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Ferricrete biochemical degradation on the rainforest–savannas boundary of Central African Republic

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1 **Ferricrete biochemical degradation on the rainforest-savannas**

2 **boundary of Central African Republic**

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38 **Abstract**

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40 In southeastern Central African Republic the lateritic weathering mantles are
41 capped by two to five meters thick ferricretes, which previously formed under a
42 seasonal tropical climate. The actual humid tropical climatic conditions result in the
43 biophysical disaggregation of the ferricretes everywhere the forest develop that lead to a
44 soil formation composed of ferricrete relicts and ferruginous nodules embedded in a soft
45 bioturbated micro-aggregated clay-ferruginous matrix. The potential effect of the
46 biological activity (e.g., termites) on the soil and vegetation dynamics and therefore on
47 the evolution of the previous consolidated ferricrete is discussed. Following its
48 mechanical disaggregation by the forest tree roots, the ferricrete underwent a chemical
49 degradation under the combined effect of hydration and redox conditions, which result
50 from the biodegradation and oxidation of the organic matter. The transformation of the
51 ferricrete into a soft bioturbated micro-aggregated clay-ferruginous soil matrix implies
52 the hematite dissolution, and the kaolinite transformation into gibbsite, which may
53 characterize a late “bauxitization” (secondary gibbsitization of kaolinite) of previous
54 ferricrete profiles linked to a late Quaternary environmental (climate and vegetation)
55 change. However, the geochemical and mineralogical pattern of the matrix not only
56 reflects the geochemistry of the parental ferricrete but also depends on the physical
57 transfers of quartz and heavy minerals from the lower horizons of the profile. Hence,
58 the use of geochemical indexes such as Ti and/or Zr for mass balance calculations in the
59 lateritic weathering profiles is precluded because these supposedly inert chemical
60 elements are not simply accumulated by *in situ* chemical weathering process.

61
62 *Keywords:* Biochemical weathering; Ferricrete; Bauxitization; Termites; Central
63 African Republic

64
65 *Beauvais, 2008*

65 1. Introduction

66
67 Long term rock chemical weathering throughout the intertropical zone led to the
68 formation of several tens meters of lateritic weathering profiles, many being capped by
69 two to ten meters thick ferricretes. From the bottom to the top, a ferruginous lateritic
70 weathering profile is generally composed of a saprolite, a mottled clay horizon, a soft
71 ferricrete and/or a soft nodular horizon and a ferricrete (Nahon, 1986; Tardy, 1997;
72 Beauvais, 1999). The ferricretes developed under a seasonal tropical climate and
73 represent the ultimate stage of the ferruginization process that started earlier in the
74 mottled clay horizon (Tardy and Nahon, 1985; Nahon, 1986, 1991; Thomas, 1994;
75 Tardy, 1997; Beauvais, 1999). With the increasing ferruginization, the geochemical
76 signature of parent rocks is progressively blurred until nearly complete deletion in the
77 ferricrete (Tardy et al., 1988; Tardy, 1997). The large intertropical areas over which the
78 ferricretes actually outcrop suggest paleoclimatic changes towards drier conditions
79 (Tardy and Roquin, 1998) that led to the degradation of the vegetation cover with a
80 consecutive mechanical erosion of the upper leached horizon, which previously overlay
81 the buried ferricrete (Büdel, 1982; Millot, 1983; Butt, 1987).

82 However, the exposed ferricretes may disaggregate and geochemically degrade
83 under the wet and warm climatic conditions characterizing the rainforest environments
84 (Novikoff, 1974; Nahon *et al.*, 1989; Thomas, 1994; Tardy, 1997). The degradation of
85 previously consolidated ferricretes implies a complete reorganization of the uppermost
86 part of the profile under the effects of biological activity and almost permanent
87 moisture. Therefore, the disaggregated ferricrete is progressively transformed into a soil
88 containing blocks and debris of ferricrete of various sizes including centimeter size
89 ferruginous nodules embedded in a bioturbated micro-aggregated clay ferruginous
90 matrix similar to that of many red ferruginous tropical soils. Such a transformation is

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91 investigated (1) by comparing the main geochemical outlines of an undisturbed
92 ferricrete profile and a disaggregated ferricrete horizon, and (2) by defining the
93 geochemical differentiation pattern of two disaggregated ferricrete horizons at the top of
94 lateritic weathering profiles profile developed upon different parent rocks. The
95 biophysical and geochemical processes involved in the ferricrete degradation are
96 discussed. In particular, the potential role of the biological activity (e.g., termites) on the
97 degradation processes of previous undisturbed ferricrete profiles is approached.

98

99 **2. Field description**

100

101 The study area (“Haut Mbomou”) is located in southeastern Central African
102 Republic (CAR) (Fig. 1a). The climate is humid seasonal tropical with a dry season
103 from December to February and a mean annual rainfall of 1600 mm (Fig. 1a), a mean
104 annual temperature of 25°C and a mean annual relative humidity of the air of 80%. The
105 southern part of CAR hosts forests belonging to the Congo-Guinean domain (Sillans,
106 1958), where *Terminalia superba*, *Albizia zygia*, *Triplochiton scleroxylon* and *Celtis sp.*
107 are the main identified species (Boulvert, 1986; Beauvais, 1991).

108 The vegetation of the study area is a mosaic of grass savanna interspersed with
109 patches of dense rain forest. About 79.3 % of the total landsurface of the previous
110 mapped area (545 km²) are covered by grass savanna where consolidated ferricrete is
111 outcropping on plateaus and hillslopes, while the rain forest occupies the remaining
112 20.7 % where the ferricrete is disaggregated resulting in the formation of dismantled
113 ferricrete soils (Beauvais and Roquin, 1996; Fig. 1b). The extension of forest against
114 savanna in the Mbomou area was dated from the Holocene period using C isotopic
115 analyses of organic matter in soils and alluvial sediments (Runge, 2002) that also
116 characterize a climatic change towards more humidity. A semi-humid forest with

Beauvais, 2008

117 *Anogeissus leiocarpus* and *Albizia zygia* effectively develops around the highest
118 plateaus (10.6% of the total surface) at a topographic slope gradient change (Fig. 1c),
119 while a Guinean selvage forest with *Triplochiton scleroxylon* and *Celtis sp.* occupies
120 relatively incised thalwegs (10.1% of the total surface). A Soudano-Guinean savanna
121 with *Daniella oliveri* and *Terminalia glaucescens* alternates with Gramineae such as
122 *Ctenium newtonii* and *Loudetia annua* (Sillans, 1958), where ferricrete effectively
123 outcrops on the plateaus (Boulvert, 1986; Beauvais, 1991).

124 The degradation processes of the ferricrete are investigated on vertical profiles located
125 in the forested transition area between the high plateaus and the bare hillslope (Figs. 1b
126 and 1c), which carry massive or protonodular and protopisolitic ferricretes, respectively,
127 as previously established from a combined geomorphological and petrological study of
128 the main ferricretes in the “Haut-Mbomou” region (Beauvais and Roquin, 1996). In the
129 “Haut-Mbomou” area, the moderate epeirogenesis resulted in insufficient river incision
130 and erosion that did not allow a clear differentiation of stepped lateritic
131 paleolandsurfaces (bauxitic and ferruginous) like those characterizing the West African
132 landscapes (Eschenbrenner and Grandin, 1970, Michel, 1973; Grandin, 1976; see also
133 Beauvais et al., 1999). The long-term (Cenozoic) climatic change gradient was higher in
134 West Africa than in CAR (Tardy and Roquin, 1998). Paleoclimates evolved from humid
135 to dry in West Africa, and from arid to seasonal humid tropical in CAR that led to
136 continuous ferricrete formation during Tertiary (Beauvais, 1991; Beauvais and Colin,
137 1993; Tardy and Roquin, 1998) instead of successive development of bauxite and
138 ferruginous glacis (pediments). However, the high plateaus and hillslopes or low
139 plateaus of the “Haut-Mbomou” could be analogous of the West African intermediary
140 and high glacis landsurfaces, respectively (Boulvert, 1996).

141 The “Haut-Mbomou” landscape is also characterized by “mushroom” termite
142 mounds of *Cubitermes fungifaber*, which are systematically erected on gently sloping
143 surfaces bearing a ferricrete (Fig. 3a), called “lakéré” (Sillans, 1958; Boulvert, 1986).
144 Runge and Lammers (2001) counted five to six hundred termite mounds per hectare for
145 an area of 75,000 km² (Mbomou plateau) that imply a denudation rate of 0.1 mm.ha⁻¹
146 .year⁻¹ corresponding to 0.94 t. ha⁻¹.year⁻¹ of material removed by termites from the
147 lower weathered horizons (saprolite and mottled clays). This material is therefore
148 available for surface runoff erosion and dispersion over the outcropping ferricretes (Fig.
149 3b) that may favor the forest growth at the expenses of savanna under humid tropical
150 climatic conditions.

151

152 **3. Material and analytical techniques**

153 The degradation patterns of the ferricrete are studied and analyzed in the
154 uppermost-disaggregated parts (1 to 4.5 m) of two vertical lateritic weathering profiles
155 (Figs. 2c and 2d) at Guenekoumba and Finzani in southeastern CAR (Figs. 1a). The two
156 vertical profiles are located in the forest fringe (forested hillslope) between the high
157 plateau and the bare hillslope both bearing undisturbed ferricrete profiles (Fig. 1b). The
158 weathering profile of Guenekoumba is developed on amphibole schist (Beauvais and
159 Colin, 1993) while epimetamorphic schist intruded by granite constitutes the parent
160 rocks of the Finzani weathering profile. Based on geological map, the amphibole schist
161 rocks were observed and collected on outcrops and in riverbeds, while the
162 epimetamorphic schist was deduced by the direct observation of saprolites (Beauvais,
163 1991; Beauvais and Colin, 1993). A typical disaggregated ferricrete horizon is
164 composed of three main components (Fig. 2b to 2d). A first component corresponds to
165 the disaggregated ferricrete of 1-2 to 3 m thickness, which is often affected by

167 horizontal joints (Fig. 2c and 2d), the edges of which being overlain by lamellar
168 goethitic brown secondary deposits. Decimetric and metric fragments and blocks of
169 ferricrete characterize this sub-horizon. The second component is composed of
170 hematitic ferruginous nodules and clasts of ferricrete of size ranging between 1 and 10
171 cm. This sub-horizon can also contain some humus in its uppermost part. The nodules
172 are larger at the top than at the base of the horizon. The third component consists of the
173 bioturbated micro-aggregated clay-ferruginous matrix, in which the nodules and clasts
174 of ferricrete are embedded and the biological activity is highly developed (Fig. 2b).

175 Fifty-three samples and sub-samples were collected between 0 and 4.5 meters
176 (Figs. 2c and 2d): thirty-three samples for Guenekoumba (15 ferricrete relicts, 9 nodules
177 and 9 matrices) and twenty samples for Finzani (6 ferricrete relicts, 6 nodules and 7
178 matrices). Subsamples of nodules and matrices were extracted from a same sample.

179 XRD was used to determine the mineral composition of each sample category, i.e.,
180 the quantity of quartz, kaolinite, gibbsite, hematite and goethite. Mineral contents were
181 estimated by measuring characteristic intensity of X-ray peak weighted by a calibration
182 coefficient defined for each mineral, using normative calculations (Mazaltarim, 1989).
183 The estimation error ranges from 1 to 3 %. Each sample was therefore defined by five
184 mineralogical variables, corresponding to the estimated contents of kaolinite (Ka),
185 quartz (Q), gibbsite (Gi), goethite (Go), hematite (He), and also by the ratios, RGH
186 equal to $100 * \text{goethite}/(\text{goethite} + \text{hematite})$, and RKGi equal to $100 * \text{kaolinite}/(\text{gibbsite} + \text{kaolinite})$
187 as defined by Beauvais and Roquin (1996). Scanning
188 electron microscopy has been also used to define the crystalline morphology of the main
189 mineral phases for each ferricrete degradation component.

190 Spark emission spectrometry has provided chemical composition for major
191 elements, Si, Al, Fe, Mn, Mg, K, Ti, P. Inductively coupled plasma atomic emission

192 spectrometry (ICP-AES) was used to dose the trace elements, Sr, Ba, V, Ni, Co, Cr, Zn,
193 Cu, Sc, Y, Zr, La, Ce, Yb, Nb.

194 Mineralogical and chemical data were statistically analyzed by a principal component
195 analysis (PCA) using StatView F- 4.5 (1995) that allowed differentiation of the main
196 geochemical patterns of each sample category. The eigenvectors are first determined with
197 their associated Eigen values from the correlation matrix, followed here by an application of
198 the orthogonal Varimax rotation procedure (Lebart *et al.*, 1979). The principal components
199 (factorial axes) describe the main differentiation trends in the data set. These independent
200 synthetic variables are characterized by correlation loadings with chemical elements and
201 minerals, as previously applied to tropical soils (Litaor *et al.*, 1989; Donkin and Fey, 1991),
202 bauxitic weathering profiles and ferricretes regional distribution (Boski and Herbosch, 1990;
203 Roquin *et al.*, 1990; Beauvais and Roquin, 1996). Within each factor, the correlation loadings
204 ranging from -0.4 to 0.4 were considered as non-significant regarding to the samples number.
205 The projection of samples on factor score diagrams highlights the differentiation patterns
206 within and between each samples category, allowing discussion of the geochemical and
207 mineralogical evolution induced by the development of the weathering and ferruginization
208 and/or the ferricrete degradation process.

209

210 **4. Results and discussion**

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212 *4.1. Petrographical outlines of the ferricrete degradation*

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214 The formation processes of undisturbed lateritic weathering profiles (Fig. 2a) were
215 previously studied (Beauvais and Colin, 1993; Beauvais, 1999). The present study
216 focuses on the uppermost part (ferricrete) of such profiles, which is apparently
217 disaggregated and degraded under the forest (Fig. 2b). The ferruginous nodules of such

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218 horizon have the same petrographical fabric as the ferricrete. However, many nodules
219 exhibit peripheral goethite brown rims (Fig. 4a) composed of many thin crystals, which
220 develop perpendicular to the edge of the hematitic core of the nodules (Fig. 4b). Other
221 nodules previously composed of hematite and kaolinite (Beauvais, 1999) show gibbsite
222 crystals formed at the expense of the kaolinite (Fig. 5a). Secondary gibbsite crystals of
223 10 μ m size are also observed within vacuolar voids of 20 to 50 μ m sizes (Fig. 5b). The
224 bioturbated micro-aggregated clay ferruginous matrix is also characterized by the
225 formation of smaller size (2 μ m) gibbsite crystals within the vacuolar and tubular
226 porosity (Fig. 6a and 6b). This gibbsite is not inherited but comes from the process of
227 ferricrete transformation, contemporaneously with the secondary gibbsite forming in the
228 kaolinitic saprolite of undisturbed profiles (Beauvais and Colin, 1993; Beauvais, 1999).
229 The degradation matrix also contains small size (10 μ m) quartz grains (Fig. 6c and 6d),
230 which may be mechanically transferred from other parts of the profile through the
231 termite activity (Eschenbrenner, 1986; Tardy, 1997; Thomas, 1994).

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233 *4.2. Undisturbed versus disaggregated ferricrete profile*

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235 A comparison between a previously studied undisturbed lateritic weathering profile with
236 consolidated ferricrete (Beauvais and Colin, 1993) and the disaggregated ferricrete horizon of
237 an adjacent profile in the Guenekoumba site (Figs. 2a, 2b and 2c) allows differentiation
238 between the advancing ferruginization and the geochemical degradation of ferricretes. The
239 development of the undisturbed weathering profile is a function of two complementary
240 processes: saprolitization and ferruginization (Beauvais and Colin, 1993), during which iron
241 first increases by relative accumulation (saprolitization) and secondly by absolute
242 accumulation that leads to the ferricrete development (Beauvais, 1999). These processes are
243 characterized by analyzing the behavior of Fe against Sc (Brown et al., 2003). Except for the

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244 absolute Fe depletion due to local reduction process in the saprolite, Fe and Sc increase in
245 same proportions (relative Fe accumulation) during the first stage of *in situ* rock chemical
246 weathering. However, Fe and Sc show a more contrasted behavior during the ferruginization
247 process driven by oxidation processes that lead to the development of the soft nodular and
248 ferricrete horizons by absolute Fe accumulation (Fig. 7a).

249 The ferricrete geochemical degradation first leads to a decrease of Sc compared to
250 the ferricrete of the undisturbed profile, then to a decrease of Fe with approximately
251 constant Sc (Fig. 7a). The nodules of the disaggregated horizon are richer in Fe than the
252 nodules of the soft nodular layer underlying the ferricrete of the undisturbed profile.
253 The first effectively derive from the physical disaggregation and geochemical
254 degradation of the ferricrete, whereas the second are advanced ferruginized forms of
255 mottled clays (Tardy and Nahon, 1985; Nahon, 1986, 1991; Tardy, 1997). The matrices
256 of the disaggregated ferricrete horizon show less Sc content than the saprolite and the
257 mottled clays of the undisturbed ferricrete profile (Fig. 7a). These matrices are also
258 enriched in Zr and Si (Quartz), and show similar Ti contents as the saprolite and mottled
259 clays of the undisturbed ferricrete profile (Figs. 7b-d). Ti and Zr are not correlated in
260 the undisturbed profile while they co-vary in the disaggregated ferricrete horizon (Fig.
261 7d). They may relatively enrich from the ferricrete degradation or absolutely
262 accumulate by some mechanical transfer from other parts of the profile.

263 A principal component analysis of the geochemical and mineralogical data of the
264 undisturbed and disaggregated profiles yields four factorial axes describing 75.2% of
265 the total variance (Table 1). The first factorial axis (37.3 % of the total variance)
266 discriminates the saprolitization with its residual parent rock mineralogical inheritance
267 (quartz + heavy minerals) from the advancing ferruginization (hematite and goethite)
268 processes (Fig. 8). The second factorial axis (23.6 % of the total variance) characterizes

269 the ferricrete degradation by discriminating the clay-ferruginous matrices from the
 270 ferricrete relicts and nodules (Fig. 8). The figure 8 also shows the differentiation of the
 271 degradation matrices from the saprolite and mottled clays of the undisturbed ferricrete
 272 profile. Compared to the parental ferricretes the degradation matrices are enriched in
 273 quartz, gibbsite and heavy minerals and impoverished in iron, hematite and kaolinite.
 274 The third factorial axis (7.2 % of the total variance) clearly described the transformation
 275 of kaolinite into gibbsite in the undisturbed ferricrete profile (Beauvais and Colin, 1993)
 276 but also in the degradation matrices (Table 1 and Figs. 6a-b) that could characterize the
 277 late “bauxitization” (i.e., secondary gibbsitization according to Tardy, 1997) of the
 278 previous ferricrete profiles. This “bauxitization” may result from the development of
 279 the forest at the expenses of savanna linked to a more humid climate since the Holocene
 280 (7.5 to 7 ka) (Runge, 2002). The fourth factorial axis (7.1 % of the total variance)
 281 collates Ce, Ba, Sr and La, which reflect some parent rock geochemical inheritance
 282 (Table 1). Secondary minerals such as florencite may also form as it was suggested in
 283 similar lateritic weathering profiles of Cameroon (Braun et al., 1990). Cerianite (Ce-
 284 oxide) was also identified at the bottom of the soft nodular horizon in the undisturbed
 285 ferricrete profile of Guenekoumba (Beauvais and Colin, 1993).

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287 *4.3. Geochemical differentiation pattern of two disaggregated ferricrete horizons*

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289 The average geochemical and mineralogical compositions of each ferricrete
 290 degradation components (ferricrete elements, nodules and soft matrices) are given in the
 291 table 2. The degradation components of the Guenekoumba profile are, on the average,
 292 less rich in silica, alumina, MgO, and K₂O but richer in Fe₂O₃, Mn₃O₄, TiO₂ and P₂O₅
 293 than those of the Finzani profile. These geochemical differences reflect differences of
 294 parent rocks, which are also emphasized by differences in V, Cr, Cu, Zn, Y, Ba, La and

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295 Ce contents (Table 2). A relatively high amount of K₂O and Ba has been noted in the
296 Finzani ferricrete relicts as well as some Mg (Table 2) that may indicate a relatively
297 quick ferruginization of saprolite still embedding poorly weathered micas prior to the
298 hardening of the ferricrete (Beauvais, 1991, 1999). Therefore, the differences of
299 alumina contents may be explained by the accumulation of relict micas and kaolinite
300 higher in the Finzani profile than in the Guenekoumba profile (Table 2).

301 The geochemical differentiation patterns of each sample category (ferricrete relicts,
302 nodules, and matrix) are also deciphered, by applying a Principal Component Analysis
303 (PCA) to the geochemical and mineralogical data that allows definition of three
304 factorial axes accounting for 76.4 % of the total variance (Table. 3). The first factorial
305 axis (44.1 % of the total variance) discriminates the group (ferricrete relicts + the
306 ferruginous nodules) from the embedding clay-ferruginous matrices (Fig. 9). These
307 latter are enriched in quartz (Figs. 6c-d and 10a) and heavy minerals (Fig. 10b) and they
308 are propitious to the development of gibbsite (Figs. 6a-b and 11a), which results from
309 the late weathering of micas and/or from the desilification and hydration of kaolinite
310 (Beauvais and Roquin, 1996). With quartz, the heavy minerals compose the residual
311 mineral phase, which may be relatively enriched by *in situ* geochemical degradation of
312 ferricrete containing them (Figs. 9 and 10b) or mechanically transferred with the clay-
313 silt materials from other parts of the profile through the termite activity (Tardy and
314 Roquin, 1992). The variation of Zr content in matrices at constant Fe (Fig. 11b) may
315 also suggest, at least partially, an absolute input of small size zircon. Hence, the
316 common use of Ti and Zr for mass balance calculations should be considered with much
317 caution. Zircon may also dissolve in the lateritic geosphere (Colin *et al.*, 1993). Mass
318 balance calculations based on geochemical indexes may be applied for non-perturbed
319 weathering horizons (Beauvais and Colin, 1993) but they are inappropriate for

1 320 quantifying the geochemical mass balance transfers in the upper ferruginous horizons
2 321 that are bioturbated and often rework allochthonous materials (Beauvais et al., 1999).
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4 322 The geochemical degradation of the ferricrete therefore leads to a release of Fe_2O_3 ,
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6 323 Sr, Ba, V, and Cr, with an accumulation of silica, alumina, Mn_3O_4 , MgO, K_2O and TiO_2
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8 324 in the matrices, and also, Ni, Y, Zr, Yb and Nb. The amounts of P_2O_5 , and Co, Zn, Cu,
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10 325 Sc, La, and Ce remain relatively constant (Table 2). The increasing of magnesium and
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12 326 potassium in the matrices of degradation profiles may reflect the occurrence of poorly
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14 327 weathered micas as phengites that is indicated by the negative loading of the second
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16 328 factorial axis (20.9 % of the total variance). Previous geochemical analyses of saprolite
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18 329 and mottled clays of Guenekoumba undisturbed profile revealed similar Mg and K
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20 330 contents, which related to poorly weathered relict micas optically identified on thin
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22 331 sections (Beauvais and Colin, 1993). The second factorial axis also characterizes the
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24 332 association of goethite with Cu, TiO_2 , Zn, P_2O_5 , Mn_3O_4 , and Sc (Table 3), which may
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26 333 indicate the presence of anatase and/or residual ilmenite in the degradation matrices as
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28 334 previously shown in undisturbed weathering profile (Beauvais and Colin, 1993). The
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30 335 factor 2 therefore discriminates the Ti-rich Guenekoumba degradation profile from the
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32 336 Ba-Mg-K rich Finzani degradation profile (Fig. 9) that suggests incomplete micas
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34 337 dissolution in this profile although a part of the kaolinite may derive from their late
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36 338 weathering in the degradation matrices (Table 2). The third factorial axis (11.4 % of the
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38 339 total variance) discriminates La–Sr–Ce–V from Co–Cu–Sc– Ni that reflects some
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40 340 geochemical dependence to the parent rock.
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53 342 *4.4. Factors of the ferricrete biochemical degradation*

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55 343 The mechanical disaggregation (tree roots effect) and biochemical degradation of
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57 344 the ferricrete result in the loosening of the ferruginous cements and their bioturbation by
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346 burrowing animals such as worms and termites. Termites microdivide the mineralogical
347 assemblages and transfer nutrients and clay-silts from the saprolite to the upper
348 ferruginous horizons and the topsoils (Eschenbrenner, 1986, 1987; Gleeson and Poulin,
349 1989; Tardy and Roquin, 1992; Thomas, 1994). Many topsoils of Central Africa are
350 formed, at least in part, from imported material from deeper horizons by termite activity
351 (De Heinzelin, 1955; De Ploey, 1964). The termite material may be spread at the ground
352 surface by erosion (Fig. 3b) that effectively contributed to the soil restoration and
353 hillslope forestation (Mando et al., 1996; Runge and Lammers, 2001), which are further
354 sustained by the nutrients transferred from the bottom to the top of the profiles
355 (Miedema et al., 1994; Berner and Berner, 1996). The forest biochemically degrades the
356 ferricrete transforming its main mineralogical constituents (Tardy and Roquin, 1992;
357 Birkeland, 1999). Notice that many ferruginous “stone lines” of the tropical forest
358 savanna transition areas may result from the combined termite activity and ferricrete
359 biophysical degradation (Eschenbrenner, 1986, 1987).

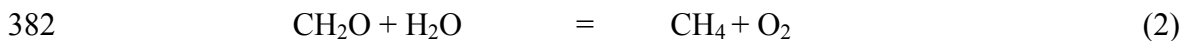
360 In spite of the lack of specific biogeochemical data, some interesting idea based on
361 field observations may be discussed before to be tested in future investigations. The
362 increasing biological activity generates bioturbation and aeration of the lateritic
363 weathering profiles by creating channels, chambers and pedotubules that improve the
364 hydrological properties of soils (drainage) and the plants development (Humphreys,
365 1994; Mando et al., 1996; Runge and Lammers, 2001). The digestion of the organic
366 matter by termites modifies the redox conditions of the vadoze zone. In the lateritic
367 profiles evolving under a forest cover the organic matter biodegradation may result in a
368 degassing of a mixture of carbon monoxide and methane. The occurrences of degassing
369 and water at the bottom of 10 to 15 m thick profiles may have a biogeochemical impact
370 on the geochemical and mineralogical patterns of the lateritic weathering profiles.

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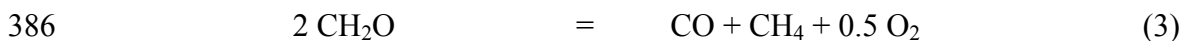
371 Although the gases were not analytically identified, they were highly suspected by acid
372 smells owing to the organic matters decomposition, by experimenting burn rope (CO)
373 and observing termite activity (CH₄) at the transition between the saturated and
374 unsaturated zone of profiles (10 to 15 meter depth). Carbon monoxide derives from the
375 partial oxidation of organic matter as:



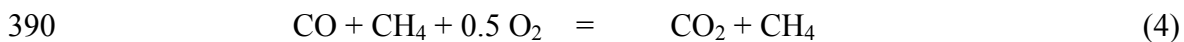
378
379 Methane result from the biodegradation of organic matter in termites' guts (Berner and
380 Berner, 1996; Mackenzie, 1998) according to the following reaction:



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384 It results from (1) and (2) the global dissociation reaction of organic matter:



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388 That leads to carbon dioxide production with methane as:



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392 It would be certainly interesting to analytically characterize the organic species in
393 the degradation matrices and in the solutions draining the disaggregated ferricrete
394 profiles as well as to get C isotopic signatures of the organic matters, soil solutions, and
395 gaseous phases. For instance, the measure of ¹³C/¹²C ratios would be useful to

396 distinguish bacterial from non-bacterial sources of methane (Conny and Currie, 1996).

397 However, the geochemical degradation of the ferricrete including the transformation of

398 its mineralogical constituents may be primarily controlled by the degree of hydration of

399 the profile (Tardy, 1997), and by the redox conditions change owing to the

400 biodegradation of organic matters producing H^+ protons (Berner and Berner, 1996).

401

402 *4.5. Mineralogical outcomes of the ferricrete biochemical degradation*

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404 The increasing biological dynamics and soil moisture (pore water activity) therefore

405 result in an increase of gibbsite and in a lesser part goethite with respect to kaolinite and

406 hematite. Goethite content does not significantly increase (Table. 1), but hematite is

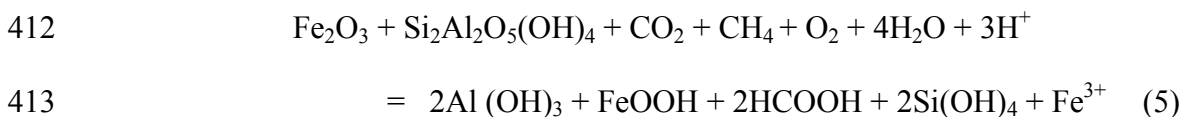
407 partly dissolved under the combined effect of redox and hydration process.

408 The organic matter biodegradation (reaction 4) and hydration processes may effectively

409 create the conditions of the disruption of the hematite – kaolinite mineral association

410 according to the following reaction:

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415 The released Fe may be exported towards the lower parts of the profiles and

416 reincorporated in a newly formed ferricrete essentially composed of goethite (Beauvais,

417 1999), according to local redox conditions also favorable to the formation of Ce and

418 Mn-oxhydroxydes (Beauvais and Colin, 1993).

419 The matrices and ferruginous nodules of the Guenekoumba profile are a little more

420 gibbsitic but less kaolinitic than those of the Finzani profile (Figs. 10a and 11a).

421 Nodules and ferricretes of Finzani contain more kaolinite than those of Guenekoumba

422 (Fig. 11a) but the same gibbsite quantities. According to Tardy (1997), the
423 transformation of kaolinite into gibbsite is limited in quartz-rich matrices, while this
424 transformation is important in matrices impoverished in quartz. But our results show
425 that relatively high quantities of small size quartz in bioturbated matrices (Figs. 6c-d
426 and 10a) do not preclude the transformation of kaolinite into gibbsite (Figs. 6a-b and
427 11a). In tropical soils this transformation is driven by high water activity ($[H_2O] = 1$) in
428 large pores (Tardy, 1997). Gibbsite effectively derives from kaolinite according to
429 desilification and hydration processes that lead to a decrease of kaolinite in the matrices
430 compared with the contents measured in the ferricrete and nodules (Fig. 11a). However
431 in soils with similar physical chemical properties (porosity, water activity and Eh-pH
432 conditions), the presence of silicates as phengites and quartz maintains relatively high
433 amounts of Si, Al, and (Ba, K, Mg) within the matrices (Table 2) that may limit the
434 transformation of kaolinite into gibbsite (Fig. 10a). This is the case of matrices of the
435 Finzani degradation profile (Fig. 11a) where the quantity of poorly weathered micas
436 inherited from the deeper horizons is higher than in the Guenekoumba profile.
437 Therefore, a part of the kaolinite may derive from the late weathering of micas if the
438 water activity in matrix pores is ≤ 0.9 ; but hematite could remain stable (Trolard and
439 Tardy, 1987). However, it was previously shown that kaolinite deriving from micas is
440 large and well crystallized and could be a mineralogical tracer of the late ferricrete
441 degradation (Beauvais and Bertaux, 2002). Both micas and kaolinite may however
442 transform into gibbsite if the water activity > 0.9 (Tardy, 1997), and the hematite is
443 dissolved and partly transformed into goethite (Trolard and Tardy, 1987).

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445 **5. Conclusion**

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447 In transitional humid tropical environments between savanna and rainforest, the
448 degradation of ferricrete previously composed of hematite and kaolinite results in the
449 development of a softer material relatively richer in gibbsite and in a lesser part in
450 goethite. The ferricrete degradation horizon is composed of chemically unsaturated
451 ferricrete relicts and ferruginous nodules embedded in a bioturbated micro-aggregated
452 clay ferruginous matrix. This matrix is also enriched in poorly weathered parent
453 minerals such as micas inherited from lower saprolite, and also with small size quartz
454 and heavy minerals, which may be biomechanically transferred by termites from the
455 lower horizons of the lateritic weathering profiles. The nutrient supplies by termites
456 may sustain the forest recrudescence on previous savanna areas implying the
457 biophysical dismantling and the geochemical degradation of the ferricrete. Such an
458 ecosystem may self-organize according to a positive feedback loop in that, the more
459 humid becomes the climate, the faster the forest grows in area enriched in nutrients
460 imported by termites, the more the ferricrete transforms into a micro-aggregated soil,
461 which sustains the forest development and therefore its destructive effect on the
462 ferricrete. The resulting hydration and biological processes lead to the biodegradation
463 and oxidation of organic matters modifying the redox conditions that also trigger the
464 ferricrete degradation. These processes result in the preferential dissolution of hematite,
465 and the transformation of kaolinite into gibbsite provide the moisture (water activity) be
466 sufficient that may also characterize the late “bauxitization” (Holocene) of previous
467 ferricrete profiles.

468 **Acknowledgements** – This is an IRD (UMR 161 CEREGE) contribution, which was
469 previously supported by the research program PIRAT (INSU-CNRS-ORSTOM). Two
470 anonymous reviewers are thanked for their helpful remarks and suggestions.

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597

598 **Figures caption**

599

600 **Figure 1.** (a) Location of the study area in Central African Republic (CAR). The black
 601 rectangle represents the previous mapped land area (Beauvais and Roquin, 1996;
 602 Beauvais, 1999). (b) Geomorphic distribution of the different forms of ferricrete. The
 603 black square is for the location of the disaggregated-ferricrete profile at Guénékoumba.
 604 (c) Geomorphological transect across c shown in (b).

605

606 **Figure 2.** (a) Sketch of a typical undisturbed profile, (b) Macroscopic patterns of the
 607 disaggregated ferricrete, (c) and (d) disaggregated ferricrete profiles of Guenekoumba
 608 and Finzani, respectively. The grey and black squares represent the analyzed samples.

609

610 **Figure 3.** (a) Gently sloping surface (bare hillslope) colonized by termite mounds, (b)
 611 Detail of the mounds at the transition between the grassy and forested hillslope (the size
 612 of the foreground ferricrete block is 0.5-0.6 m).

613

614 **Figure 4.** Transformation of a red-black hematite-kaolinite nodule into yellow goethite,
 615 (a) Polarised optical microscope view, (b) Scanning electron microscope view (Go =
 616 goethite crystals developing perpendicular to the nodule edge; kHe = kaolinite-hematite
 617 core of the nodule).

618

619 **Figure 5.** Transformation of kaolinite into gibbsite in a nodule, (a) Polarised optical
 620 microscope view. (b) Scanning electron microscope view. (K= kaolinite; G= Gibbsite).

621

622 **Figure 6.** Scanning electron micrographs of the bioturbated micro-aggregated clay
 623 ferruginous matrix. (a) Microcrystalline newly formed gibbsite, (b) detail of (a), (c)
 624 relict quartz grain and (d) relict quartz grain with dissolution-crystallization figures.
 625 (kHe = kaolinite-hematite; G = gibbsite; Q = quartz).

626

1 627 **Figure 7.** Geochemical comparison between undisturbed ferricrete profile (grey) and
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3 628 the disaggregated ferricrete horizon (black) of Guenekoumba, (a) Fe vs. Sc, (b) Fe vs.
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5 629 Zr, (c) Si vs. Zr, and (d) Ti vs. Zr, (the dashed line represents the relative accumulation
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8 630 and/or depletion of chemical elements).

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10 632 **Figure 8.** Geochemical differentiation pattern of the components in the undisturbed and
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13 633 disaggregated profiles of Guenekoumba by the factor score diagram Fs1 vs. Fs2, (see
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15 634 the table 1 for the factor loadings, and the figure 7 for the labels explanation). (Af =
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17 635 advancing ferruginization; Fd = ferricrete degradation).

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21 637 **Figure 9.** Geochemical differentiation pattern of the degradation components in the
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23 638 disaggregated ferricrete horizons of Guenekoumba (black) and Finzani (grey) by the
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25 639 factor score diagram Fs1 vs. Fs2, (see the table 3 for the factor loadings, and the figure
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27 640 7 for the labels explanation).

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28 642 **Figure 10.** Comparison between each disaggregated ferricrete profile, (a) quartz content
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31 643 vs. ratio RKGi in the degradation matrices ($RKGi = 100 * \text{kaolinite} / \text{kaolinite} +$
32
33 644 gibbsite), (b) Ti vs. Zr (see Figures 7 and 9 for labels explanation).

645

34 646 **Figure 11.** Comparison between the two disaggregated ferricrete profile (a) kaolinite vs.
35
36 647 gibbsite contents, (b) Fe vs. Zr (see Figures 7 and 9 for labels explanation)

648

649 **Tables caption**

650

651 **Table 1.** Correlation of chemical elements and minerals with each orthogonal
 652 factorial axis defined by the Principal Component Analysis for the undisturbed
 653 and disaggregated ferricrete profiles (σ %= % of explained variance; loading
 654 values are given in parentheses)

655

656 **Table 2.** Mean chemical and mineralogical compositions of the ferricrete
 657 degradation components (N = number of samples; m = mean; $\sqrt{\sigma}$ = standard
 658 deviation; wt.= weight; LOI = lost on ignition (1000°C); RHG= 100 * hematite /
 659 hematite + goethite; RKGi= 100 * kaolinite / kaolinite + gibbsite).

660

661 **Table 3.** Correlation of chemical elements and minerals with each orthogonal
 662 factorial axis defined by the Principal Component Analysis for the two
 663 disaggregated ferricrete profiles (σ %= % of explained variance; loading values
 664 are given in parentheses)

665

666

Figure

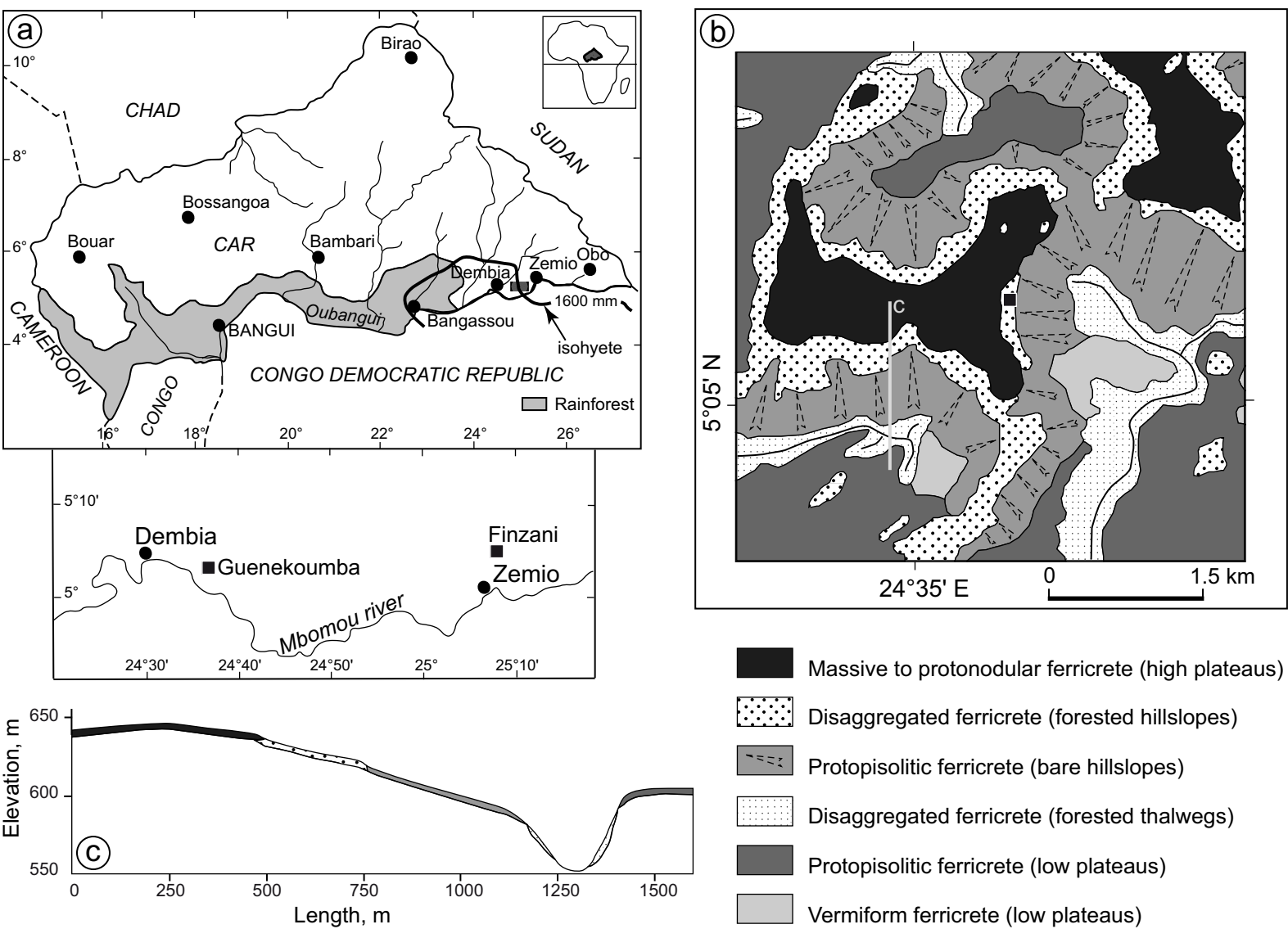


Fig. 1

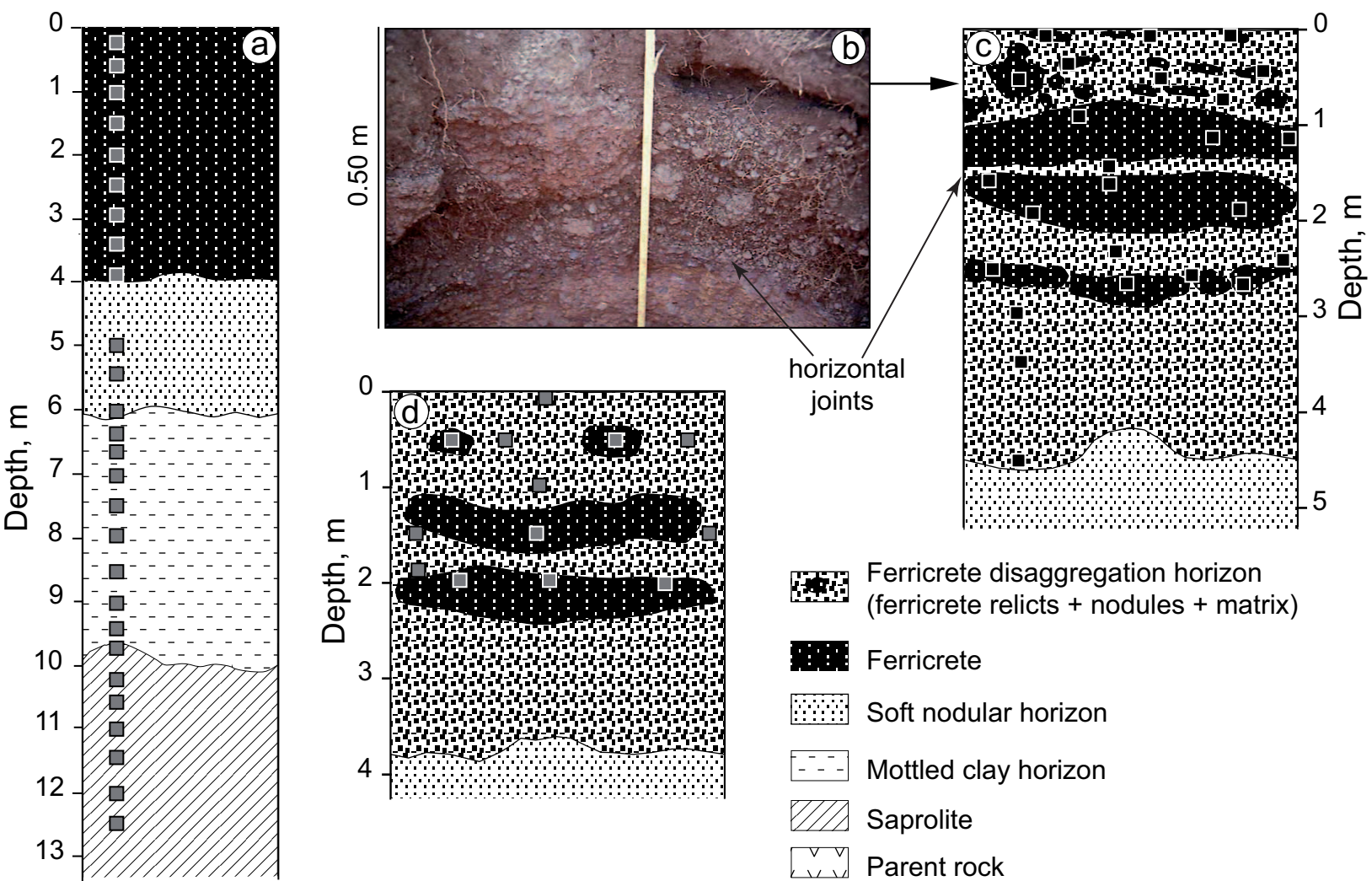


Fig. 2



Fig. 3

Beauvais, 2008

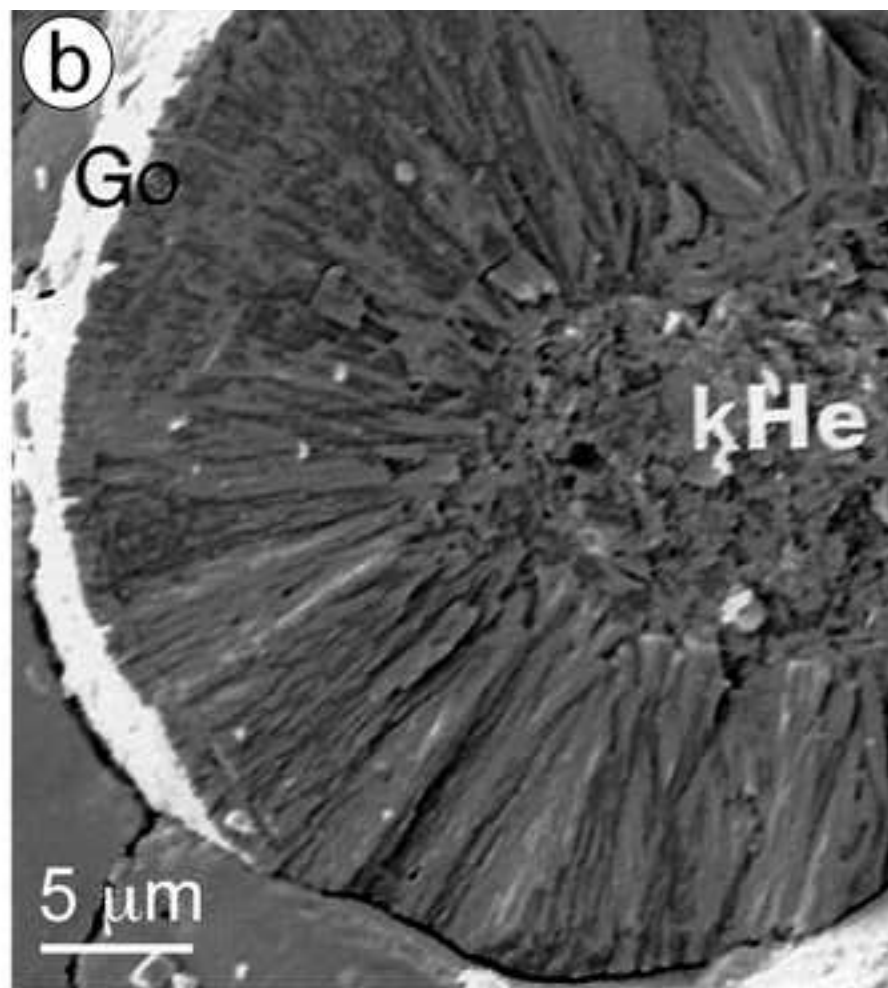
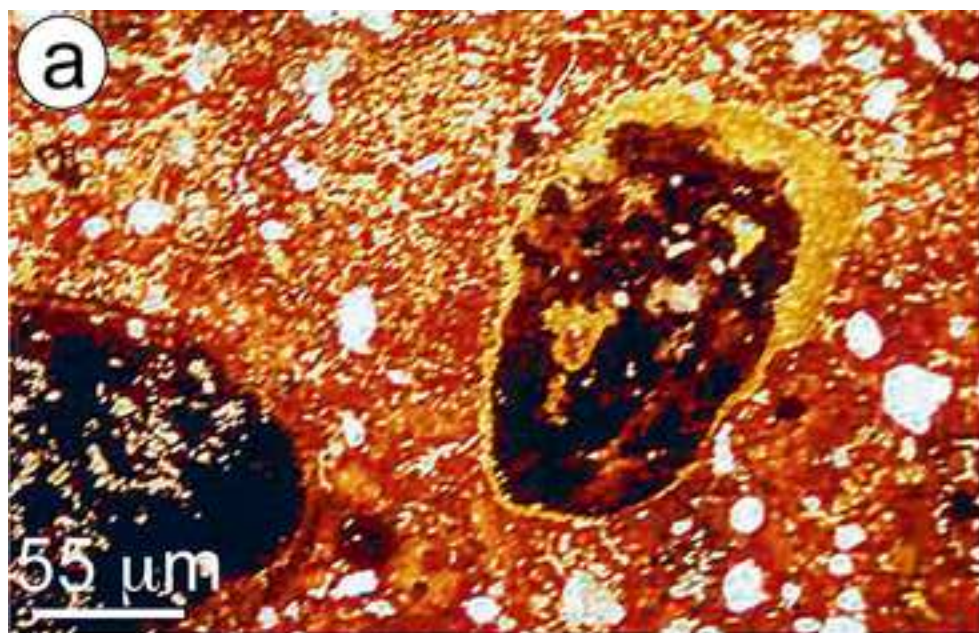


Fig. 4

Beauvais, 2008

Figure
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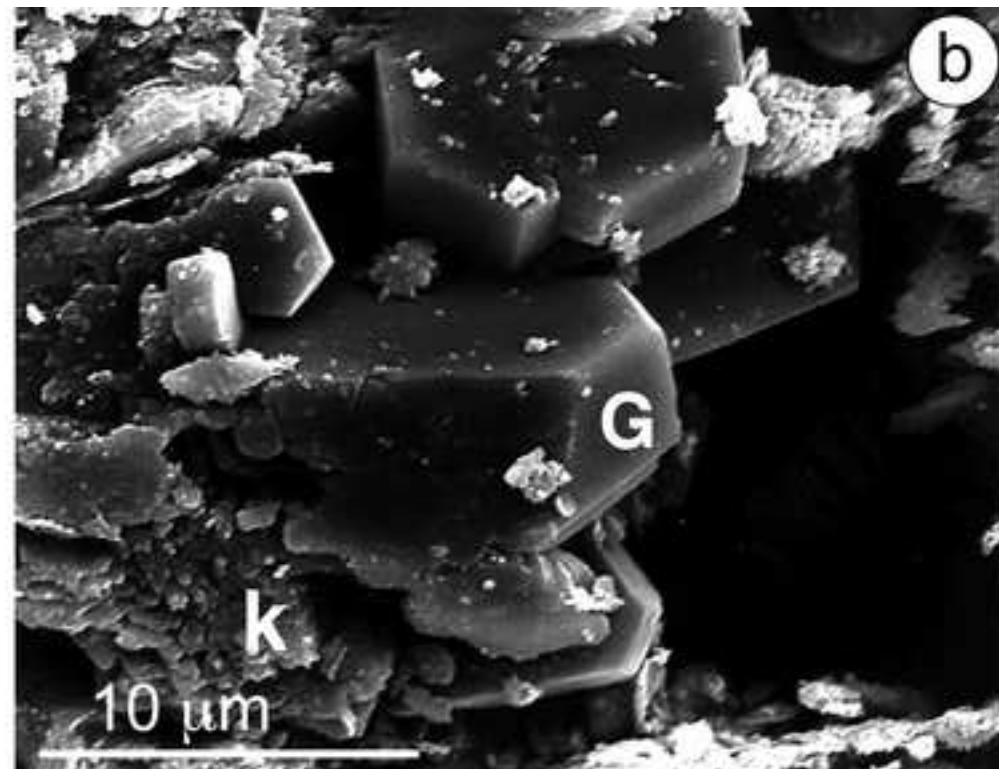
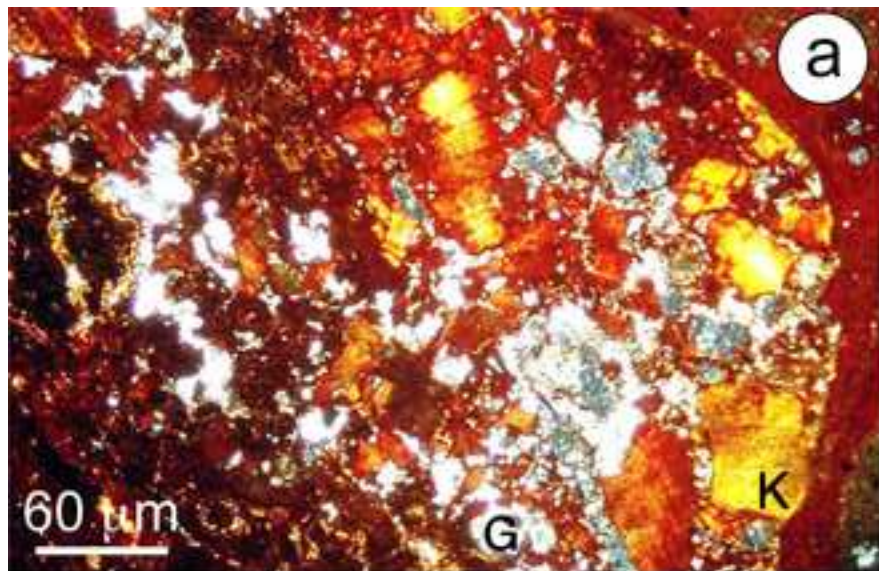


Fig. 5

Beauvais, 2008

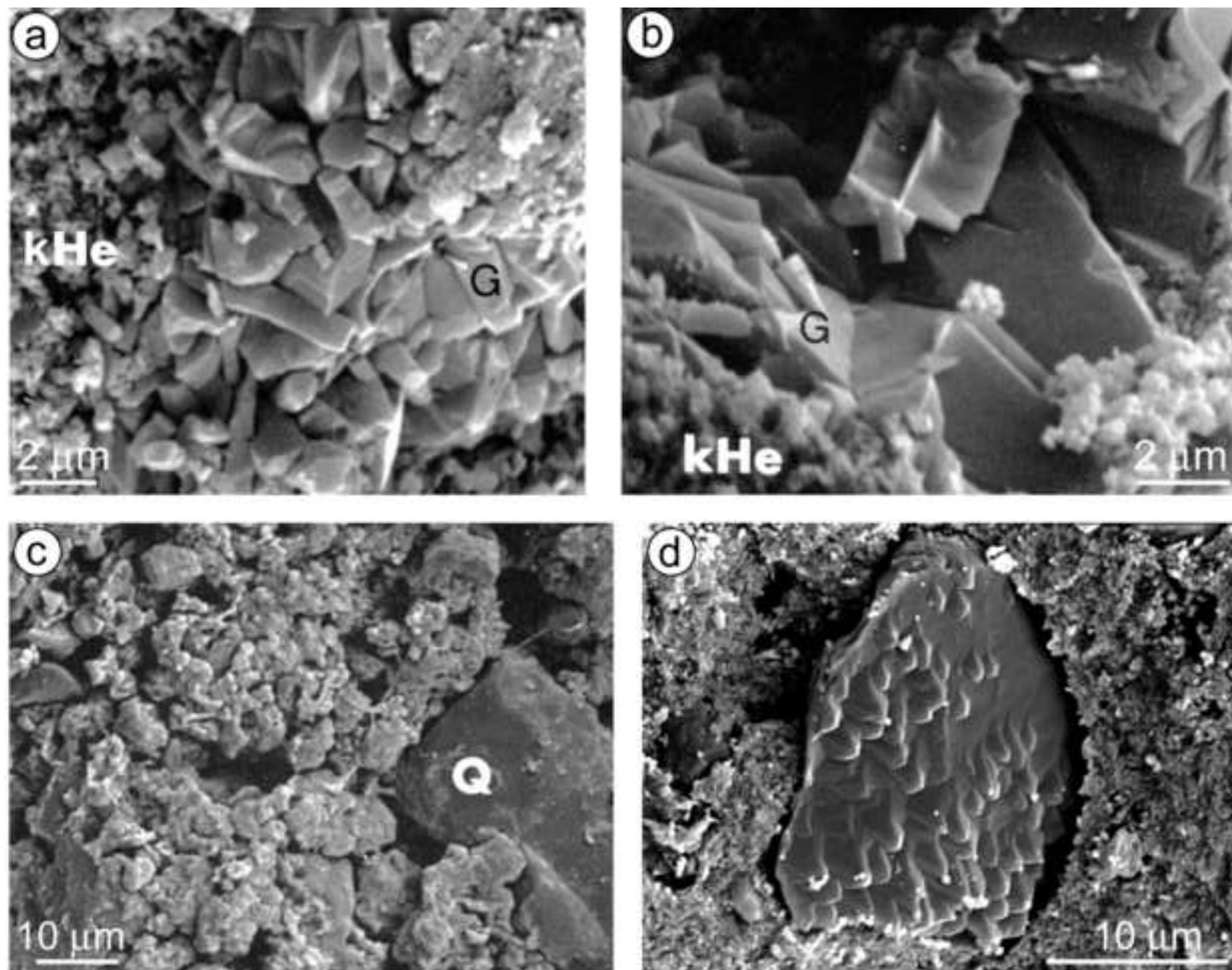


Fig. 6

Beauvais, 2008

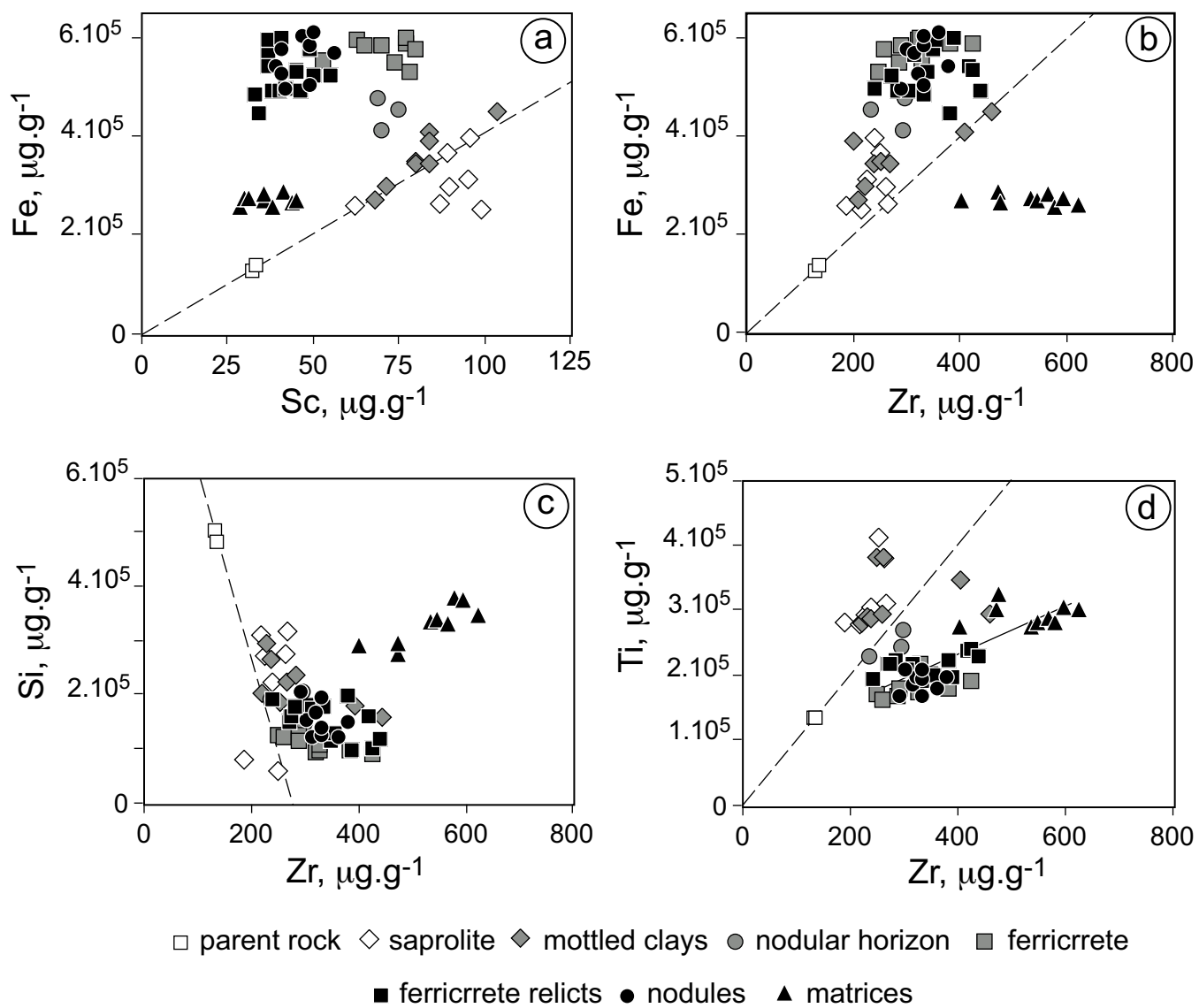


Fig. 7

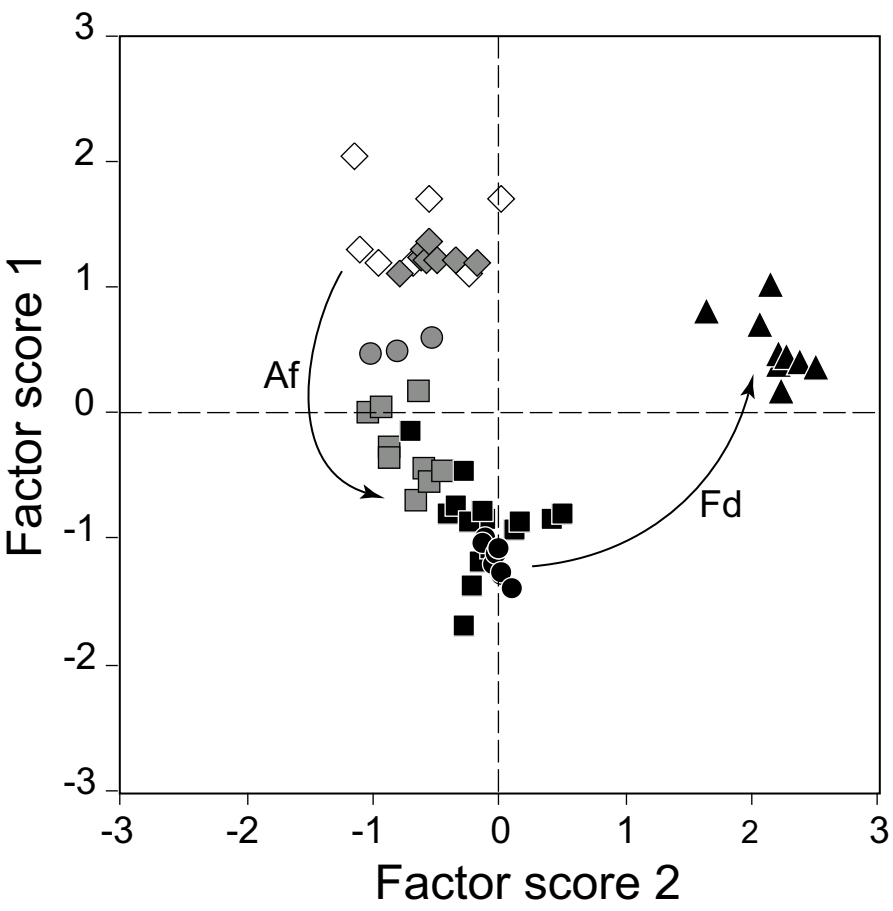


Fig. 8

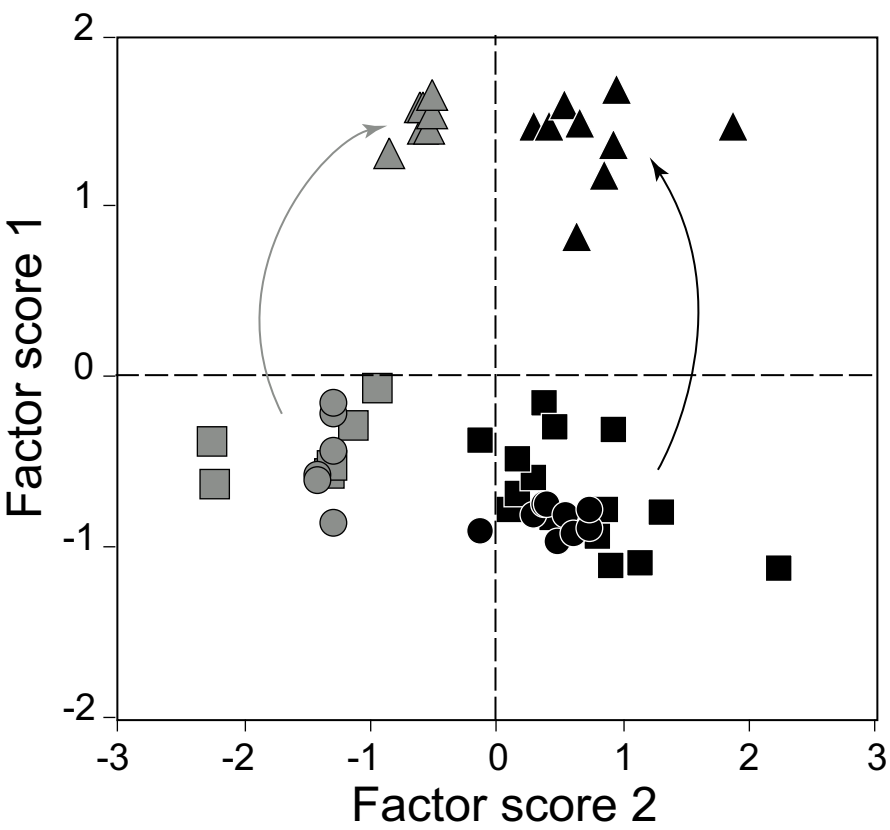


Fig. 9

Beauvais, 2008

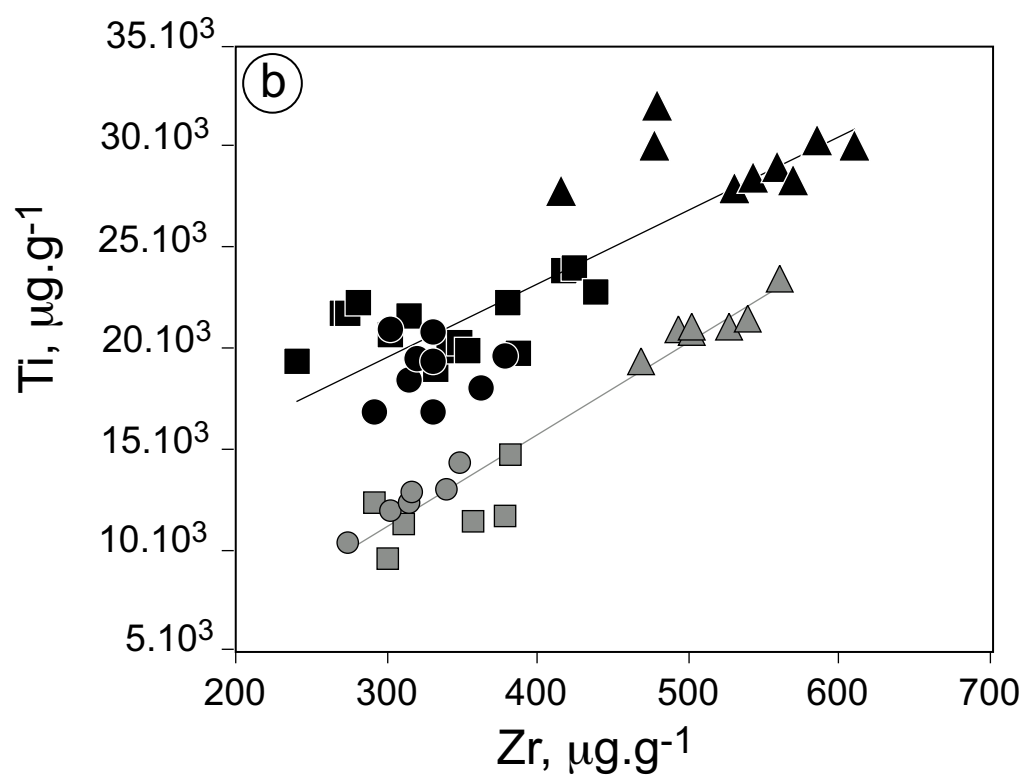
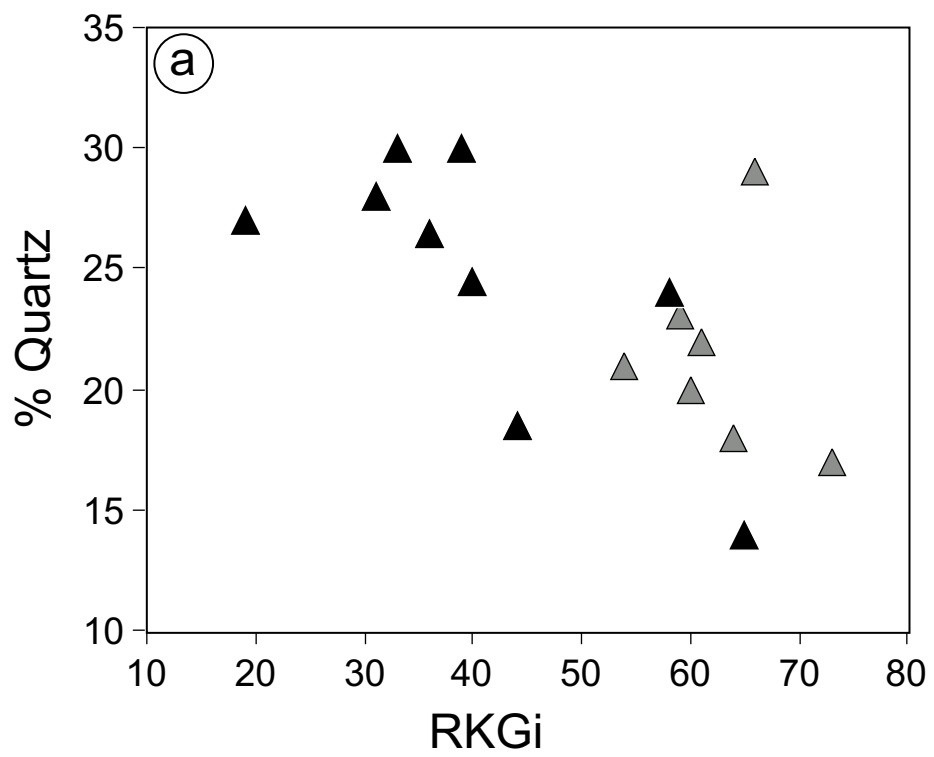


Fig. 10

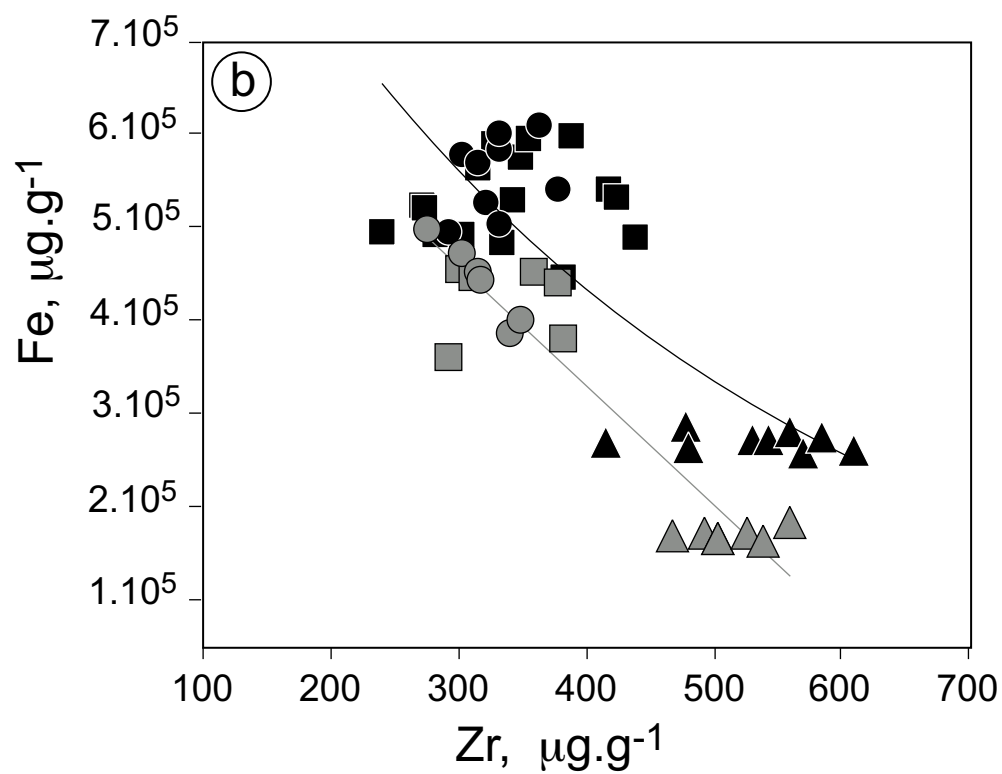
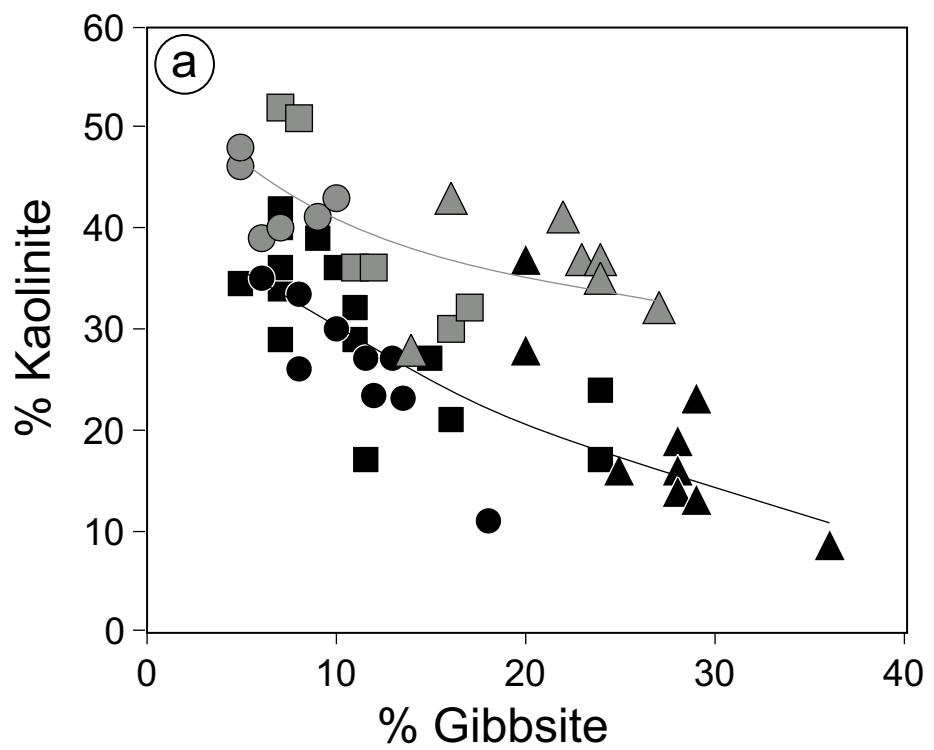


Fig. 11

Factorial Axis	σ %	Positive loading	Negative loading
F1	37.3	Mn ₃ O ₄ (0.87) TiO ₂ (0.81) Al ₂ O ₃ (0.76) Y (0.71) Ni (0.71) Zn (0.71) Sc (0.66) Goethite (0.60) SiO ₂ (0.53) Kaolinite (0.52) Cu (0.50)	Hematite (0.94) Fe ₂ O ₃ (0.81) Cr (0.76) P ₂ O ₅ (0.75) La (0.57) V (0.56) Sr (0.56)
F2	23.6	Quartz (0.93) Nb (0.89) Zr (0.87) MgO (0.73) Yb (0.71) SiO ₂ (0.63) Gibbsite (0.52) Y (0.52)	V (0.66) Sc (0.65) Goethite (0.57) Cu (0.53) Fe ₂ O ₃ (0.48) Kaolinite (0.43)
F3	7.2	Gibbsite (0.76)	Kaolinite (0.66) SiO ₂ (0.47)
F4	7.1	Ce (0.80) Ba (0.77) Sr (0.76) La (0.69)	

Table 1.

Table

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Location:	Guenekoumba profile						Finzani profile					
Facies:	Ferricrete		Nodules		Matrices		Ferricrete		Nodules		Matrices	
<i>N</i> :	15		9		9		6		6		7	
	m	$\sqrt{\sigma}$	m	$\sqrt{\sigma}$	m	$\sqrt{\sigma}$	m	$\sqrt{\sigma}$	m	$\sqrt{\sigma}$	m	$\sqrt{\sigma}$
SiO ₂ wt.%	14.89	3.35	15.17	3.11	32.83	3.15	21.73	3.94	22.75	2.4	37.87	1.52
Al ₂ O ₃	19.21	2.44	17.27	1.15	24.53	1.62	23.47	1.63	21.93	2.2	29.67	1.15
Fe ₂ O ₃	52.55	4.38	55.6	4.16	27.03	0.91	42.27	4.06	44.2	4.2	17.03	0.67
Mn ₃ O ₄	0.06	0.02	0.04	0.01	0.09	0.02	0.02	0.01	0.03	0	0.05	0.02
MgO	0.03	0.01	0.04	0.01	0.17	0.07	0.23	0.14	0.22	0.02	0.37	0.02
K ₂ O					0.11	0.02	0.61	0.55	0.46	0.06	0.35	0.08
TiO ₂	2.12	0.15	1.89	0.15	2.93	0.14	1.18	0.17	1.25	0.12	2.12	0.12
P ₂ O ₅	0.39	0.06	0.38	0.05	0.25	0.04	0.19	0.03	0.19	0.01	0.18	0.02
LOI	10.11	1.39	9.27	0.95	11.63	1.45	10.65	0.99	9.11	1.02	12.85	0.35
Sr ppm	39	32	48	9	18	5	34	20	35	7	21	2
Ba	32	24	51	14	40	7	223	179	157	19	95	12
V	1369	280	1298	66	634	29	827	202	757	69	344	14
Ni	47	19	36	6	78	23	35	10	51	6	79	21
Co	13	5	11	2	13	4	9	8	16	3	20	4
Cr	340	142	426	117	155	20	403	157	414	79	91	1
Zn	52	19	50	5	62	16	34	14	40	8	40	8
Cu	133	64	121	19	116	29	58	9	75	5	89	5
Sc	42	6	46	6	37	5	36	3	37	1	40	2
Y	8	2	8	1	23	2	12	2	12	3	31	2
Zr	341	60	329	27	530	61	337	40	316	26	513	31
La	47	39	51	12	23	5	34	12	39	6	33	5
Ce	114	80	99	27	126	20	62	33	65	18	107	11
Yb	1	0	1	0	3	0	2	0	2	0.5	4	0
Nb	18	4	19	2	36	3	16	2	14	3	33	4
% Quartz	1	1	3	3	25	5	3	2	3	1	22	4
Kaolinite	31	8	27	7	19	9	40	10	44	3	38	5
Hematite	41	6	45	5	17	1	33	6	37	4	9	1
Goethite	16	6	14	3	12	1	12	3	8	1	9	1
Gibbsite	11	6	11	4	27	5	12	4	8	2	22	5
RHG	72	10	76	6	57	4	73	8	82	3	52	3
RKGi	72	14	71	14	41	14	76	10	86	4	63	6

Table 2.

Factorial Axis	σ %	Positive loading	Negative loading
F1	44.1	Y (0.95) Yb (0.95) Quartz (0.94) SiO ₂ (0.92) Zr (0.91) Nb (0.90) Al ₂ O ₃ (0.82) Gibbsite (0.78) Ni (0.66) MgO (0.62) TiO ₂ (0.59) Mn ₃ O ₄ (0.40)	Fe ₂ O ₃ (0.94) Hematite (0.91) V (0.78) Cr (0.74) P ₂ O ₅ (0.57) Sr (0.40)
F2	20.9	Cu (0.75) TiO ₂ (0.75) Zn (0.71) P ₂ O ₅ (0.69) Mn ₃ O ₄ (0.67) Goethite (0.63) Sc (0.48)	K ₂ O (0.79) Ba (0.77) kaolinite (0.65) MgO (0.60)
F3	11.4	Co (0.59) Cu (0.52) Sc (0.40) Ni (0.40)	Ce (0.78) La (0.75) Sr (0.75) V (0.42)

Table 3.