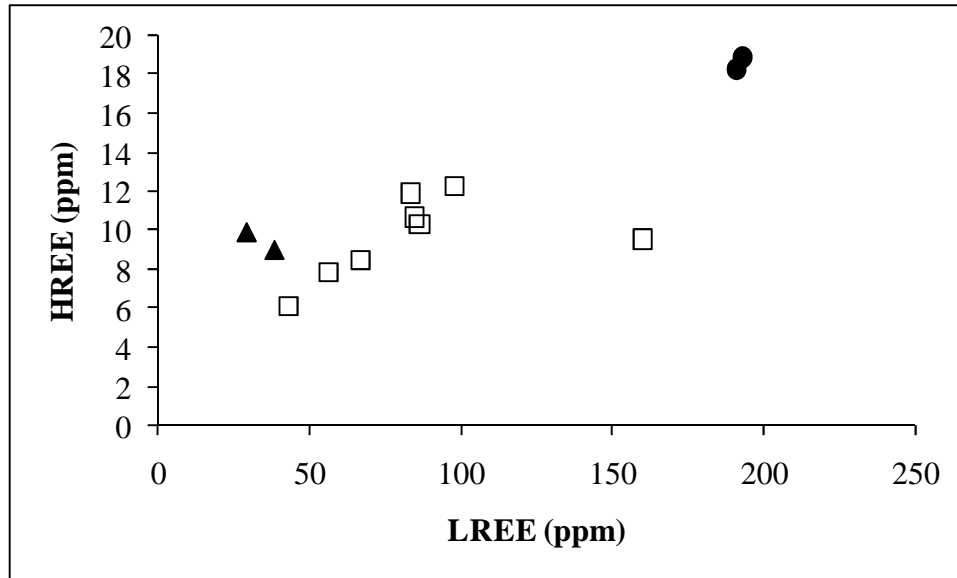
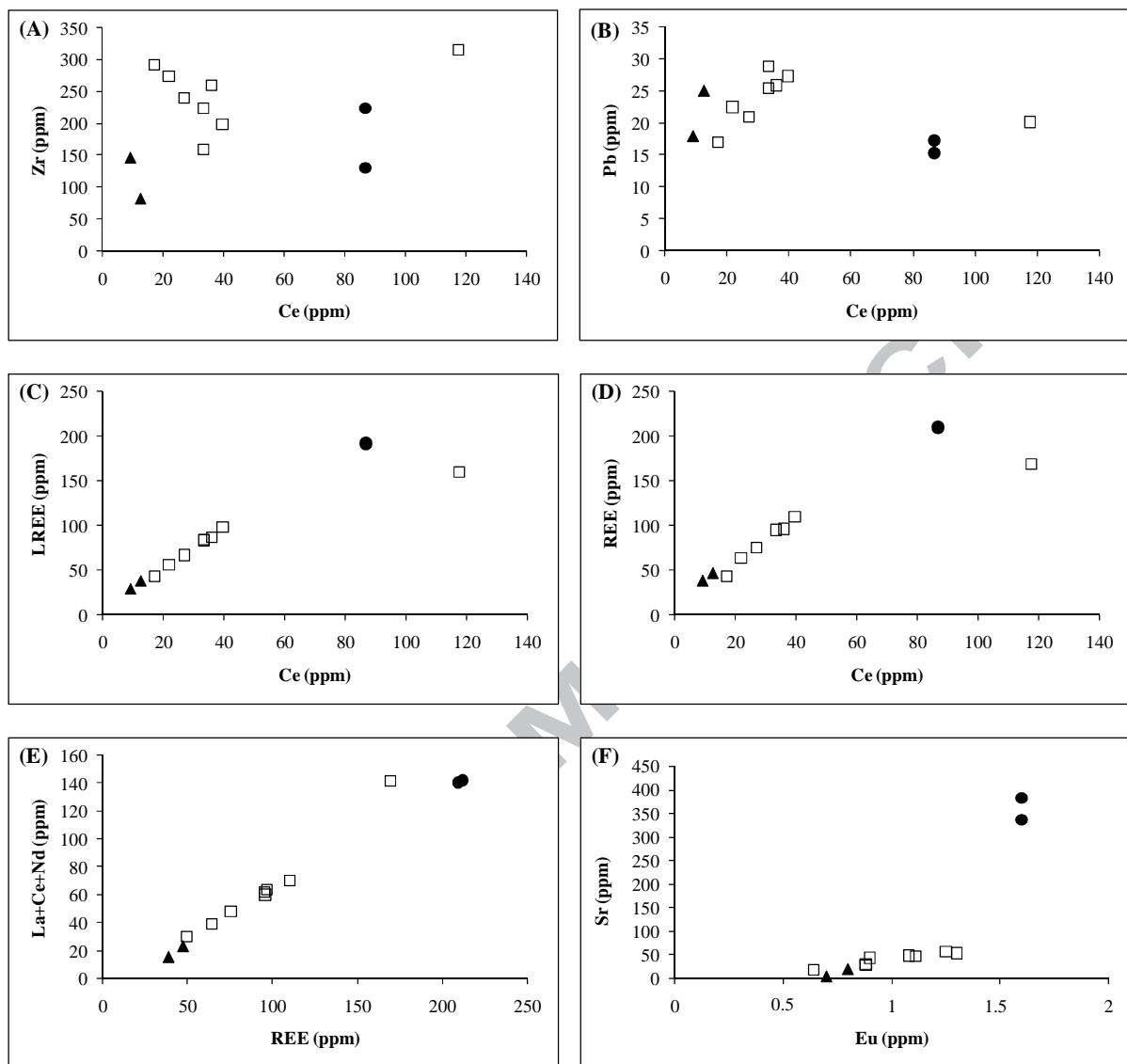


Figure 9



□ Loose materials    ▲ Iron duricrust    ● Parent rock

Figure 10



□ Loose materials    ▲ Iron duricrust    ● Parent rock

Figure 11

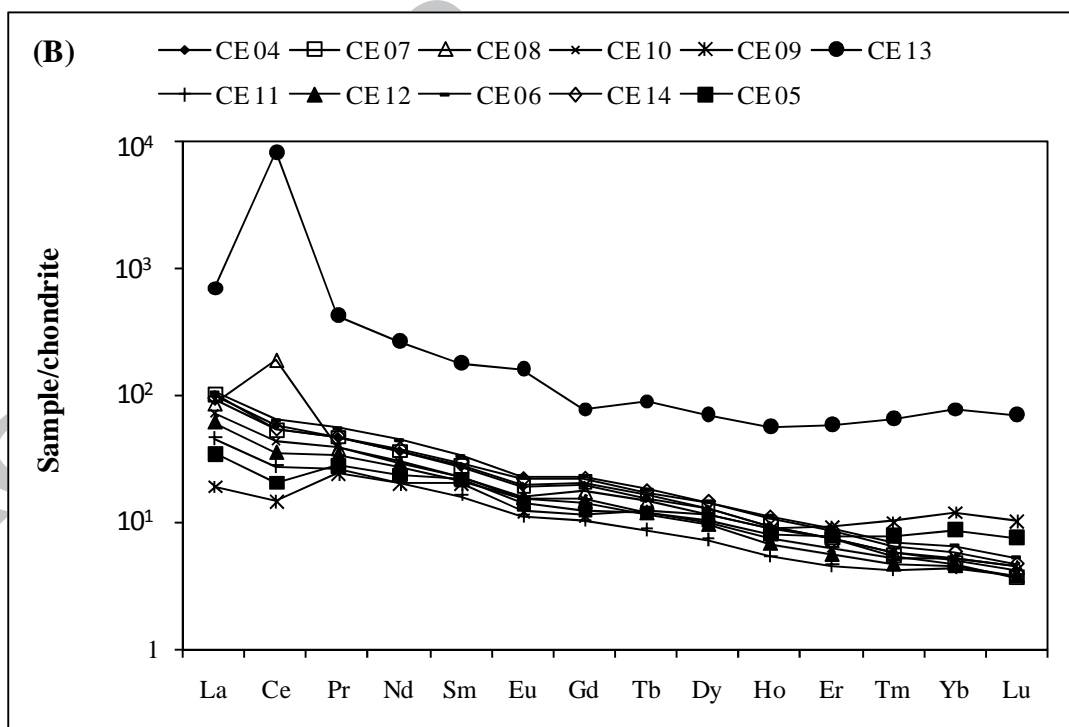
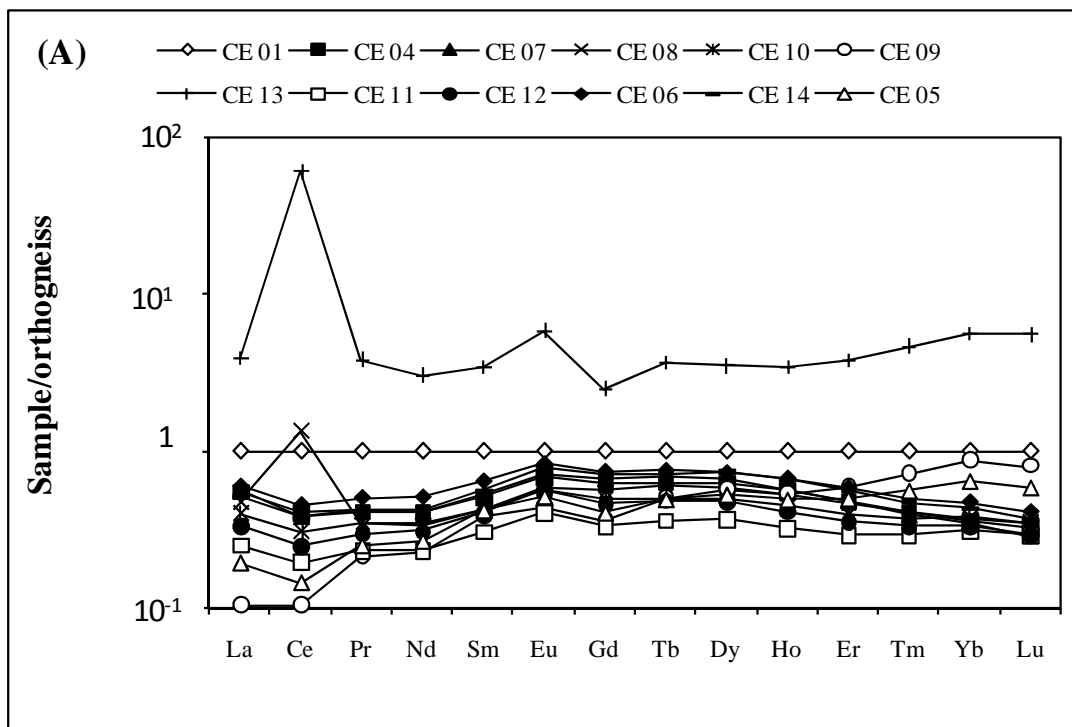


Figure 12

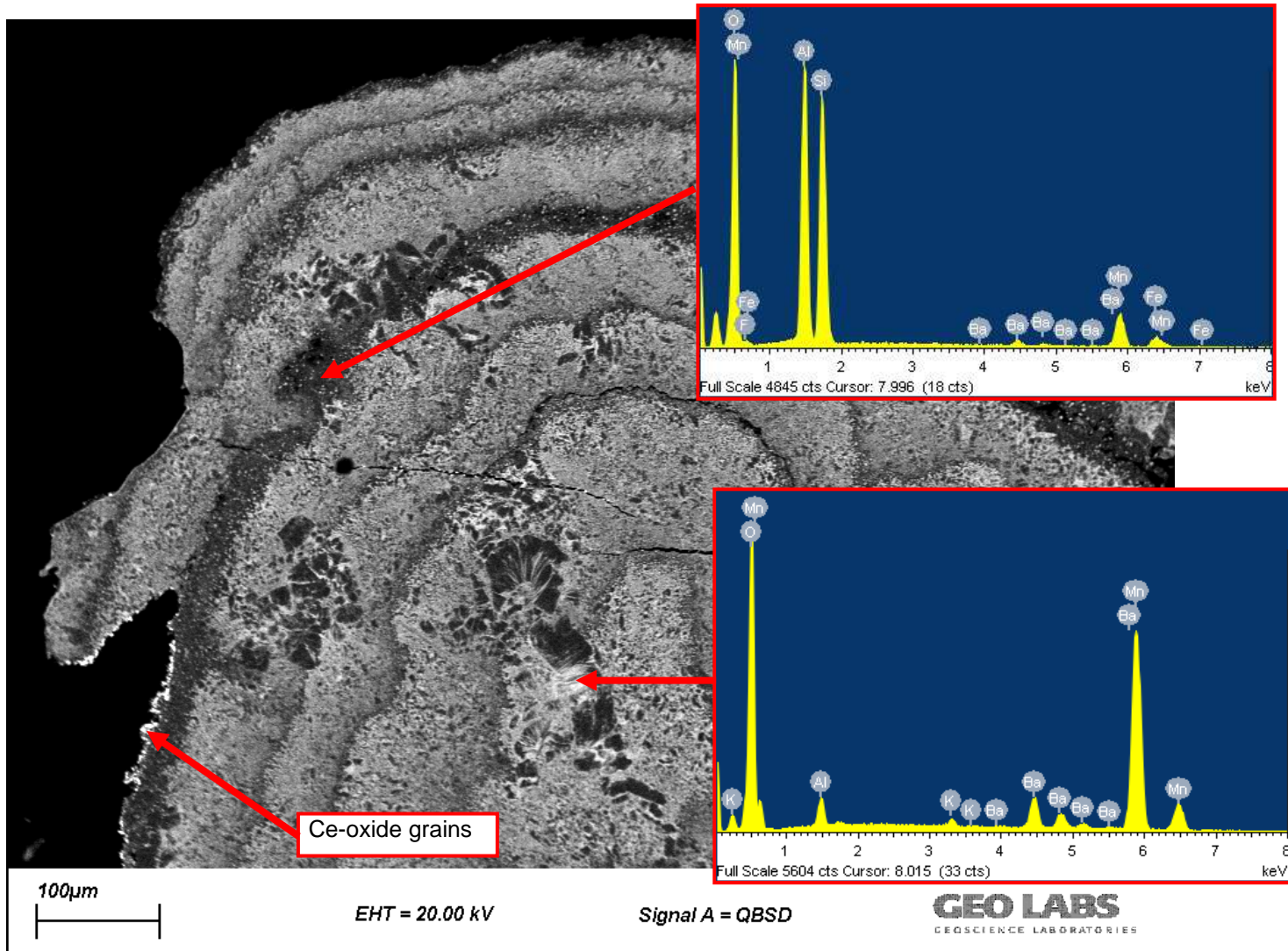


Figure 13

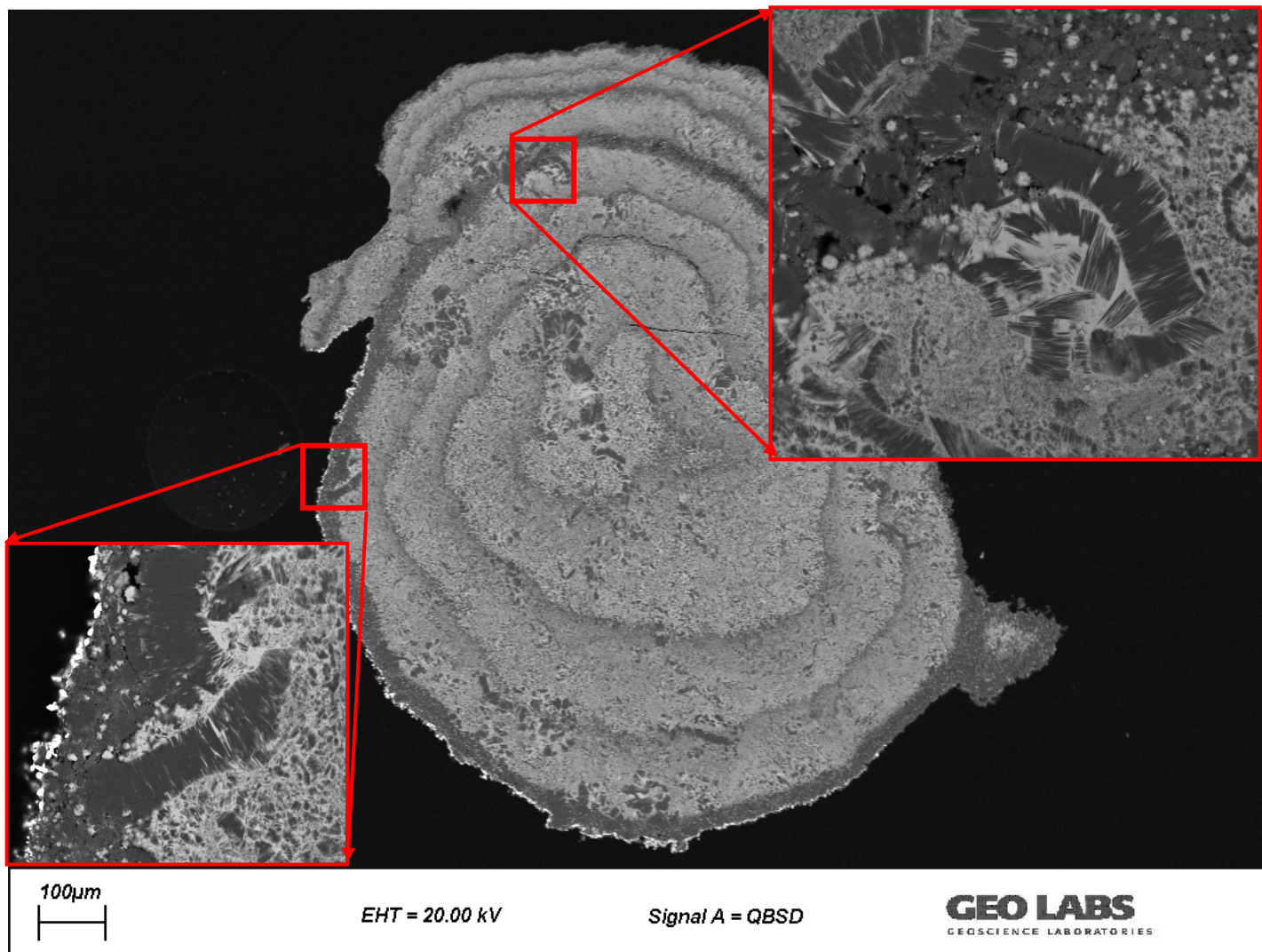


Figure 14



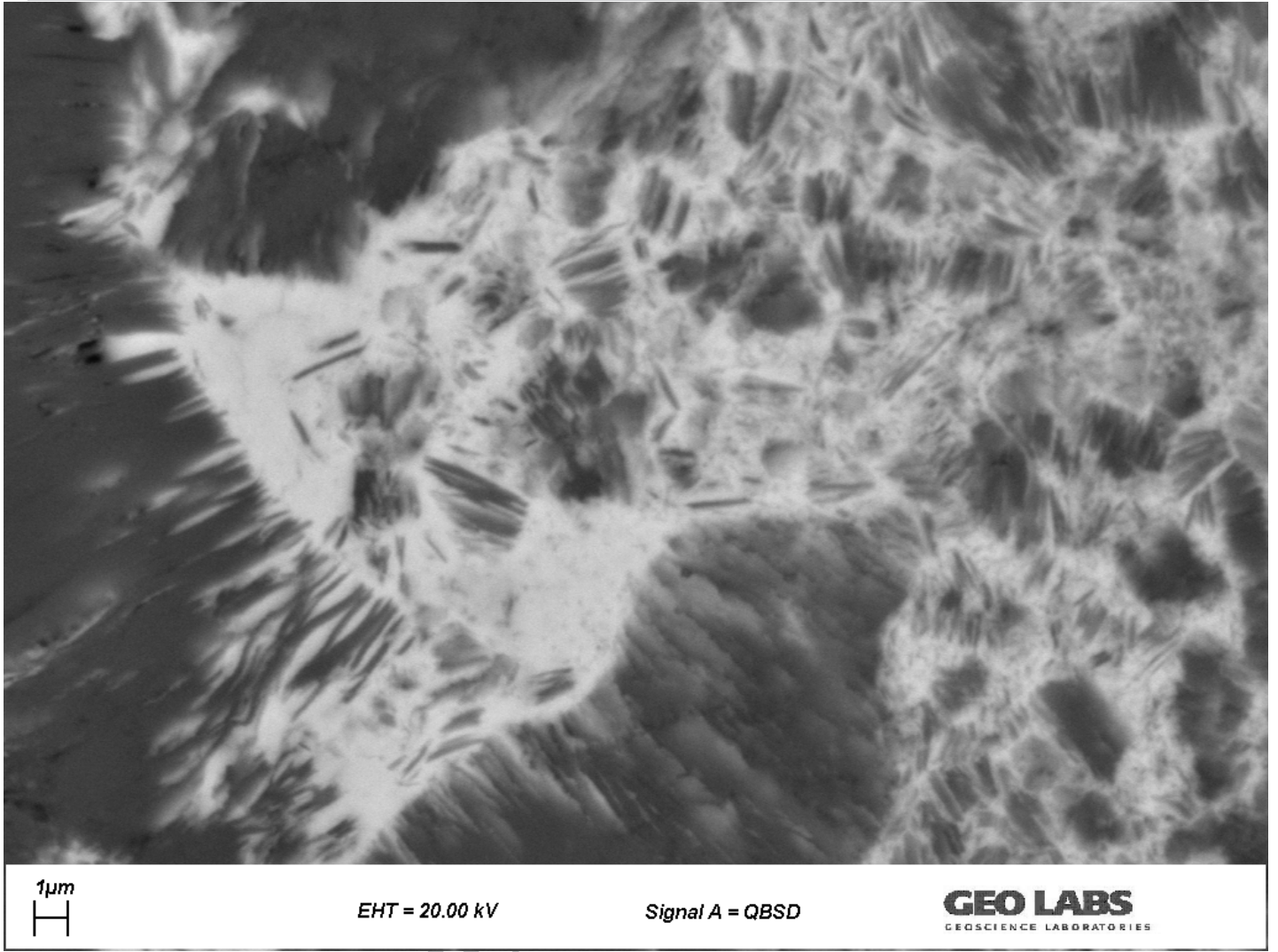


Figure 15

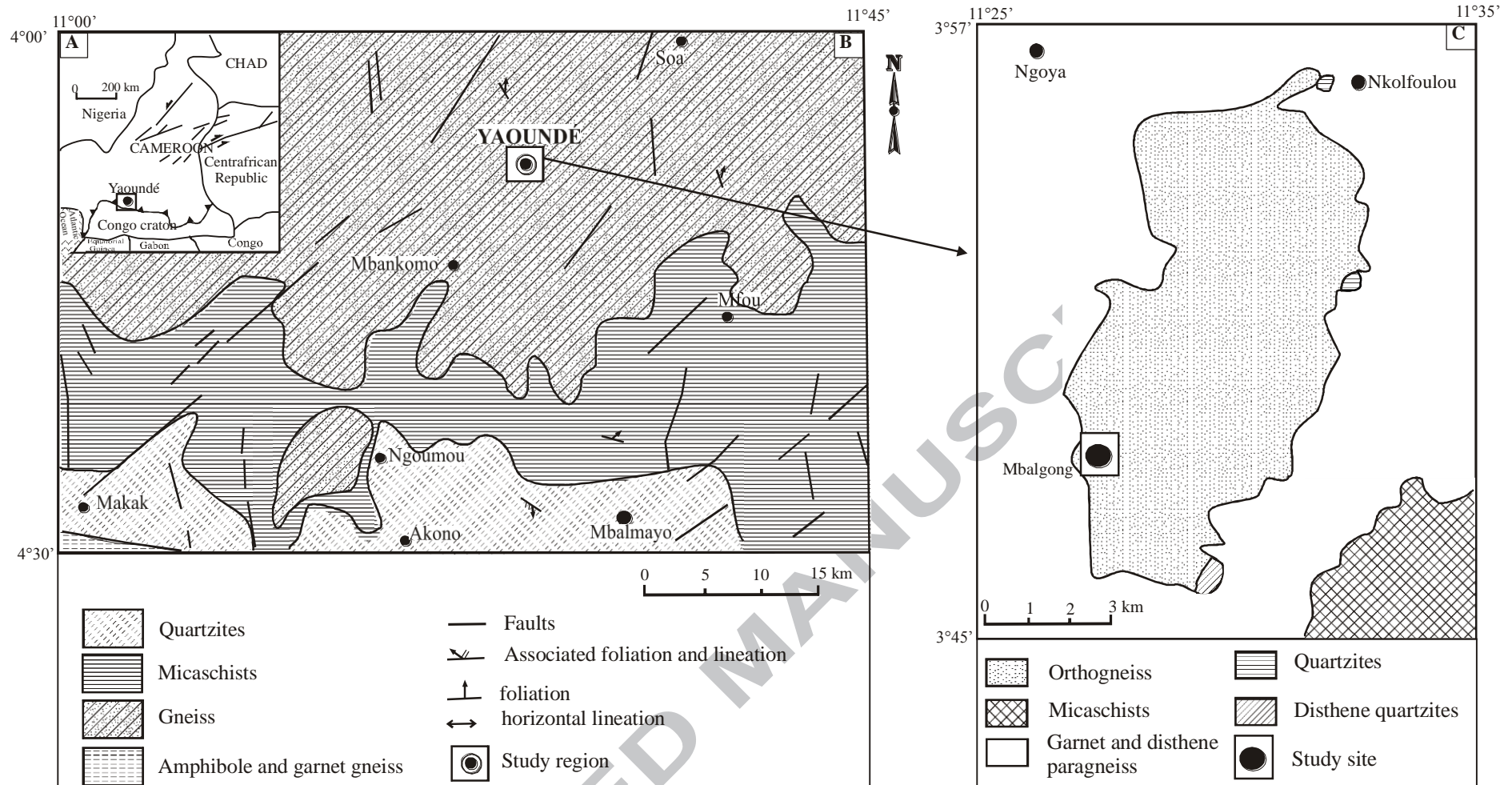
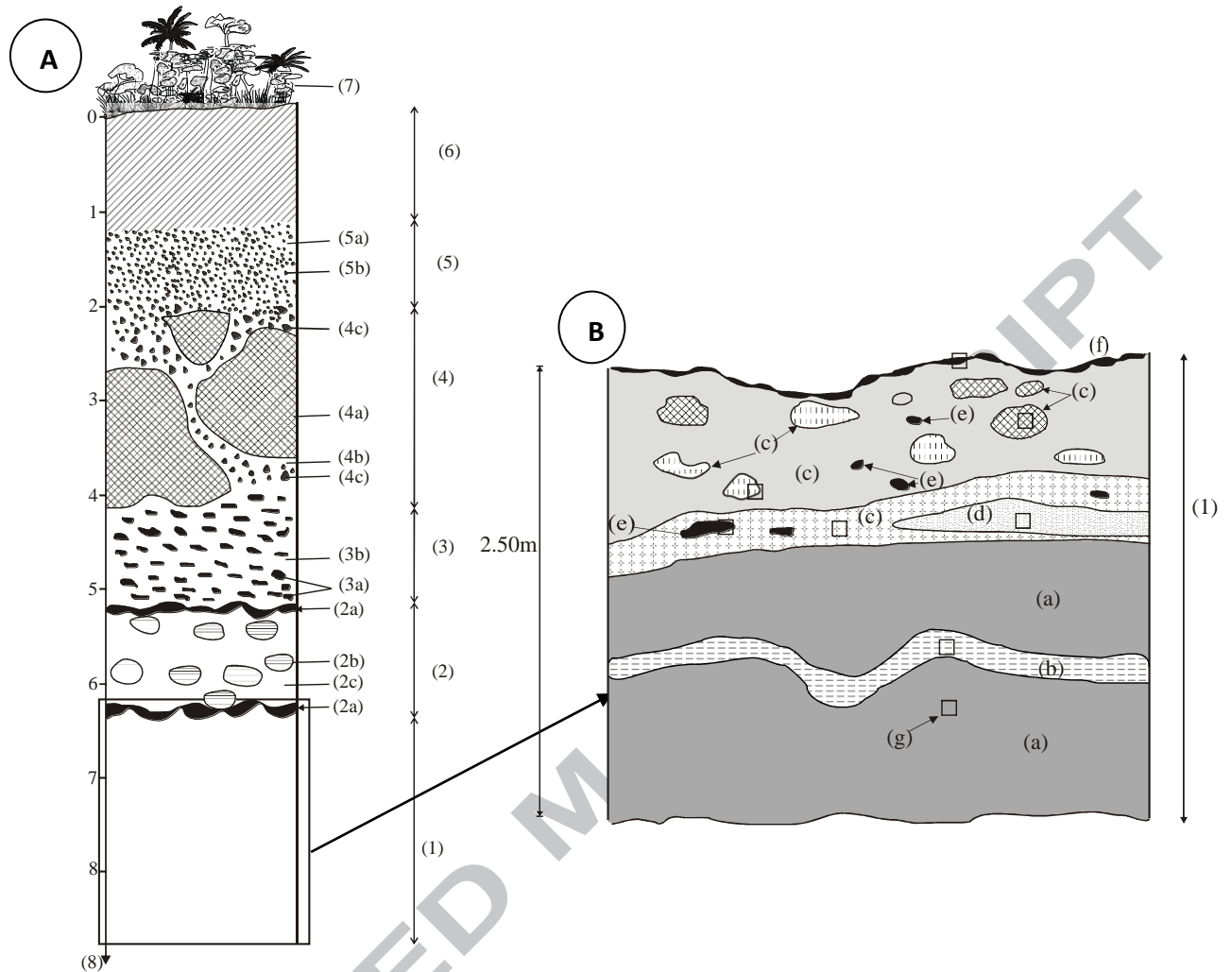


Fig. 1



1. coarse sapolite (a. brown materials; b. white veins; c. yellowish brown plates; d. dark red iron duricrust; e. black plates; f. dusky red iron duricrust; g. sample location); 2. fine sapolite (2a: iron duricrust (plates); 2b: plates with relic structure; 2c: patched materials); 3. lower nodular horizon (3a: flattened nodules with relic structure; 3b: dark red matrix); 4. iron duricrust horizon (4a: metric blocks of the nodular iron duricrust; 4b: red matrix; 4c. nodules); 5. upper nodular horizon (5a: red matrix; 5b: nodules); 6. clayey loose horizon; 7. vegetation; 8. Depth.

Figure 2

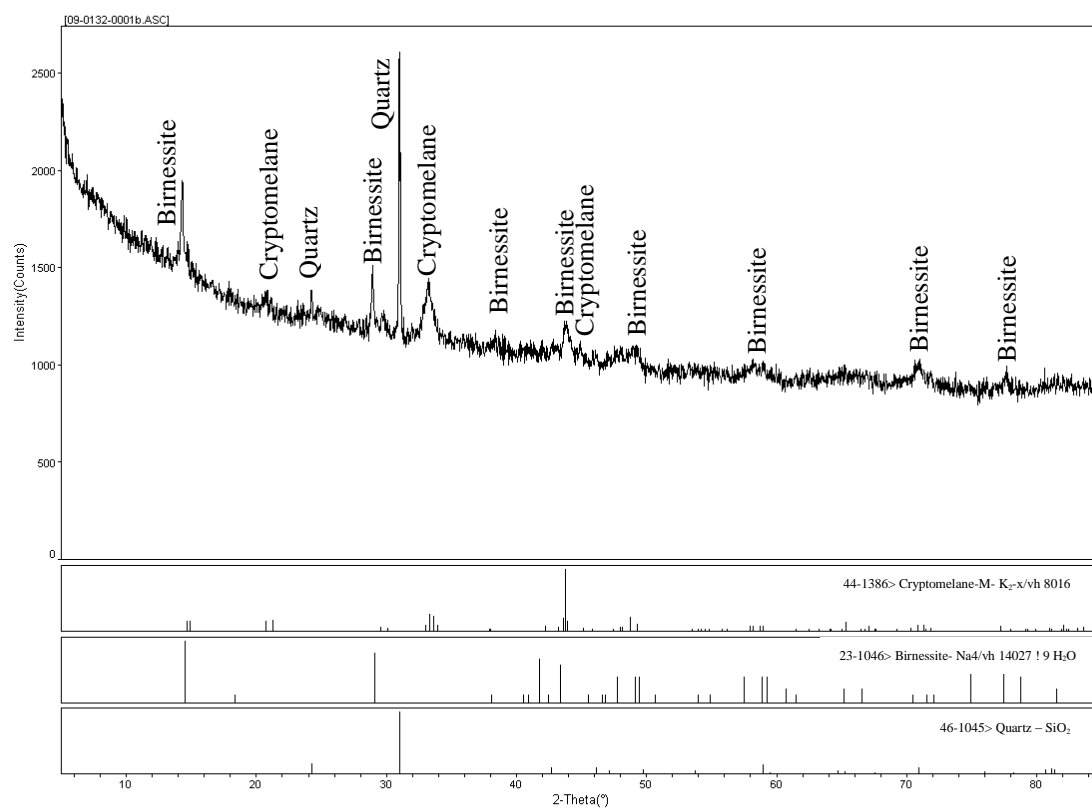


Figure 5