



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

Paul-Désiré Ndjigui, Anicet Beauvais, Soureiyatou Fadil-Djenabou, Jean-Paul Ambrosi

► To cite this version:

Paul-Désiré Ndjigui, Anicet Beauvais, Soureiyatou Fadil-Djenabou, Jean-Paul Ambrosi. Origin and evolution of Ngaye River alluvial sediments, Northern Cameroon: Geochemical constraints. Journal of African Earth Sciences, 2014, 100, pp.164 - 178. 10.1016/j.jafrearsci.2014.06.005 . ird-01419945

HAL Id: ird-01419945

<https://ird.hal.science/ird-01419945>

Submitted on 20 Dec 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

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

P.-D. Ndjigui, M.F.B. Badinane, B. Nyeck, H.P.K. Nandjip, P. Bilong

PII: S1464-343X(12)00225-7

DOI: <http://dx.doi.org/10.1016/j.jafrearsci.2012.11.008>

Reference: AES 1813

To appear in: *African Earth Sciences*

Received Date: 23 November 2011

Revised Date: 27 August 2012

Accepted Date: 13 November 2012



Please cite this article as: Ndjigui, P.-D., Badinane, M.F.B., Nyeck, B., Nandjip, H.P.K., Bilong, P., Mineralogical and geochemical features of the coarse saprolite developed on orthogneiss in the SW of Yaoundé, South Cameroon, *African Earth Sciences* (2012), doi: <http://dx.doi.org/10.1016/j.jafrearsci.2012.11.008>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

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

⁴ 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*

Corresponding author: lndjigui@yahoo.fr

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 SiO₂ (61.56
 38 wt.%), Ba (916 ppm) and REE (209 ppm), moderate content in Al₂O₃ (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 SiO₂ (56 to 64.83 wt.%) and Al₂O₃ (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)_N 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 Fe₂O₃ (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 Fe₂O₃ (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)_N 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

71

72

73

74

75

76

77

78

79

80

81

82

83

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}U - ^{235}U - ^{230}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 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 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°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% Al₂O₃. 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 HClO₄) at 120°C in a closed container for one week, and then rinsed from their
178 containers with dilute HNO₃ and dried. The residues were dissolved in an acid mixture (HCl
179 and HClO₄) and oven-dried for a second time before they were then dissolved in an acid
180 mixture (HNO₃, 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 (ρ_w) was
188 obtained by the paraffin method. The grain densities (ρ_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 heterograngular 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 SiO₂, and moderate Al₂O₃, Fe₂O₃, MgO, CaO, K₂O and Na₂O contents (Table 2). The slightly
207 weathered sample is characterized by an increase in SiO₂, Al₂O₃, K₂O, TiO₂ and P₂O₅
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 Al_2O_3 (22.48 wt.%) and TiO_2 (1.36 wt.%) relative to
231 the orthogneiss (Table 2). The Fe_2O_3 , MnO , MgO , CaO , Na_2O and K_2O 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 SiO₂ (64.83 wt.%), Al₂O₃ (22.76 wt.%) and TiO₂ (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 Fe₂O₃ content is 53.26 wt.% and those of SiO₂ and Al₂O₃ 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 SiO₂ (27.97 wt.%) and Al₂O₃ (12.16
253 wt.%). The Fe₂O₃ 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 Fe_2O_3 (45.60 wt.%) and moderate contents in SiO_2 (30.79 wt.%) and
263 Al_2O_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 SiO_2 has positive correlations with Al_2O_3 , TiO_2 , P_2O_5 , Y and U (Fig. 7). However,
297 correlations of SiO_2 with Fe_2O_3 , Zr, Cr and V are negative. K_2O , Rb and Th have no
298 significant correlations with SiO_2 (Fig. 7). The binary diagrams show that Fe_2O_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 ~ 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 ~ 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 kg/m³ 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
$$K_{jm} = \{((C_{jw} \times \rho_w) / (C_{jp} \times \rho_p)) - 1\} \times 100 \quad (1)$$

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 , ρ_{jw}
 357 is the bulk density of the weathered material w , and ρ_{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, ρ_p is the bulk density of the parent rock in 10^3 kg/m^3 , V_p is the volume of the parent
 363 rock in 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 m³ 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 K₂O is due to adsorption and the increase in Al₂O₃ 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 (Nguenkam 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 SiO₂ 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 SiO₂ with Al₂O₃, TiO₂, P₂O₅, 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 SiO₂
443 and Fe₂O₃ 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 Fe₂O₃ 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 (LREEPO₄.nH₂O) (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 (Σ 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 Ce⁴⁺ or to the probable Ce precipitation as cerianite (CeO₂) 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 Ce⁴⁺ than REE³⁺ (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 $[\text{Ce(OH)}]^{3+}$ and $[\text{Ce(OH)}_2]^{2+}$. 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 REE³⁺ (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 Ca²⁺ and Sr²⁺ 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 (Dequencéy 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 (Dequencéy 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

523 **Acknowledgements**

524 This work was partially supported by the Geoscience Laboratories (Sudbury, Canada)
525 from the stages of sample preparation to laboratory analysis; we wish to thank Clement
526 Merilla, John Hechler and Dave Crabtree for the SEM observations. The authors gratefully
527 acknowledge the editor and two anonymous reviewers for their detailed comments that have
528 considerably improved the manuscript.

529

530 **References**

- 531 Beauvais, A., 1999. Geochemical balance of lateritization processes and climatic signatures in
532 weathering profiles overlain by ferricretes in Central Africa. *Geochimica et Cosmochimica
533 Acta* 63 (23/24), 3939-3957.
- 534 Beauvais, A., 2009. Ferricrete biochemical degradation on the rainforest-savannas boundary
535 of Central African Republic. *Geoderma* 150, 379-388.
- 536 Beauvais, A., Colin, F., 1993. Formation and transformation processes of iron duricrust
537 systems in tropical humid environment. *Chemical Geology* 106, 77-101.
- 538 Beauvais, A., Nahon, D., 1985. Nodules and pisolites from manganiferous weathering profiles
539 under lateritic influences. Examples from Ivory Coast and Gabon. *Bulletin Sciences
540 Géologiques* 38 (4), 359-381.
- 541 Bitom, D., Volkoff, B., Angue-Abossolo, M., 2003. Evolution and alteration in situ of a
542 massive iron duricrust in Central Africa. *Journal of African Earth Sciences* 37, 89-101.
- 543 Boulad, A.P., Muller, J.-P., Bocquier, G., 1977. Essai de détermination de l'âge et de la
544 vitesse d'altération d'un sol ferrallitique camerounais à l'aide de la méthode du déséquilibre
545 radioactif uranium/thorium. *Bulletin Sciences Géologiques* 30, 175-188.
- 546 Boulangé, B., Colin, F., 1994. Rare earth element mobility during conversion of nepheline
547 syenite into lateritic bauxite at Passa Quatro. Minais Gerais, Brazil. *Applied Geochemistry* 9,
548 701-711.
- 549 Bourgauth, R.R., Rabenhorst, M.C., 2011. Genesis and characterization of manganiferous
550 soils in the Eastern Piedmont, USA. *Geoderma* 165(1), 84-94.
- 551 Braun, J.-J., Ndam Ngoupayou J.R., Viers, J., Dupre, B., Bedimo Bedimo J.-P., Boeglin, J.-
552 L., Robain, H., Nyeck, B., Freydier, R., Sigha Nkamdjou, L., Rouiller, J., Muller, J.-P., 2005.
553 Present weathering rates in a humid tropical watershed: Nsimi, South Cameroon. *Geochimica
554 et Cosmochimica Acta* 69, 357-387.

- 555 Braun, J.-J., Pagel, M., Herbillon, A., Rosin, C., 1993. Mobilization and redistribution of
556 REEs and Th in syenitic lateritic profile: - a mass-balance study. *Geochimica et*
557 *Cosmochimica Acta* 57, 4419-4434.
- 558 Braun, J.-J., Viers, J., Dupre, B., Polve, M., Ndam, J., Muller, J.-P., 1998. Solid/liquid REE
559 fractionation in the lateritic system of Goyoum, East Cameroon: the implication for the
560 present dynamics of the soil covers of the humid tropical regions. *Geochimica et*
561 *Cosmochimica Acta* 62, 273-299.
- 562 Brimhall, G.H., Dietrich, W.E., 1987. Constitutive mass-balance relations between chemical
563 composition, volume, density, porosity and strain in metasomatic hydrochemical systems:
564 results on weathering and pedogenesis. *Geochimica et Cosmochimica Acta* 51, 567-587.
- 565 Brindley, G.W., Brown, G., 1980. Crystal structures of clay minerals and their x-ray
566 identification. Mineralogical Society, London, p. 495.
- 567 Burnham, O.M., Schweyer, J., 2004. Trace element analysis of geological samples by
568 inductively Coupled Plasma Mass Spectrometry at the Geoscience Laboratories: revised
569 capabilities due to improvements to instrumentation. Summary of Field Work and Other
570 Activities 2004, Ontario Geological Survey, Open file report 6145, 54, 1-20.
- 571 Chabaux, F., Dequincey, O., Lévèque, J.-J., Leprun, J.-C., Clauer, N., Riotte, J., Paquet, H.,
572 2003. Tracing and dating recent chemical transfers in weathering profiles by trace-element
573 geochemistry and ^{238}U - ^{234}U - ^{230}Th disequilibria: the example of the Kaya lateritic
574 toposequence (Burkina-Faso). *C.R. Geoscience* 335, 1219-1231.
- 575 Colin, F., Ambrosi, J.-P., 1993. Gold mass transfer during lateritic weathering under
576 equatorial rainforest conditions. *Chemical Geology* 107, 285-288.
- 577 Colin, F., Veillard, P., Ambrosi, J.-P., 1993. Quantitative approach to physical and chemical
578 gold mobility in equatorial rainforest lateritic environment. *Earth Planetary Science Letters*
579 114, 269-285.

- 580 Coppin, F., Berger, G., Bauer, A., Castet, S., Loubet, M., 2002. Sorption of lanthanides on
581 smectite and kaolinite. *Chemical Geology* 182, 57-68.
- 582 Cornu, S., Lucas, Y., Lebon, E., Ambrosi, J.-P., Luizão, F., Rouiller, J., Bonnay, M., Neal, C.,
583 1999. Evidence of titanium mobility in soil profiles. Manaus, Central Amazonia. *Geoderma*
584 91, 281-295.
- 585 Davranchise, M., Pourret, O., Gruau, G., Dia, A., Jin, D., Gaertner, D., 2008. Competitive
586 binding of REE to humic acid and manganese oxide: impact of reaction kinetics on
587 development of cerium anomaly and REE adsorption. *Chemical Geology* 247, 154-170.
- 588 Davranchise, M., Pourret, O., Gruau, G., Dia, A., Le Coz-Bouhnik, M., 2005. Adsorption of
589 REE(III)-humate complexes onto MnO₂, experimental evidence for cerium anomaly and
590 lanthanide tetrad effect suppression. *Geochimica et Cosmochimica Acta* 69, 4825-4835.
- 591 Delvigne, J.E., 1998. Atlas of micromorphology of mineral alteration and weathering. The
592 Canadian Mineralogist, special publication 3, p. 494.
- 593 Dequençey, O., Chabaux, F., Clauer, N., Sigmarsson, O., Liewig, N., Leprun, J.-C., 2002.
594 Chemical mobilizations in laterites: Evidence from trace elements and ²³⁸U-²³⁴U-²³⁰Th
595 disequilibria. *Geochimica et Cosmochimica Acta* 66, 1997-1210.
- 596 Dequençey, O., Chabaux, F., Leprun, J.-C., Paquet, H., Clauer, N., Larque, P., 2006.
597 Lanthanide and trace element mobilization in a lateritic toposequence: inferences from the
598 Kaya laterite in Burkina Faso. *European Journal of Soil Science* 57, 816-830.
- 599 Etame, J., Suh, C.E., Gerard, M., Bilong, P., 2012. Phillipsite formation in nephelinitic rocks
600 in response to hydrothermal alteration at Mount Etinde, Cameroon. *Chemie der Erde-
601 Geochemistry* 72, 31-37.
- 602 Feng, J.L., 2008. Behaviour of rare earth elements and yttrium in ferromanganese concretions,
603 gibbsite spots, and surrounding terra rossa over dolomite during chemical weathering.
604 *Chemical Geology* 271, 112-132.

- 605 Galán, E., Fernández-Caliani, J.C., Miras, A., Aparicio, P., Márquez, M.G., 2007. Residence
606 and fractionation of rare earth elements during kaolinization of alkaline peraluminous granites
607 in NW Spain. *Clays Minerals* 42 (3), 341-352.
- 608 Golightly, J.-P., 1979. Geology of Soroako nickeliferous laterite deposits. AIME International
609 laterite Symposium, pp. 38-55.
- 610 Gromet, P.L., Silver, L.T., 1983. Rare earth element distributions among minerals in a
611 granodiorite and their petrogenetic implications. *Geochimica et Cosmochimica Acta* 47 (5),
612 925-939.
- 613 Harvalan, Y., Erel, Y., Blum, J.D., 2009. Coupled release of REE and Pb to the soil labile
614 pool with time by weathering of accessory phases, wind river mountains, WY. *Geochimica et*
615 *Cosmochimica Acta* 73, 320-336.
- 616 Huang, C., Wang, C., 2004. Geochemical characteristics and behaviors of rare earth elements
617 in process of vertisol development. *Journal of Rare Earths* 22 (4), 552-557.
- 618 Kamgang Beyala, V., Ekodeck, G.E., 1991. Altération et bilans géochimiques des biotites des
619 gneiss de Nkolbisson (NW de Yaoundé, Cameroun). *Géodynamique* 6 (2), 191-199.
- 620 Kamgang Kabeyene Beyala, V., Onana V.L., Ndome Effoudou Priso, E., Parisot, J.-C.,
621 Ekodeck, G.E., 2009. Behaviour of REE and mass balance calculations in a lateritic profile
622 over chlorite schists in South Cameroon. *Chemie der Erde-Geochemistry* 69, 61-73.
- 623 Koppi, A.J., Edis, R., Field, D.J., Geering, H.R., Klessa, D.A., Cockayne, D.J.H., 1996. Rare
624 earth element trends and cerium-uranium-manganese associations in weathered rock from
625 Koongarra, Northern Territory, Australia. *Geochimica et Cosmochimica Acta* 60, 1695-1707.
- 626 Lambiv Dzemua G., Mees F., Stoops G., Van Ranst E., 2011. Micromorphology, mineralogy
627 and geochemistry of lateritic weathering over serpentinite in south-east Cameroon. *Journal of*
628 *African Earth Sciences* 60, 38-48.

- 629 Laufer, F., Yariv, S., Steinberg, M., 1984. The adsorption of quadrivalent cerium by kaolinite.
- 630 Clay Minerals 19, 137-149.
- 631 Laveuf, C., Cornu, S., 2010. A review on the potentiality of rare earth elements to trace
- 632 pedogenetic processes. Geoderma 154, 1-12.
- 633 Letouzey, R., 1985. Notice explicative de la carte phytogéographique du Cameroun à
- 634 l'échelle de 1/500 000. Institut de la Carte Internationale de la Végétation, Toulouse, p. 240.
- 635 Leybourne, M.I., Goodfellow, W.D., Bowle, D.R., Hall, G.M., 2000. Rapid development of
- 636 negative Ce anomalies in surface waters and contrasting REE patterns in ground waters
- 637 associated with Zn-Pb massive sulphide deposits. Applied Geochemistry 15, 695-793.
- 638 Llorca, S., Monchoux, P., 1991. Supergene cobalt minerals from New Caledonia. Canadian
- 639 Mineralogist 29, 149-161.
- 640 Loges, A., Wagner, T., Barth, M., Bau, M., Göb, S., Markl, G., 2012. Negative Ce anomalies
- 641 in Mn oxides: the role of Ce⁴⁺ mobility during water-mineral interaction. Geochimica et
- 642 Cosmochimica Acta 86, 296-317.
- 643 Marsh, J.S., 1990. REE fractionation and Ce anomalies in weathered Karoo dolerite.
- 644 Chemical Geology 90, 189-194.
- 645 Mathieu, D., Bernat, M., Nahon, D., 1995. Short-lived U and Th isotope distribution in a
- 646 tropical laterite derived from granite (Pitinga River Basin, Amazonia, Brazil): application to
- 647 assessment of weathering rate. Earth Planetary Science Letters 136, 703-714.
- 648 Maurizot, P., Abessolo, A., Feybesse, A., Johan, V., Lecomte, P., 1986. Etude et prospection
- 649 minière du Sud-Ouest Cameroun. Synthèse des travaux de 1978 à 1985. 85-CMR 066 BRGM.
- 650 McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. Chemical Geology 120,
- 651 223-253.
- 652 McFarlane, M.J., 1976. Laterite and landscape. Academic Press, London, p. 151.

- 653 Millot, G., Bonifas, M., 1955. Transformations iso-volumiques dans les phénomènes de
654 latéritisation et de bauxitisation. Bulletin du Service de la Carte Géologique d'Alsace-
655 Lorraine 8, 8-10.
- 656 Mishra, P.P., Mohapatra, B.K., Singh, P.P., 2007. Contrasting REE signatures on manganese
657 ores of iron ore group in North Orissa, India. Journal of Rare Earths 25, 749-758.
- 658 Moroni, M., Girardi, V.A.V., Ferrario, A., 2001. The Serra Pelada Au-PGE deposit, Serra dos
659 Cerajás (Pará State, Brazil): geological and geochemical indications for a composite
660 mineralising process. Mineralium Deposita 36, 768-785.
- 661 Mungall, J.E., Martin, R.F., 1994. Severe leaching of trachyte glass without devitrification,
662 Terceira, Azores. Geochimica et Cosmochimica Acta 58, 75-83.
- 663 Nandjip K.P.H., 2010. Contribution à l'étude pétrologique d'une isaltérite développée sur
664 orthogneiss au SW de Yaoundé : recherche des indices de cérium dans les matériaux
665 ferruginisés. Master, Univ. de Yaoundé I, p. 70.
- 666 Ndjigui, P.-D., Bilong, P., Bitom, D., 2009. Negative cerium anomalies in the saprolite zone
667 of serpentinite lateritic profiles in the Lomié ultramafic complex, South-East Cameroon.
668 Journal of African Earth Sciences 53, 59-69.
- 669 Ndjigui, P.-D., Bilong, P., Bitom, D., Dia, A., 2008. Mobilization and redistribution of major
670 and trace elements in two weathering profiles developed on serpentinite in the Lomié
671 ultramafic complex, South-East Cameroon. Journal of African Earth Sciences 50, 305-328.
- 672 Ndjigui, P.-D., Bilong, P., Nyeck, B., Eno Belinga, S.-M., Vicat, J.-P., Gérard, M., 1998. Les
673 produits d'altération du gneiss à biotite et amphibole dans la plaine côtière de Douala.
674 Annales Fac. Sci., série Sci. Nat. et Vie, vol. 34, 191-216.
- 675 Nguetnkam, J.-P., Yongue-Fouateu, R., Bitom, D., Bilong, P., Volkoff, B., 2006. Etude
676 pétrologique d'une formation latéritique sur granite en milieu tropical forestier sud-

- 677 camerounais (Afrique centrale). Mise en évidence de son caractère polyphasé. Etude et
678 Gestion des Sols 13, 89-102.
- 679 Ohnuki, T., Ozaki, T., Kozai, N., Nankawa, T., Sakamoto, F., Sakai, T., Suzuki, Y., Francis,
680 A.J., 2008. Concurrent transformation of Ce(III) and formation of biogenic manganese
681 oxides. Chemical Geology 253, 23-29.
- 682 Ohta, A., Kawabe, I., 2001. REE(III) adsorption onto Mn dioxide ($\delta\text{-MnO}_2$) and Fe
683 oxyhydroxide: Ce(III) oxidation by ($\delta\text{-MnO}_2$). Geochimica et Cosmochimica Acta 65 (5),
684 695-703.
- 685 Owona, S., Mvondo Ondoа, J., Essono, J., Tjomb, B., Enama Mengong, M., 2003.
686 Géomorphologie et cartographie de deux faciès paradérivés et un orthodérivé de la région de
687 Yaoundé. Sci. Technol. Dev., Vol. 10 (1), 81-91.
- 688 Panahi, A., Young, G.M., Rainbird, R.H., 2000. Behavior of major and trace elements
689 (including REE) during Paleoproterozoic pedogenesis and diagenetic alteration of an
690 Archaean granite near Ville Marie, Québec, Canada. Geochimica et Cosmochimica Acta 64
691 (13), 2199-2220.
- 692 Singh, B., Sherman, D.M., Gilkes, R.J., Wells, M.A., Mosselmans, J.F.W., 2002.
693 Incorporation of Cr, Mn and Ni into goethite ($\alpha\text{-FeOOH}$): mechanism from extended X-ray
694 absorption fine structure spectroscopy. Clay Minerals 37, 636-649.
- 695 Suchel, J.-B., 1987. Les climats du Cameroun. Thesis, Université de Bordeaux III, p. 1186.
- 696 Takahashi, Y., Manceau, A., Geoffroy, N., Marcus, M.A., Usui, A., 2007. Chemical and
697 structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides.
698 Geochimica et Cosmochimica Acta 71, 984-1008.
- 699 Takahashi, Y., Shimizu, H., Usui, H., Kagi, H., Nomura, M., 2000. Direct observation of
700 tetravalent cerium in ferromanganese nodules and crusts by x-ray-absorption near-edge
701 structure (XANES). Geochimica et Cosmochimica Acta 17, 2929-2935.

- 702 Tanaka, K., Tani, Y., Takahashi, Y., Tanimizu, M., Suzuki, Y., Kozai, N., Ohnuki, T., 2010.
703 A specific Ce oxidation process during sorption of rare earth elements on biogenic Mn oxide
704 produced by *Acremonium sp.* Strain KR21-2. *Geochemica et Cosmochimica Acta* 74, 5463-
705 5477.
- 706 Tardy, Y., 1993. Pétrologie des latérites et des sols tropicaux. Masson, Paris, p. 459.
- 707 Tollari, N., Barnes S.-J., Cox, R.A., Nabil, H., 2008. Trace element concentrations in apatites
708 from the Sept-Îles intrusive suite, Canada – Implications for the genesis of nelsonites.
709 *Chemical Geology* 252, 180-190.
- 710 Toteu, S., Penaye, J., Deloule, E., Van Schmus, W.R., Tchameni, R., 2006. Diachronous
711 evolution of volcano-sedimentary basins north of the Congo craton: insights from U-Pb ion
712 microphobe dating zircon from Poli, Lom and Yaoundé groups (Cameroon). *Journal of*
713 *African Earth Sciences* 44, 428-442.
- 714 Traoré, D., 2005. Serpentinisation hydrothermale et altération latéritique des roches
715 ultrabasiques en milieu tropical: évolution géochimique et minéralogique de la minéralisation
716 en platine de la rivière des Pirogues (Nouvelle-Calédonie). Thesis, Université de la Nouvelle
717 Calédonie, p. 191.
- 718 Tripathi, J.K., Rajamani, V., 2007. Geochemistry and origin of ferruginous nodules in
719 weathered granodioritic gneisses, Mysore Plateau, Southern India. *Geochimica et*
720 *Cosmochimica Acta* 71 (7), 1674-1688.
- 721 Vasconcelos, I.F., Haack, E.A., Maurice, P.A., Bunker, B.A., 2008. EXAFS analysis of
722 cadmium (II) adsorption to kaolinite. *Chemical Geology* 249, 237-249.
- 723 Yoshida, T., Ozaki, T., Ohnuki, T., Francis, A.J., 2004. Adsorption of rare earth elements by
724 γ -Al₂O₃ and *Pseudomonas fluorescens* cells in the presence of desferrioxamine B: implication
725 of siderophores for the Ce anomaly. *Chemical Geology* 212, 239-246.
- 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 Fe_2O_3 with selected ferromagnesian trace elements: A. Fe_2O_3 vs. Cr;
749 B. Fe_2O_3 vs. Ni; C. Fe_2O_3 vs. Co; D. Fe_2O_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.

786

787

788

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			Yellowish brown plates			
			Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Black phases	(a)	(b)	(c)	(d)
Depth (m)	-	-	-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	+1.80	+2.10	+2.40
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
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					
				Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases					
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 ₂	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 ₂ O ₃	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 ₂ O ₃	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	33.86	0.01	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 ₂ O	0.01	2.72	2.58	<dl	<dl	<dl	0.02	<dl	0.11	0.02	0.02	<dl	0.02	<dl
K ₂ 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 ₂	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 ₂ O ₅	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 ₂ /Al ₂ O ₃	-	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 ₂ O ₃ /K ₂ 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			Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust
			Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust	Mn-phases			Yellowish brown plates	Dusky red iron duricrust		
Depth (m)	-	-	-	+ 0.10	+ 0.40	-	+1.70	+1.70	(a)	(b)	(c)	(d)	+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			Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust
				Whole fraction	Brown material	White veins	Whole fraction					(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	
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	<dl	<dl	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	<dl	
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			Mn-phases			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 14	CE 05	
		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 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		
Σ REE	-	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		
Σ LREE	-	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		
Σ HREE	-	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		
(La/Yb) _N	-	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.

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

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

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

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

For rock samples: (La/Yb)_N = (La_{orthogneiss}/La_{chondrite})/(Yb_{orthogneiss}/Yb_{chondrite}).For weathered samples: (La/Yb)_N = (La_{weathered sample}/La_{orthogneiss})/(Yb_{weathered sample}/Yb_{orthogneiss}).

Table 6

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

Coarse saprolite											
Depth (m)	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)	
	-	+ 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	6.19	-11.87	-0.44	8.48	4.87	-5.24	-3.87	-31.47
Fe	-53.82	-64.54	-82.48	-25.31	849.56	67.64	-13.64	-39.91	-61.44	-38.73	433.42
Mn	-95.10	-96.44	-95.79	-94.72	-90.32	30482	-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	7.13	7.89	-79.36	16.45	5.36	-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	1288	909	1075	1492	2541	3281	1617	1525	1241	1333	1867

Table 7

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

Coarse saprolite											
	Bottom		Top		Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
	Whole fraction	Brown material	White veins	Whole fraction			(a)	(b)	(c)		
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	390.50
Ni	-84.17	-88.94	-89.44	-78.96	-50.84	10.88	-78.01	-80.96	-82.15	-83.97	-82.21
Co	-92.89	-95.41	-95.99	-93.32	-66.46	7275	-92.79	-94.71	-95.29	-91.92	-83.77
Zn	-75.74	-83.26	-80.72	-64.69	85.81	170.61	-58.28	-68.10	-71.37	-67.60	12.48
Sc	-13.89	-34.01	-20.71	3.38	141.73	86.79	15.60	0.75	-21.37	-9.93	128.99
Cu	-68.74	-74.27	-70.56	-33.49	-24.74	923.61	-19.02	-46.16	-64.61	-41.69	77.03
V	0.13	-32.53	-22.68	20.52	163.50	9.93	29.25	5.83	-1.74	-22.36	181.00
Ba	-77.78	-83.66	-81.38	-86.38	-97.44	6526	-92.67	-88.66	-80.16	-76.14	-90.42
Pb	7.80	-22.89	-27.75	-5.77	48.08	9991	-21.04	-3.42	1.20	20.81	35.49
Y	-71.29	-80.25	-76.55	-77.29	-69.65	60.84	-84.29	-80.87	-70.55	-67.23	-78.77
Ga	-5.15	-31.94	-12.34	0.99	-9.80	45.75	0.71	-6.38	-3.34	-7.05	-26.11
Th	-6.13	-40.60	66.74	-0.43	23.62	-36.47	-23.03	-20.90	-4.07	-12.31	227.44
U	-7.61	-33.21	-5.65	20.23	120.09	35.47	31.17	11.32	-16.07	-19.68	105.02
Zr	25.43	-21.48	31.01	25.35	40.17	14.74	56.81	36.82	-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	961.36	594.03	1177	587	1368	5966	-	-	1034	327.86	1,414
Nb	-18.66	-38.47	-13.89	-4.97	-16.75	-32.95	-3.83	-22.15	-19.49	-25.85	-48.69
Hf	20.58	-22.25	31.73	20.81	32.75	15.17	47.86	29.55	-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	21667	-93.58	-93.11	-94.45	-86.54	-80.36
Mo	-73.74	-79.32	-73.79	-66.26	-70.16	129.32	-72.96	-77.30	-72.83	-61.18	-14.97
Sn	-15.81	-38.26	-18.33	-11.79	-4.53	0.69	-21.70	-11.15	0.26	-25.09	-64.20
Tl	-98.52	-99.37	-98.94	-97.35	-98.30	7616	-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			Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
Depth (m)	Whole fraction	Brown material	White veins	Whole fraction	Dark red iron duricrust		(a)	(b)	(c)		
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	355.28	-82.09	-77.78	-66.05	-66.48	-84.00
Ce	-73.71	-82.29	-26.05	-78.70	-86.76	6919	-86.08	-83.57	-74.23	-75.37	-88.02
Pr	-73.37	-80.73	-81.43	-75.81	-72.85	346.26	-83.37	-80.36	-71.35	-72.79	-79.43
Nd	-73.79	-80.99	-81.78	-76.10	-70.99	256.21	-83.36	-79.62	-71.06	-72.59	-77.99
Sm	-66.98	-75.26	-76.76	-70.36	-51.28	298.58	-78.22	-73.26	-63.39	-63.58	-65.56
Eu	-55.84	-67.00	-68.37	-61.07	-43.40	584.75	-70.91	-62.85	-52.63	-48.75	-57.73
Gd	-60.15	-69.02	-69.23	-66.10	-54.09	192.26	-76.26	-69.25	-57.73	-54.08	-66.74
Tb	-59.40	-68.30	-67.34	-65.63	-35.85	326.70	-74.40	-68.09	-57.16	-53.34	-59.41
Dy	-59.47	-69.49	-68.38	-65.37	-28.39	310.93	-73.75	-68.29	-58.56	-52.62	-56.61
Ho	-63.83	-73.31	-70.67	-68.90	-32.27	299.72	-76.97	-72.86	-61.71	-57.10	-59.66
Er	-69.33	-77.64	-74.77	-72.54	-25.69	343.59	-79.03	-76.44	-66.63	-63.44	-59.10
Tm	-74.16	-81.89	-77.64	-73.91	-9.37	445.47	-79.01	-78.23	-71.64	-69.56	-53.99
Yb	-76.91	-83.80	-79.63	-73.34	10.60	556.56	-77.76	-78.20	-73.11	-72.24	-47.03
Lu	-79.31	-86.72	-81.01	-75.53	1.25	547.44	-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/m³).

Coarse saprolite											
	Bottom		Top		Dark red iron duricrust	Mn-phases	Yellowish brown plates			Dusky red iron duricrust	
	Whole fraction	Brown material	White veins	Whole fraction			(a)	(b)	(c)		
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	17.85	-34.22	-1.26	24.45	14.05	-15.09	-11.14	-90.69
Fe	-76.37	-91.59	-117.05	-35.92	1205	95.98	-19.36	-56.63	-	-54.96	615.05
Mn	-2.49	-2.52	-2.50	-2.48	-2.36	796.48	-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	1.31	1.44	-14.52	+3.01	+0.98	-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	11.29	78.59	92.89	128.94	217.29	284.23	139.75	131.81	107.30	115.20	161.34

Table 10

Mass balance calculations of trace elements in the coarse saprolite by isovolumetric method (g/m³).

Depth (m)	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	
-	+ 0.10	+ 0.40	-	+1.70	+1.70	+1.70	(a)	(b)	(c)	(d)	
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	2 169
Ni	-143	-151	-152	-134	-86	18	-134	-138	-140	-143	-140
Co	-51	-52	-53	-51	-36	3995	-51	-52	-52	-50	-46
Zn	-160	-176	-170	-137	181	360	-123	-144	-151	-143	26
Sc	-5	-12	-7	1	50	31	6	0	-8	-4	46
Cu	-53	-57	-54	-26	-19	711	-15	-36	-50	-32	59
V	0	-88	-61	56	443	27	79	16	-5	-61	491
Ba	-1432	-1540	-1498	-1590	-1794	120147	-1706	-1632	1476	-1402	-1665
Pb	2	-7	-9	-2	15	3073	-6	-1	0	6	+11
Y	-36	-40	-39	-39	-35	31	-43	-41	-36	-34	-40
Ga	-2	-14	-5	0	-4	19	0	-3	-1	-3	-11
Th	-1	-9	14	0	5	-8	-5	-5	-1	-3	49
U	0	-1	0	1	4	1	1	0	0	-1	+3
Zr	67	-57	82	67	107	39	51	98	-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	2	-2	2	2	2	1	4	2	-1	-2	-3
Be	-1	-2	-1	-1	-1	-1	-1	-1	-1	-1	-1
Mo	-6	-6	-6	-5	-6	11	-6	-6	-6	-5	-1
Sn	-1	-2	-1	-1	0	0	-1	-1	0	-2	-4
Tl	-1	1	-1	-1	-1	79	-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 (g/m³).

Coarse saprolite											
Depth (m)	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)	
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	307	-71	-67	-57	-58	-73
Ce	-129	-144	-46	-138	-52	12102	-151	-146	-130	-132	-154
Pr	-16	-17	-16	-16	-15	73	-18	-17	-15	-15	-17
Nd	-60	-66	-67	-62	-58	210	-68	-65	-58	-60	-64
Sm	-11	-12	-12	-11	-8	47	-12	-12	-10	-10	-10
Eu	-2	-2	-2	-2	-1	18	-2	-2	-2	-2	-2
Gd	-8	-9	-9	-8	-7	24	-10	-9	-7	-7	-8
Tb	-1	-1	-1	-1	-1	6	-1	-1	-1	-1	-1
Dy	-6	-7	-7	-6	-3	31	-7	-7	-6	-5	-6
Ho	-1	-1	-1	-1	-1	5	-1	-1	-1	-1	-1
Er	-3	-4	-4	-4	-1	17	-4	-4	-3	-3	-3
Tm	-1	-1	-1	-1	0	3	-1	-1	0	0	0
Yb	-3	-4	-4	-3	0	25	-3	-3	-3	-3	-2
Lu	-1	-1	-1	0	0	3	-1	-1	0	0	0

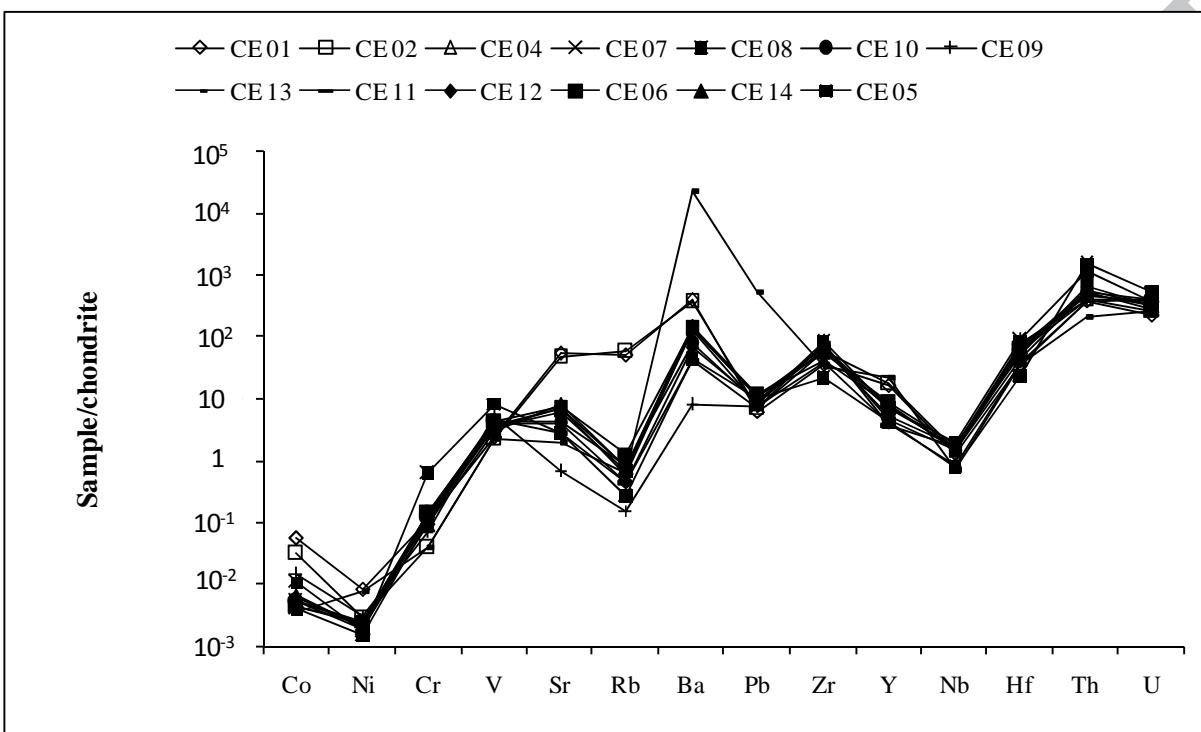


Figure 3

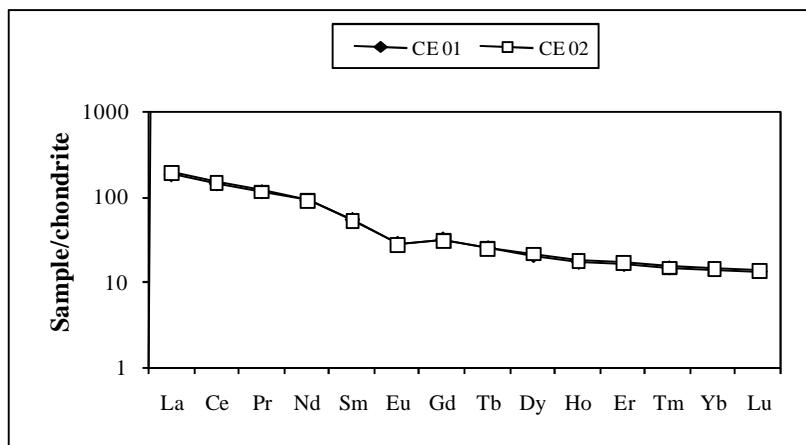


Figure 4

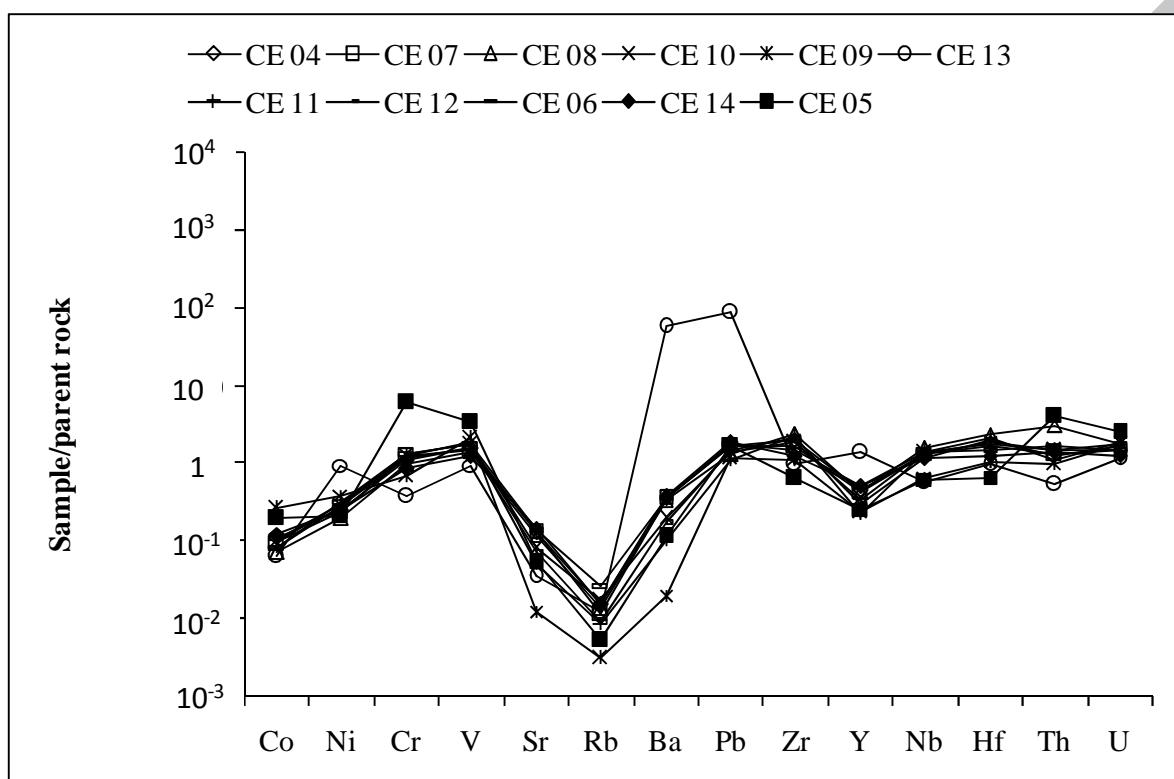
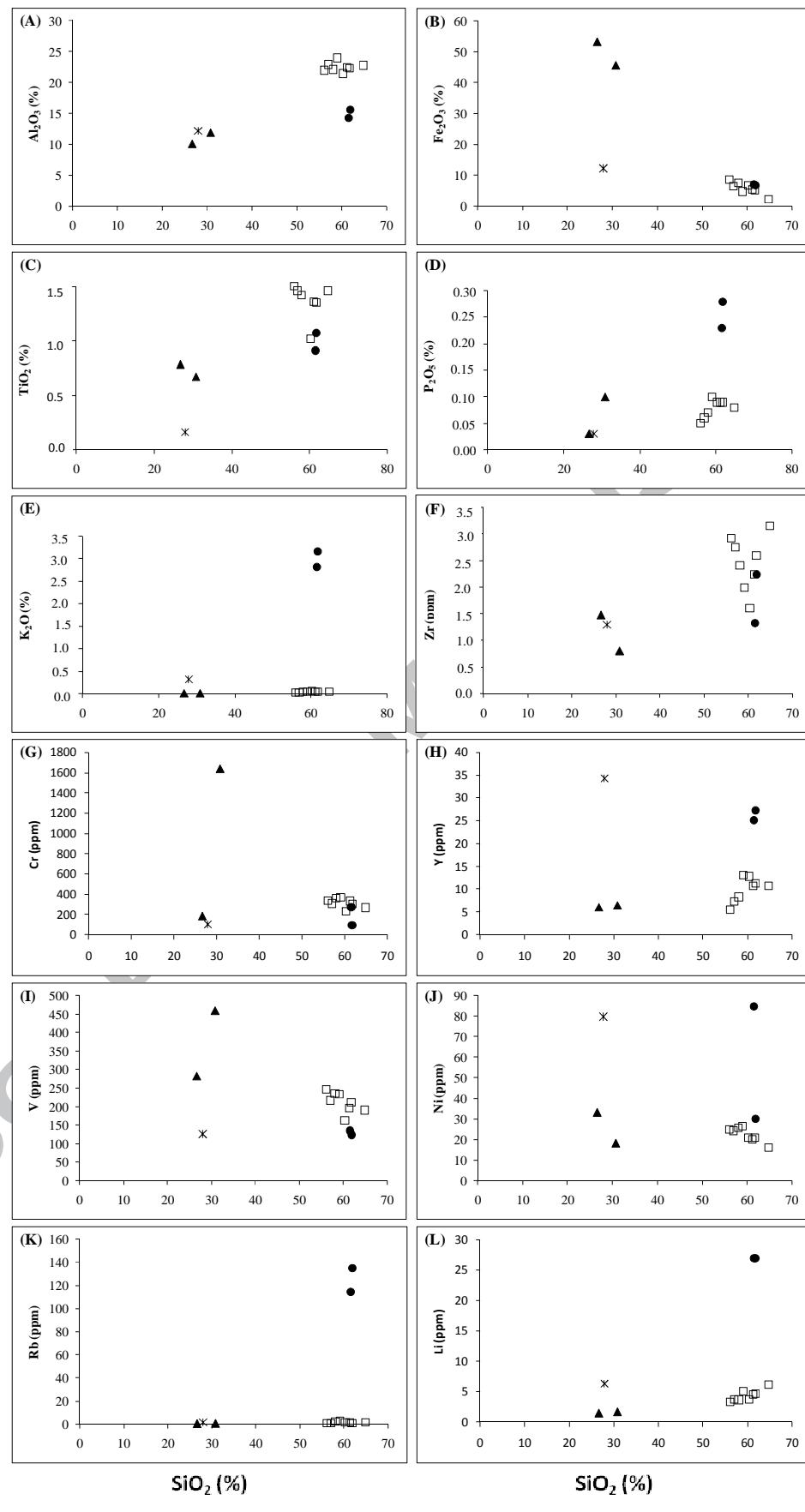


Figure 6



□ Loose materials ▲ Iron duricrust ✕ Mn-phases ● Parent rock

Figure 7

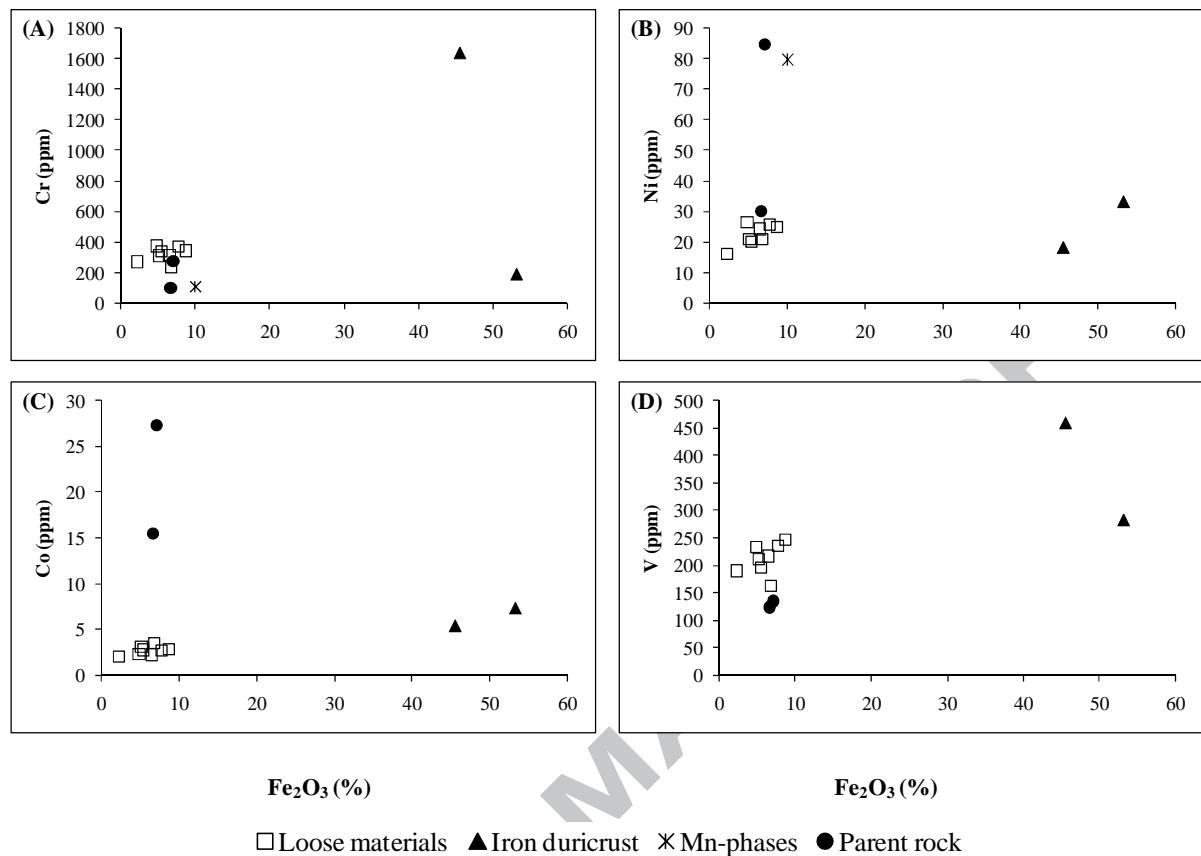


Figure 8

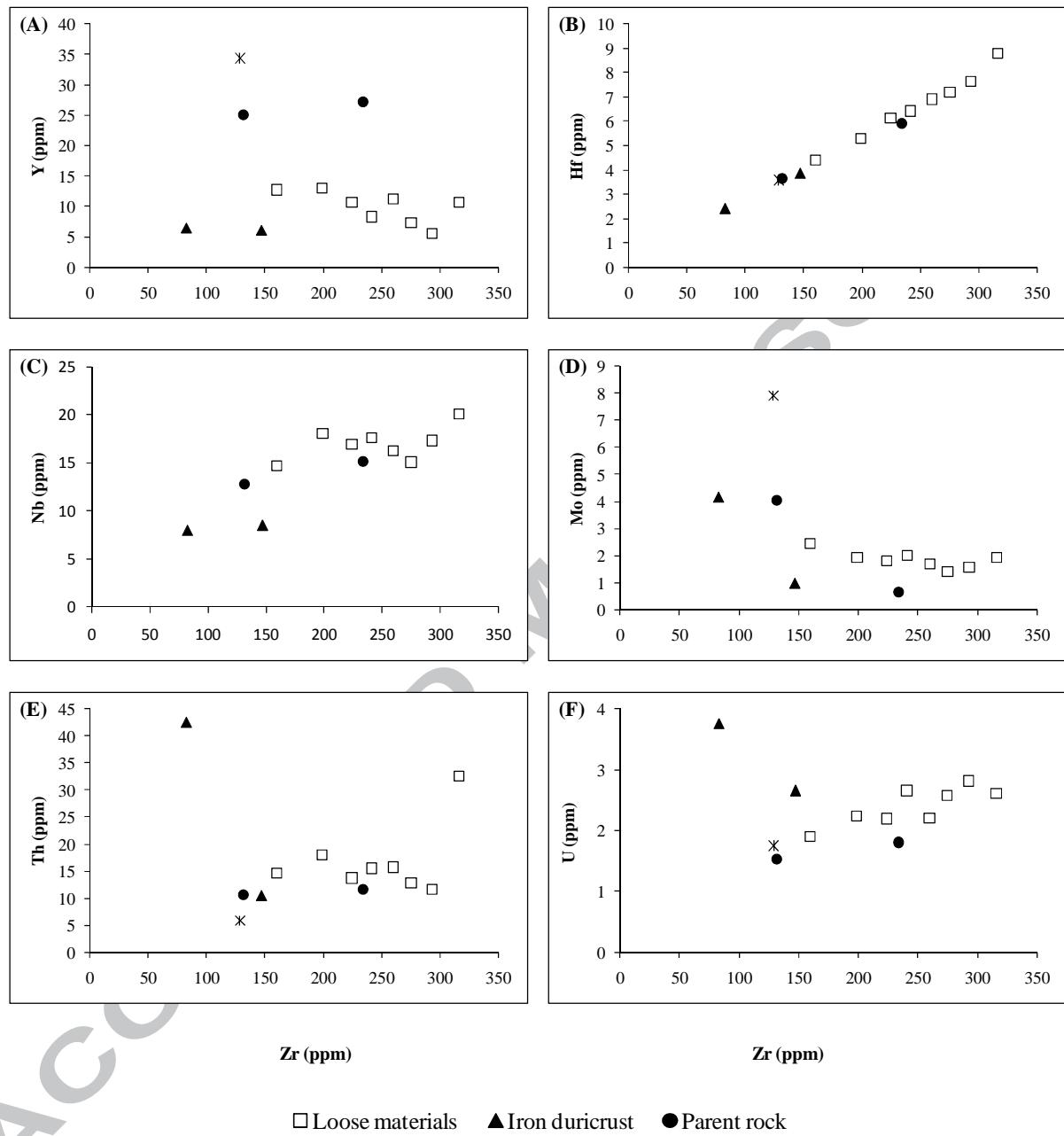


Figure 9

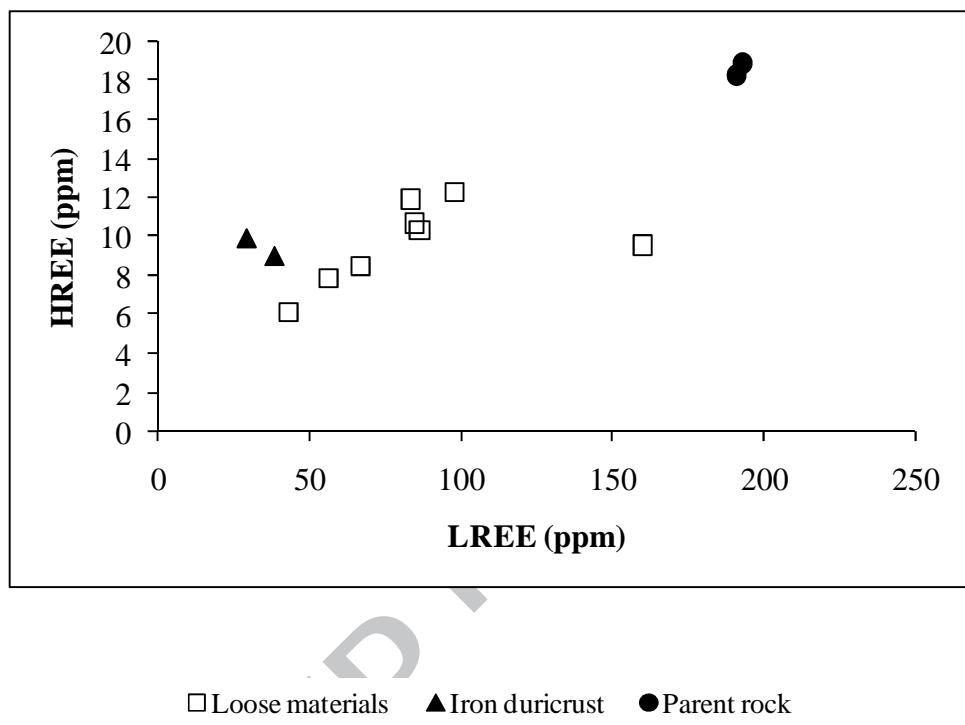


Figure 10

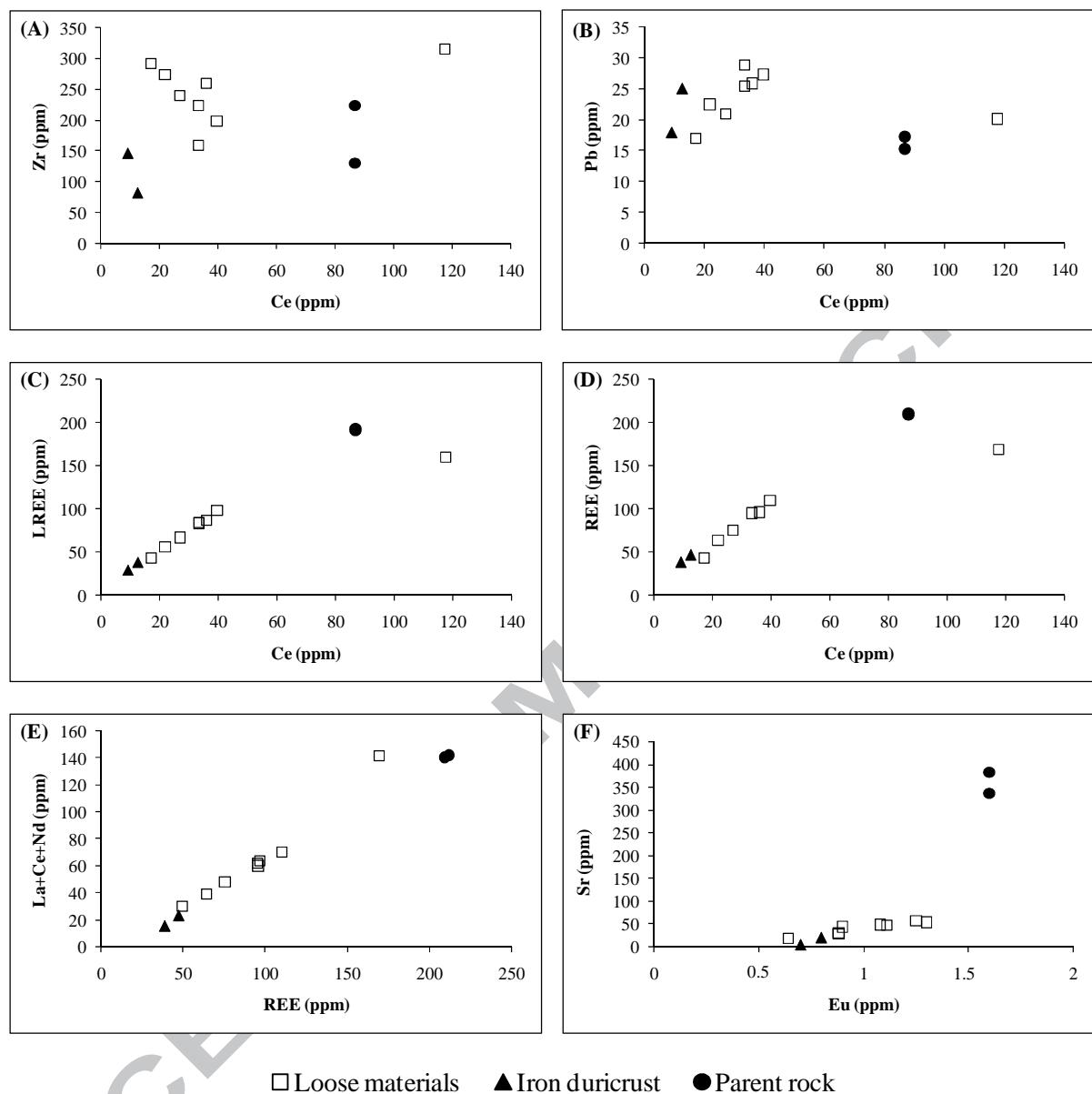


Figure 11

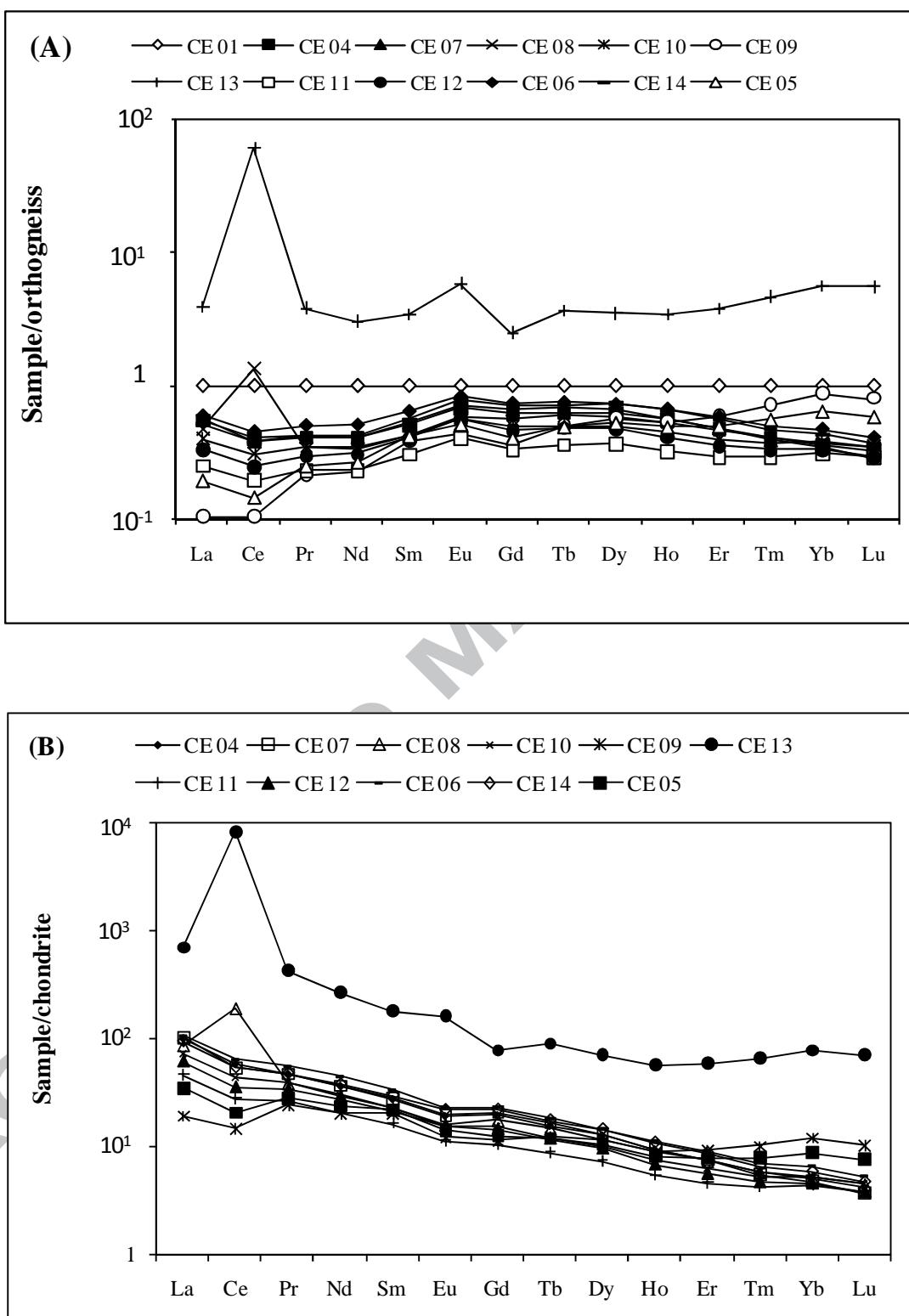


Figure 12

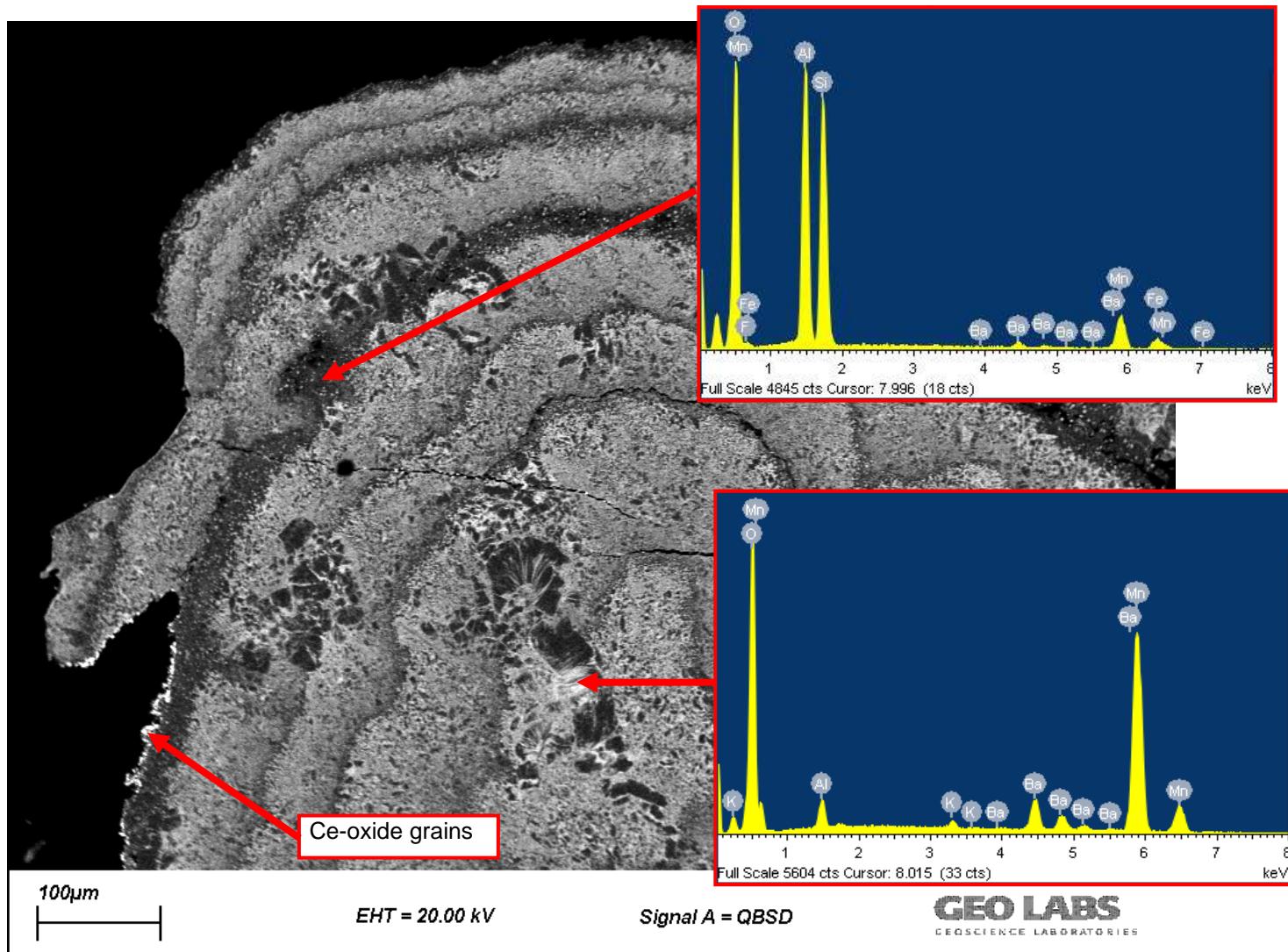


Figure 13

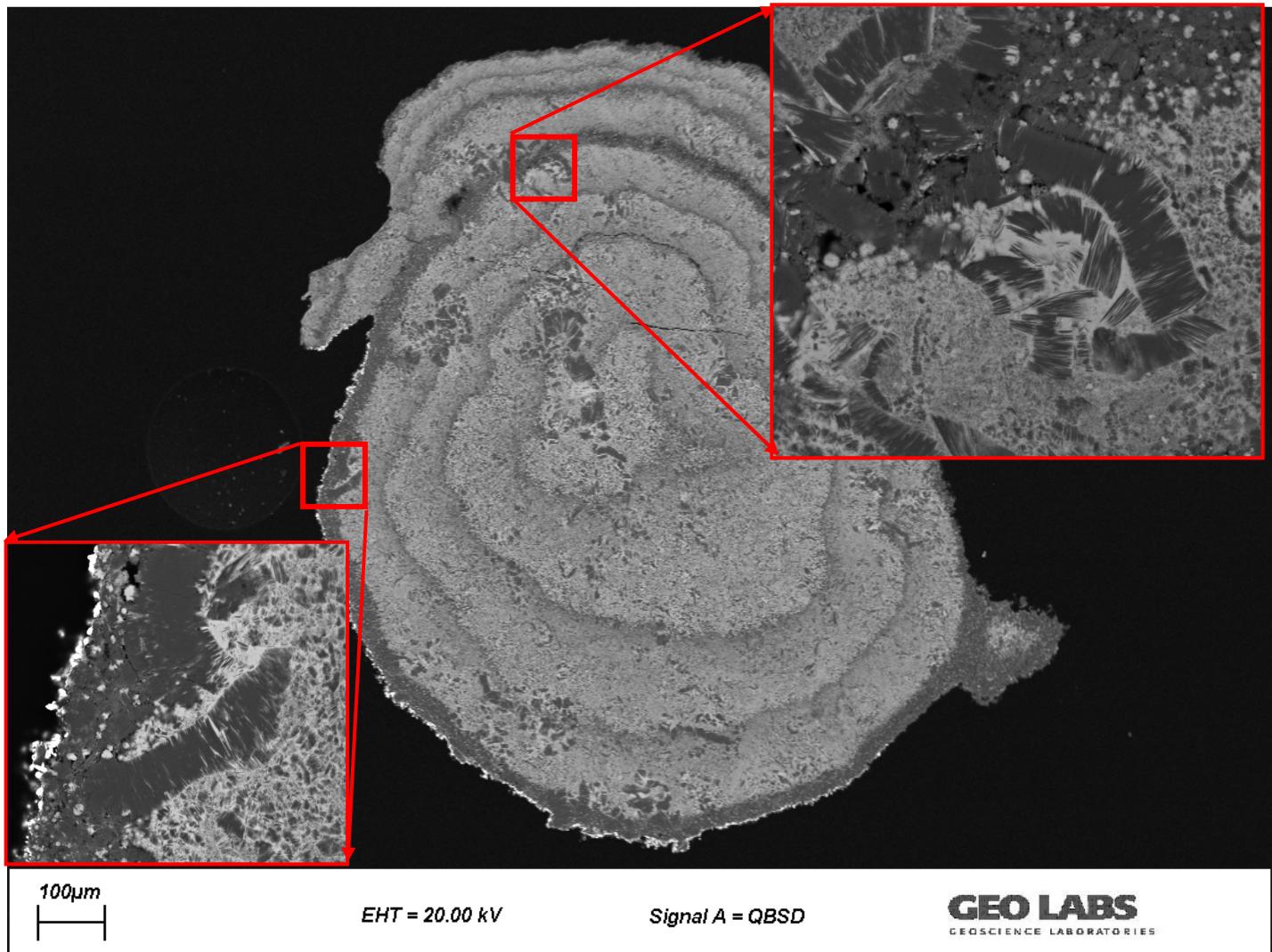
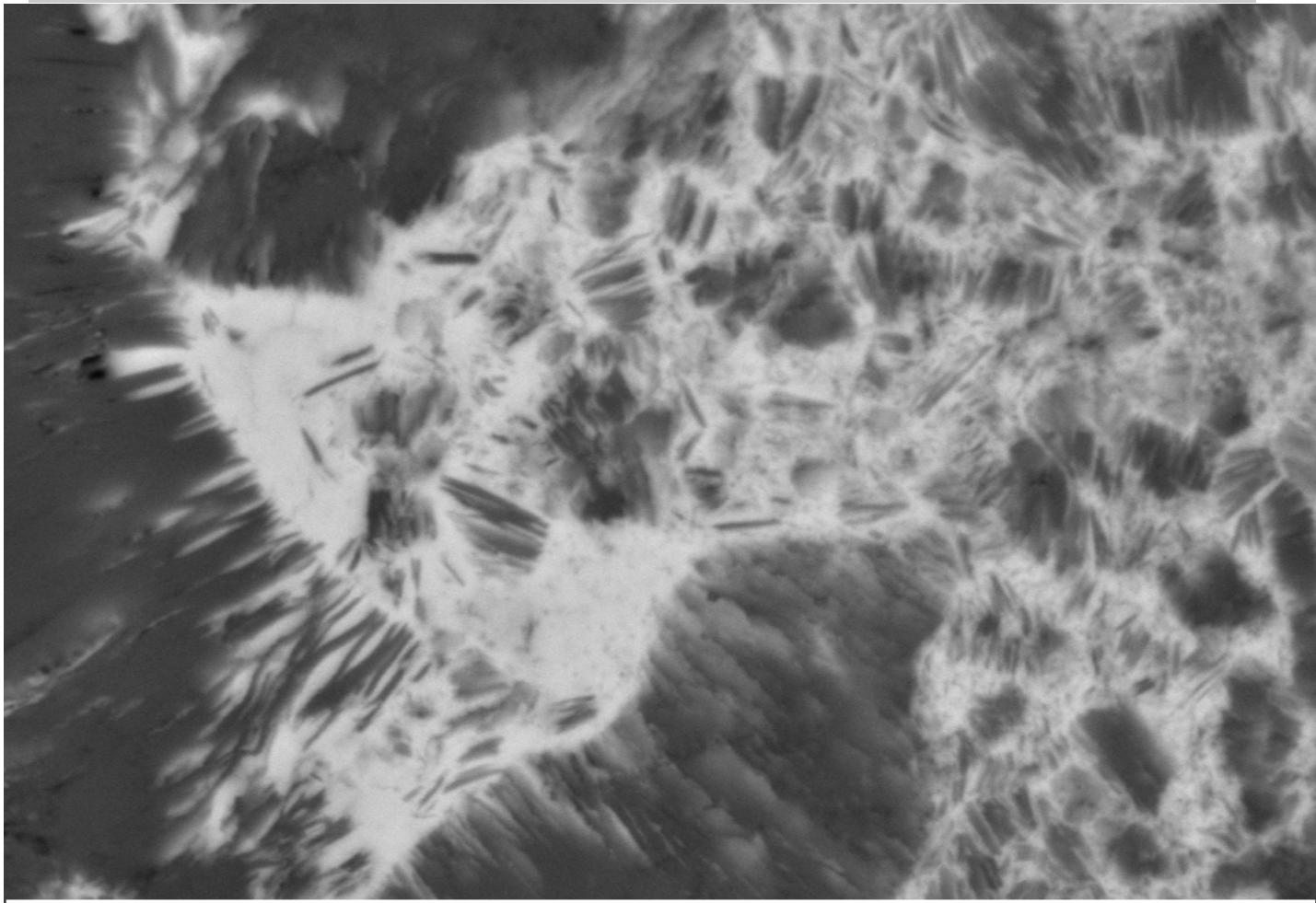


Figure 14



1 μ m
H

EHT = 20.00 kV

Signal A = QBSD

GEO LABS
GEOSCIENCE LABORATORIES

Figure 15

ACCEPTED

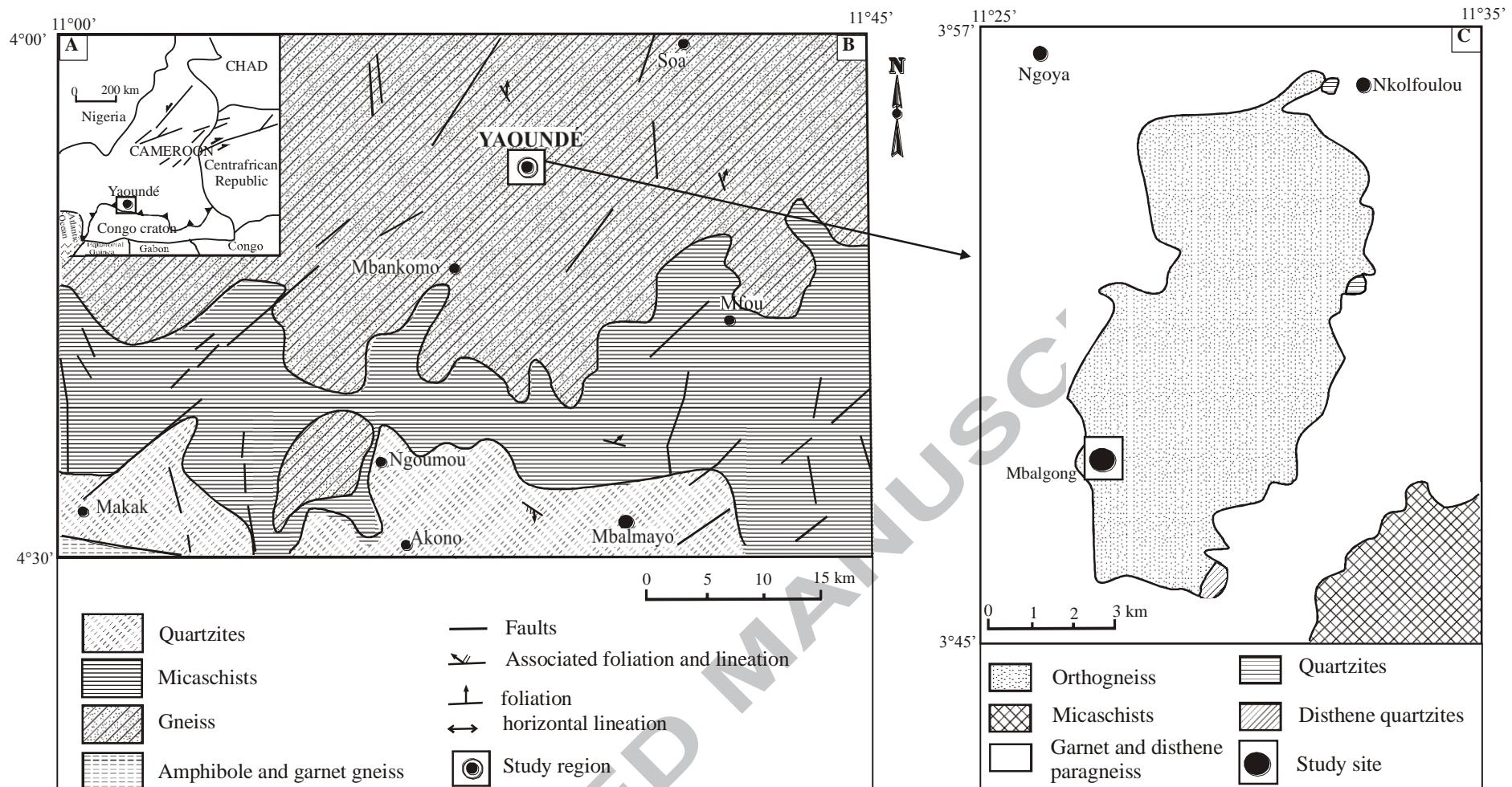
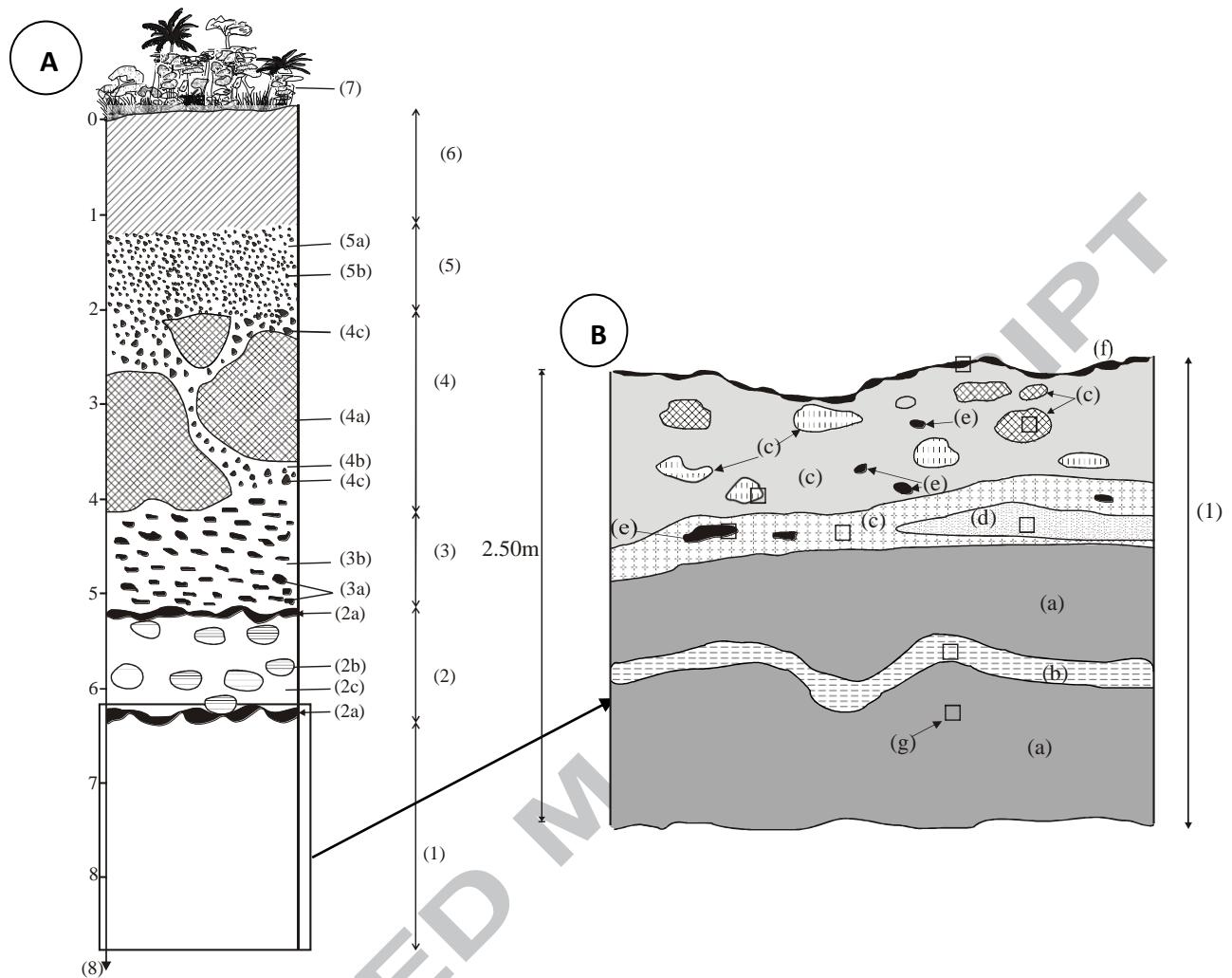


Fig. 1



1. coarse saprolite (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 saprolite (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

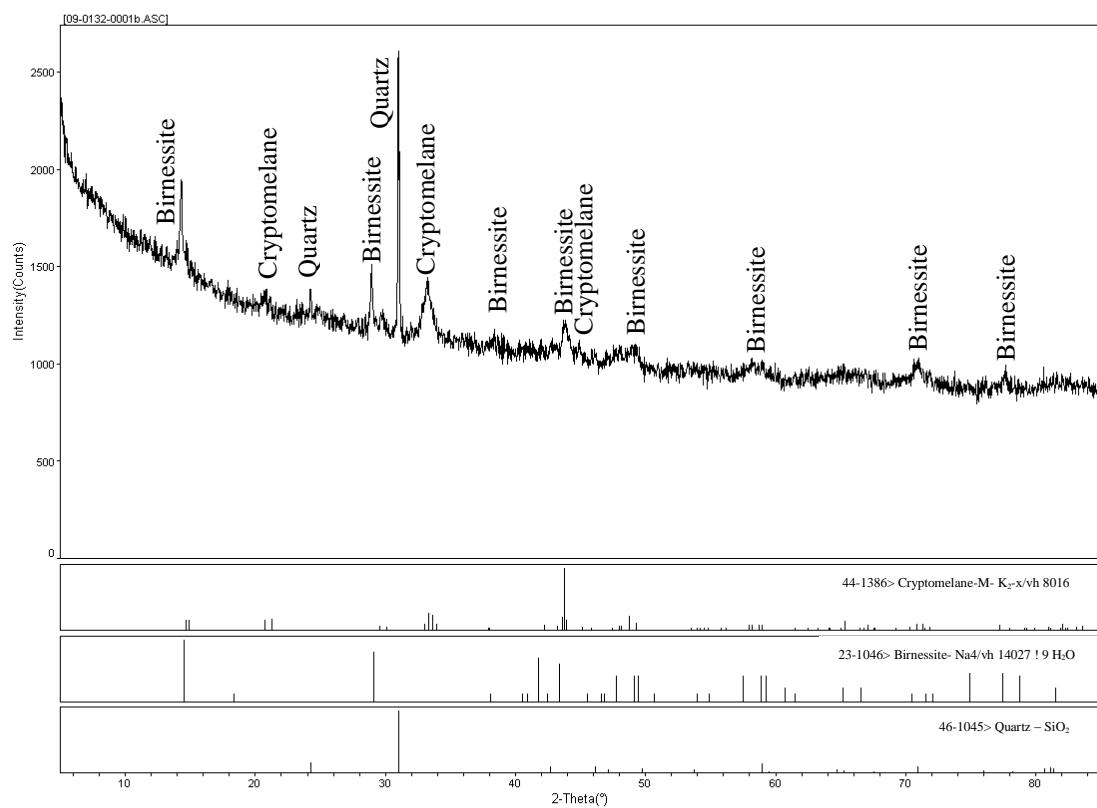


Figure 5