Geochemical balance of lateritization processes and climatic signatures in weathering profiles overlain by ferricretes in Central Africa

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Abstract—A simple geochemical balance of lateritization processes governing the development of several tens of meters of weathering profiles overlain by ferricretes is estimated on the basis of detailed mineralogical and geochemical data. The lateritic weathering mantle of the "Haut-Mbomou" area in Central Africa is composed of different weathering layers described from the base to the top of vertical profiles as a saprolite, a mottled clay layer, a soft nodular layer, a soft ferricrete, and a ferricrete in which kaolinite, gibbsite, goethite, and hematite occur in various quantities. Incongruent dissolution of kaolinite leads to the formation of gibbsite in the upper saprolite, whereas the hematite does not clearly replace the kaolinite according to an epigene process in the upper ferruginous layers of the profiles. Instead, that kaolinite is also transformed into gibbsite according to an incongruent dissolution under hydrated and reducing conditions induced by a relatively humid climatic pattern. The respective relations of the silica, iron, and aluminum balances and the Al substitution rate of the hematite on the one hand, and of RHG [RHG = 100 (hematite/hematite + goethite)] and the kaolinite on the other hand, to the consumption or the release of protons $H^+$ permit differentiation of aggrading ferruginization and degradation processes operating in the different lateritic weathering profiles. The Al substitution rate of the Fe-oxyhydroxides varies according to the nature of lateritization processes, e.g., saprolitic weathering and aggrading ferruginization vs. degradation. The observations and results indicate that the ferruginization process of the weathering materials of parent rocks is not a simple ongoing process as often thought. This suggests that the actual lateritic weathering mantle of the Haut-Mbomou area may result from different stages of weathering and erosion during climatic changes. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

On tropical African soils, lateritization processes have led to the development of weathering mantles tens of meters thick, often capped with ferricretes, at the expense of all kinds of parent rocks that may reflect a long and complex evolution, including climatic and geomorphic changes (Nahon, 1991; Tardy, 1993; Thomas, 1994; Tardy and Roquin, 1998). The term ferricrete must be understood here as ferruginous duricrust instead of iron-cemented conglomerate. It has been assumed that the underlying weathering mantle developed in situ by progressive dissolution of a previous saprolite without allochthonous iron inputs except intraprofile migrations and accumulations, that led the different layers of a weathering profile to vertically fit together during the vertical downward reduction of the regolith (Millot et al., 1976; Nahon, 1976; 1986; Leprun, 1979; Tardy, 1993). Other research based on geomorphological observations also emphasized the mechanical erosion processes, to account for the formation of many ferricretes armor- ing glacs or slope sediments of western Africa (Vogt, 1959; Michel, 1973; Grandin, 1976; Boeglin, 1990; Bambo, 1996) and etchplains (Thomas, 1965; 1994). Studies focusing on gold behavior in different regions of the African continent have also described the geochemical and the geomorphic processes controlling the detrital ore concentration patterns (Colin et al., 1989; 1992; 1997; Freyssinet et al., 1989; Lee and Colin, 1989; Freyssinet, 1990; Colin and Vieillard, 1991; Sanfo et al., 1993; Parisot et al., 1995; Ouangrawa et al., 1996).

The analysis of the geochemical and mineralogical features of lateritic residual formations can improve our understanding of the weathering and lateritization processes. The Haut-Mbomou area in Central Africa at the edge of the rainforest and savannas appears a key area to define various lateritic profile-forming processes (Fig. 1). The aim of this study is twofold: (1) to describe the mineralological and geochemical pathways of the lateritic weathering layers from the bottom to the top of profiles (Fig. 2); and (2) to derive geochemical balance and the physicochemical mechanisms of the underlying lateritization processes (i.e., saprolitic weathering and ferruginization), that will put forward an evolution model for the actual lateritic weathering mantle of the Haut-Mbomou area.

1.1. Background

It is known that the crystal chemistry of the kaolinite and Fe–oxyhydroxides of lateritic soils reflects the geochemical and physical properties of the medium in which they formed, i.e., past and present pedogenetic conditions (Fitzpatrick and Schwertmann, 1982; Fitzpatrick, 1983; Schwertmann and Kämpf, 1985; Schwertmann and Carlson, 1994; Muller et al., 1995). For instance, the Al substitution rate and crystal size of Fe–oxyhydroxides depend on pH (Nahon, 1976; Schwertmann et al., 1979; Tardy and Nahon, 1985); pH influences the dissolution rate of the kaolinite and its behavior within the weathering profiles (Carroll and Walther, 1990; Chorover and Spoor, 1995). Variations of Al substitution rates Fe–oxyhydroxides may also reflect different iron accumulation processes (Fitzpatrick, 1983).

After the seminal work of Millot and Boniåas (1955) and Millot (1970) on the isovolumetric textural changes during
Fig. 1. Location of the study area (black rectangle). The bold curve represents the mean annual rainfall (= 1600 mm).

weathering, Brimhall and Dietrich (1987) formalized a mass balance model relating the chemical composition to the bulk density, volumetric porosity, and strain according to the least mobile element as Zr. However, the correct identification of the least mobile element often poses problems because material transfers on hillslope surface with translocations through the profiles and chemical weathering of the element-bearing minerals may invalidate the iso-element method, particularly in the tropical area of Africa (Brimhall et al., 1988; Colin et al., 1992; 1993; Braun et al., 1993). Other models have coupled the stoichiometries of mineral weathering reactions to hydrological and hydrogeochemical data to calculate the mineral weathering rates (Garrels and McKenzie, 1967; Tardy, 1969; Velbel, 1985, 1986). On the basis of the mass transfer principle of Helgeson et al. (1970), Soler and Lasaga (1996) have recently developed a kinetic model to explore the mechanisms of bauxite forma-

Fig. 2. Sketch of the lateritic weathering toposequence and location of the three analyzed profiles (black arrows; smaller white arrows, other pits).
tion. The validation of the above models by field observations, however, requires two primary conditions; (1) the availability of a complete weathering profile from the unweathered parent rock to the topsoil; and (2) geochemical data regarding solutions coming in and getting out of the regolith system. Microprobe analyses of minerals and weathering phases composing the layers of lateritic profiles of western Africa have also proved useful to derive geochemical balances at the scale of mineral assemblages (Ambrosi and Nahon, 1986). A geochemical balance is derived in a similar way but at the scale of the profiles by coupling the results obtained from the bulk chemistry and mineralogy of weathering layers (Beauvais, 1991) and the microprobe analyses of each mineral component.

2. MATERIALS AND METHODS

The study area is located in the “Haut-Mbomou,” southeastern Central African Republic (Fig. 1). Plateaus and hillslopes ranging from 650 to 600 m above mean sea level (a.s.l.) are deeply dissected by thalwegs to 570 m a.s.l.—all are covered by a thick lateritic weathering mantle overlain by ferricretes. The geological basement corresponds to the Birrimian Amphibolitic-Pyroxenitic “Complex of Mbomou”, which has been tectonically quiet for ~70 My. (Mestraud, 1982; Poidevin, 1991). The humid tropical climate is characterized by a dry season from December to February, a mean annual rainfall of 1600 mm (Fig. 1), a mean annual temperature of 25°C, and a mean annual relative humidity of 80%. The vegetation cover consists of large stretches of grass and bare lands alternating on the plateaus and the hillslopes and by a dense humid forest occupying the valleys and the edges of the highest plateaus.

Sixteen pits were bored through thick lateritic weathering profiles uniformly covered by 5 to 10 m of soft ferricrete and actual ferricrete materials of various petrographic facies depending on the topographic location of the profile, because the sequence of pits extends across 1 km half drainage divide from a high plateau to a thalweg (Fig. 2). Two scarp relief of metric height resulting from mechanical erosion processes separate the sequence in three geomorphological units, the high plateau, the forested uplands, and the bare downslope (Fig. 2). The identification of parent rocks was impeded either by water occurrences, or by stinking gaseous emanations for the profiles located in the upland forested area. Methane was detected by smelling, whereas carbon dioxide was identified by observing the end of a blazing rope flame up and down when it was shook up and down in the boreholes. However, the compared observations of saprolites in some pits and of rock fragments collected on plateau surfaces and/or thalweg flats indicate an amphibole–schist facies as the most likely parent rock.

2.1. X-ray Diffraction (XRD) and Crystallo-chemical Parameter Calculation

Samples for XRD were sorted and ground, producing a powder with a sieve size of 125 μm. XRD analyses were performed over the range 2 to 80° 2θ using a Cu–Kα radiation, a step size of 1° 2θ/min, and a counting time of 5 s to quickly identify the mineral components of each weathering facies. High-resolution XRD analyses were also made on quasi-pure Fe–oxyhydroxides to calculate their unit-cell parameters by the mean of a statistical refinement program by nonlinear regression (Tournarie, 1969) and to estimate their Al substitution rates of the kaolinite, Fe–oxyhydroxides, and gibbsite but without other minerals. The normative calculation used the number of moles of SiO₂, Al₂O₃, and Fe₂O₃ to estimate the mole percentage fraction (mol%) of minerals (Ambrosi, 1984; Ambrosi and Nahon, 1986; Beauvais, 1991). The Fe substitution ratio of the kaolinite and the Al substitution rates of the Fe–oxyhydroxides were also calculated. If Al(ideal) > Si(ideal), the excess of aluminium is incorporated into the hematite or the goethite, the remaining aluminium going to the gibbsite. When Al(ideal) < Si(ideal), the excess of silicon means either the incorporation of iron into the kaolinite or free silica.

3. RESULTS AND DISCUSSION

3.1. Parent Rock Petrology

The main minerals of the amphibole–schist parent rock are green hornblendes, plagioclases, and micas as phengites, with secondary minerals as chlorites, epidotes, and garnets, and a little quartz. A summary of their petrographical outlines and an estimation of their mean chemical formula based on at least 5 microprobe analyses for each are given (Fig. 3).

Green hornblendes exhibit prismatic crystals or elongated plate forms. Their composition allows classification of them between the actual hornblende, edenite, and paragisite poles according to Deer et al. (1963), but some samples are also close to the tremolite type. Two different types of hornblende were observed: large primary magmatic crystals of actual green hornblende and smaller crystals exhibiting "tooth comb" habit reflecting uraltization process of primary pyroxenes. The mean chemical composition of actual green hornblende is (Si₆.₃₆ Al₁.₆₄) (A₁.₁₇ Ti₀.₀₇ M₇.₂₇ Fe₁₄.₈₉) (Fe₀.₀₇ Mg₀.₀₂ Ca₁₄.₇₄ Na₀.₁₆) Na₀.₃₂ K₀.₁ O₂₂ (OH)₂, which is an intermediary composition between hornblende and magnesian hastingsite (Leake, 1978). In contrast, the mean chemical composition of...
amphibole produced from uraltization of pyroxenes is (Si_{6.74} A1_{1.26}) (Al_{0.99} Ti_{0.03} Mg_{0.96} Fe_{0.03}) (Fe_{0.08} Mn_{0.03} Ca_{1.72} Na_{0.17}) Na_{0.3} K_{0.08} O_{22} (OH)_{2}, indicating a ferrous edenite-type hornblende according to Leake (1978). Actinolite was also analysed in a early weathered amphiboleschist. It is less aluminous and less ferriferous but more magnesian than the other amphibole types; its mean structural formula is (Si_{7.68} A1_{0.32}) (Al_{0.32} Ti_{0.04} Cr_{0.02} Mg_{0.03} Fe_{1.57}) (Fe_{0.05} Mn_{0.02} Ca_{1.79} Na_{0.13}) Na_{0.05} K_{0.01} O_{22} (OH)_{4} (Fig. 3).

Plagioclases are often saussuritized and form large areas associated with green hornblendes. Their mean formula was calculated as (Si_{2.97} A1_{0.03} (Al_{0.98} Fe_{0.02}) Ca_{0.01} Na_{0.04} O_{6}), indicating an albite type.

Micas are fairly well represented in the amphibole-schist rock, exhibiting small plates of 50 to 150 µm. There are phengite-type white micas with a mean structural formula of (Si_{6.55} A1_{1.43}) (Al_{0.3} Ti_{0.03} Fe_{0.39} Mg_{0.38}) Mg_{0.11} Na_{0.13} K_{1.71} B_{0.03} O_{20} (OH)_{2}.

Chlorites generally result from mica weathering. Their mean chemical composition indicates a diabantine type (Foster, 1962) as is shown by the mean structural formula, (Si_{6.68} A1_{1.32}) (Al_{1.27} Ti_{0.02} Fe_{0.32} Mg_{4.31} Mn_{0.03}) Ca_{0.07} K_{0.22} O_{20} (OH)_{4} (Fig. 3). Other chlorite exhibit curved slats, radially growing and forming typical aggregates in unweathered rock sample. Those are more ferrous and magnesian but less siliceous, close to a brusngivite type (Foster, 1962) as shown by the mean structural formula (Si_{5.57} A1_{2.44}) (Al_{2.79} Ti_{0.01} Fe_{4.35} Mg_{4.62} Mn_{0.03}) Ca_{0.01} K_{0.07} O_{20} (OH)_{16}.

Epitodes appear either as automorphous crystals or resulting from saussuritization process of plagioclases. The mean chemical composition of automorphous epitode crystals is Si_{5.04} (Al_{2.41} Ti_{0.01} Fe_{0.54}) Mn_{0.01} Mg_{0.01} Ca_{1.98} O_{12} (OH), whereas that of the epidote resulting from the saussuritization of the plagioclases is Si_{5.07} (Al_{3.58} Ti_{0.01} Fe_{0.36} Mg_{0.01} Mn_{0.01}) Ca_{1.93} O_{12} (OH).

Garnets are present as automorphous hexagonal porphyroblasts with cross-sections of 2 to 3 mm, cutting across the association amphibole-plagioclase-micas. Their chemical analyses indicate an intermediary composition between almandine (60%), grossular (19%), pyrope (13%) and spessartine (8%) as shown by the mean structural formula Si_{3.03} (Al_{1.97} Ti_{0.01} (Fe_{1.76} Mg_{0.4} Ca_{0.07} Mn_{0.23}) O_{12}. When the amphibole-schist rock starts to weather, the above mean composition changes to Si_{3.09} (Al_{1.97} Ti_{0.01}) (Fe_{1.51} Mg_{0.12} Ca_{0.48} Mn_{0.34}) O_{12} (Fig. 3). Besides being more hydrated, the weathered garnets become richer in calcium (31% grossular) and in manganese (12% spessartine) whereas they have less ferrous (53% almandine) and less magnesian (4% pyrope).

3.2. Petrology of Lateritic Weathering Profiles

Field observations revealed five different layers in the profiles; a saprolite, a mottled clay layer, a soft ferricrete and/or a soft nodular layer, and a ferricrete, the thickness of which spatially varies (Fig. 2). According to the nomenclature established by Tardy (1993), four distinct ferricrete facies were identified depending on the geomorphic location; massive and protonodular on the high plateaus and the forested upslopes, protopisolitic and vermiform on the bare downslopes (Beauvais, 1991; Beauvais and Roquin, 1996). The mineralogical and geochemical features of each layer, their variations from the bottom to the top of profiles of the high plateau and the hillside are described (Fig. 2).

3.2.1. High plateau profile

Only three layers were identified in the profile of the high plateau. The top of a mottled clay layer occurs at 10 to 12 m, the lower part being underwater, overlain by ~7 m of soft nodular layer and 3 to 4 m of ferricrete with a massive and/or a protonodular facies (Fig. 2).

The soft nodular layer consists of centimetric-size purple reddish nodules embedded in a fine clay-ferruginous matrix with aggregates of 3 to 5 mm. Microscopic observations reveal a red–yellow micronodular matrix structure with micronodules of approximately 50 to 100 µm. On average, it is composed of 18% kaolinite, 44% gibbsite, and 38% goethite substituted by 13 to 19 mol% AlOOH as estimated by the method of Schulze (1984). Additionally, this matrix contains 1.5% TiO_{2}, 0.14% P_{2}O_{5}, and 0.1% CaO, and it is richer in alumina than the ferruginous plasma composing the embedded nodules (Fig. 4A). The richness in alumina is mostly reflected by gibbsite crystallizations forming either from Al absolute accumulation in voids or from incongruent dissolution of kaolinite within the weathering plasmas in which the SEM morphology (Fig. 5A and B) recall what was previously observed in Cameroonese lateritic profiles by Muller (1987). Two types of nodules were distinguished, elongated and round polyhedral. Viewed at the optical microscope, the elongated nodules are composed of numerous kaolinite “booklets” of 10 to 20 µm embedded in a red hematitic plasma, making them appear ferruginized (Fig. 6). In fact, further SEM observations reveal that the hematit
does not simply replace kaolinite through epigene processes. Instead, it develops by epitaxy either on (001) plans parallel to c-axis of kaolinite “booklets” packing, or it exhibits round “almond” habits of 2-μm diameter on (hk0) plans (Fig. 5C and D). Microprobe analyses reveal that TiO₂ and P₂O₅ increase with increasing ferruginization, and a mean Al substitution of 2.4 mol% Al₂O₃ for the hematite, although the calculation from the unit-cell dimensions \(a = 5.04 \pm 0.001 \text{ Å}\) and \(c = 13.8 \pm 0.003 \text{ Å}\) does not show any Al substitution when applying equation (3). Even the apparently pure kaolinite “booklets” display some quantity of hematite (Fig. 4A), that is no wonder as the volume analysed by the microbeam equals 1 μm³, a size similar to that of the hematite spots (Fig. 5C and D). In round polyhedric nodules, hematite is mixed with small size kaolinite of 1 μm, which may result from the dissolution–precipitation process of previous kaolinite booklets (Ambrosi and Nahon, 1986). These nodules consist of a mixture of hematite and goethite, as it was observed under reflected light optical microscopy, the goethite spots appearing gray while the hematite is white. Additionally, secondary goethite is developed as rims and cortexes around the two types of nodules. That goethite is substituted by 10 mol% AlOOH, as estimated from microprobe analyses. It also contains 0.17% MnO, 0.2% CuO, and 0.26% P₂O₅, and it is more ferruginous than the hematite of the kaolinite “booklets” composing the core of the elongated nodules (Fig. 4A). At the bottom of the soft nodular layer, a nodular soft ferricrete facies was forming by iron absolute accumulation as reflected by secondary goethite crystals growing perpendicularly to the void edges or developing around the primary hematitic nodular domains (Fig. 5F). The unit-cell dimensions of that goethite are \(a = 4.53 \pm 0.002 \text{ Å}\), \(b = 9.76 \pm 0.003 \text{ Å}\), and \(c = 2.97 \pm 0.001 \text{ Å}\), implying an Al substitution of approximately 27 mol% AlOOH according to Eqn. 2. Further, the lower part of the soft nodular layer is also a place for a mineral paragenesis made up of lithiophorite and cerianite (Fig. 7A and B), that reflects specific redox conditions (Parc et al., 1989; Braun et al., 1990). Higher in the soft nodular layer at the transition with the ferricrete, is a level characterized by very hydrated clayey pockets with few nodules, that was previously interpreted as an iron-depleted facies (Beauvais, 1991). This layer is composed of 64% kaolinite, 20% goethite substituted by 16 mol% AlOOH, and 16% hematite substituted by 9 mol% Al₂O₃.

The ferricrete of massive and/or protonodular facies mainly consists of intimately mixed ferruginous and clay plasmas composed of hematite and kaolinite. SEM observations reveal “cauliflower” habits for the hematitic plasma, which coats inherited primary or neoformed oriented kaolinite platelets of 1 to 2 μm (Fig. 8A and B), that recalls what was seen in the round polyedric nodules of the underlying layer. This ferruginous plasma is indeed composed of 99% hematite substituted by 1.5 mol% Al₂O₃ (Fig. 4B), and 0.19% TiO₂, 0.23% P₂O₅, and 0.11% CuO. The unit-cell dimensions of that hematite are \(a = 5.11 \pm 0.001 \text{ Å}\) and \(c = 14 \pm 0.004 \text{ Å}\). The kaolinite of “booklets” is, on average, substituted by 2.4 mol% Fe₂O₃. It exhibits primary mineral habits looking like micas (Fig. 8A), which is consistent with the fact it still contains small quantities of alkalis and alkaline-earths, indicating some inheritance of a previous saprolitic material. Some kaolinite “booklets” exhibit an excess of alumina due to gibbsite crystallizations; they also contain less iron than those of elongated nodules of the soft nodular layer (Fig. 4C). The hematite associated with that kaolinite (Fig. 8A) exhibits an Al substitution higher than that contained into the elongated nodules of the underlying soft nodular layer; it is also more Al substituted than that associated with neoformed small-size kaolinite (Fig. 8B); on average, it is substituted by 4.2 mol% Al₂O₃, against 2.4 and 1.5, respectively (Fig. 4B and C). Further, that hematite also contain
Fig. 5. SEM photomicrographs in the soft nodular layer of a high plateau profile: (A) Secondary gibbsite crystal development in voids of the clay ferruginous matrix. (B) Gibbsite crystal formed from the incongruent dissolution of kaolinite. (C) Hematite crystals that exhibit either an “almond” habit of 2 mm with an epitaxic development on (001) plans of kaolinite “booklets,” or (D) a “rosette” habit on (110) plans of kaolinite platelets, both in an elongated nodule. (E) Hematite with small size kaolinite in a round polyhedral nodule. (F) Cutan of goethite developing perpendicularly to the void edges in an elongated nodule. (He, hematite crystals; K, kaolinite platelets; Go, goethitic cutan).
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Fig. 6. Optical photomicrograph of kaolinite “booklets” in light gray and hematite in white embedded in the clay ferruginous matrix of an elongated nodule of the soft nodular layer of high plateau profile.

0.23% TiO₂, 0.1% Cr₂O₃, 0.17% CuO, and 0.5% P₂O₅. Gibbsite crystals and secondary goethitic plasmas were also observed within vacuolar voids of 10 µm affecting the clay-ferruginous plasmas (Fig. 8C). In addition to developing through the porosity, secondary goethite also coats primary inherited kaolinitic structures (Fig. 8D). Microprobe analyses of this goethite reveal mean amounts of 1.61% TiO₂, 0.1% Cr₂O₃, 0.21% Ce₂O₃, and 0.23% P₂O₅. Its unit-cell dimensions are a = 4.56 ± 0.009 Å, b = 9.93 ± 0.002 Å, and c = 3.01 ± 0.007 Å, implying a substitution of ~2 mol% AlOOH.

In summary, the geochemical patterns of the high plateau profiles are governed by the association of kaolinite and Fe-oxyhydroxides in all structures. SEM observations show that the kaolinite is not clearly ferruginized by the hematite according to an epigene process as it was described in other profiles of western Africa (Ambrosi et al., 1986); instead, the two minerals appear closely associated. Aluminum is segregated, leading to gibbsite formation in the micronodular plasmas of the matrix embedding the ferruginous nodules. To a certain degree the kaolinite–gibbsite mineralogy controls the Al substitution of Fe-oxyhydroxides. The secondary goethite of cor- texes developed around the nodules is less Al substituted than the goethite neofonning at the bottom of the soft nodular layer. Hematite and secondary goethite of ferricrete are more Al substituted than those of the soft nodular layer.

3.2.2. Hillslope profiles

Five layers were identified in the profiles of the hillslope (Fig. 2); in the upslope profile, a saprolite occurring at 10 to 12 m, ~4 m of mottled clay layer, ~3 to 5 m of soft nodular layer and ~3.5 m of protonodular ferricrete; in the downslope profile, a mottled clay layer occurring at ~11 m, ~8 m of soft ferricrete layer with a vermiform facies, 1 to 2 m of soft nodular layer, and ~3 m of protopisolitic ferricrete. It is worth men- tioning that the ferricrete layer contains some decimetric size relics of massive ferricrete similar to that described in the high plateau profile.

The saprolite of the upslope profile consists of a clayey plasma composed of 95% kaolinite substituted by 2 mol% Fe₂O₃ and 5% SiO₂ as relic quartz. This plasma exhibits small-size kaolinite (≤2 µm) and kaolinite “booklets” of 50 to 100 µm; it also contains 0.1% MgO, 0.1% CaO, and trace of Mn and Cu (0.07% for each), which likely reflects the pseudo-morphic weathering of amphiboles, micas, and chlorites by kaolinite (Fig. 9A). The clayey plasma is mixed with a diffuse ferruginous plasma composed of 83% goethite substituted by 15 mol% AlOOH, 15% gibbsite, and 2% kaolinite (Fig. 10). Additionally, this goethitic plasma contains 0.75% P₂O₅, 0.14% Ce₂O₃, and 0.91% TiO₂. Higher in the layer, the clayey plasma is transformed into plasmas made up of halloysite and gibbsite (Fig. 9B and C). This latter contains minor silicon and iron (Fig. 10), and potassium and barium, which indicates it may also derive from the late weathering of phengites. In addition, a secondary gibbsite is associated with Al–goethite in sites where relic micas are still present (Fig. 9D); it invades all the previous kaolinite–goethite matrices (Fig. 9E). This gibbsite is much less siliceous and less ferruginous than the first one (Fig. 10). Al substitution of the goethite derived from microprobe analyses is ~20 mol% AlOOH.

The mottled clay layer exhibits various petrographic organizations. In the upslope profile, the bottom layer is a “patchwork” of a red goethitic plasma in which gibbsitic microdomains are differentiated, a white ochreous clayey plasma with large kaolinite “booklets” inherited from the saprolite, and a brown–orange pedoturbed plasma composed of kaolinite and goethite. The ferruginous plasma of the upslope layer consists of 86% goethite, 13% gibbsite, and only 2% kaolinite (Fig. 10). It also contains 0.48% TiO₂, 0.41% P₂O₅, and 0.1% CuO.
Goethite is substituted by 12 mol% AlOOH according to the Eqn. 2, which is a little lower than the substitution derived from the microprobe analysis; this may likely account for a little gibbsite because it is little different from that of the saprolite (Fig. 10). In the downslope profile, the mottled clay is mainly composed of a gray–white clayey plasma in which a brown–orange ferruginous plasma differentiates. The clayey plasma consists of 70% kaolinite substituted by 3 mol% Fe₂O₃, and 30% goethite (Fig. 11A). Besides exhibiting an excess of silica, it also contains 1.27% Na₂O, 3.14% MgO, and 0.25% CaO, which reflects some relic felspars and epidotes. The ferruginous plasma is composed of 75% goethite substituted by 17 mol% AlOOH and 25% pure kaolinite (Fig. 11A). It also contains 1.4% TiO₂, 0.2% Cr₂O₃, 0.22% P₂O₅, and 0.13% CuO. The Al substitution of the goethite calculated from microprobe analysis is similar to that estimated from Eqn. 2, which ranges from 13 to 19 mol% AlOOH. Although the hematitic domains are not well developed in this layer, a thorough microscopic analysis has revealed hematite substituted by 8 mol% Al₂O₃ (Fig. 11B) and containing 0.35% Cr₂O₃ and 0.15% La₂O₃. Secondary goethite, however, develops at the periphery of these hematitic domains as well as in vacuolar pores; it is only substituted by 6 mol% Al₂O₃ (Fig. 11B) and contains 0.6% P₂O₅ and 0.3% CuO.

The soft ferricrete and ferricrete with a vermiform facies are only developed in the downslope profile. Both consist of an isotropic brown plasma in which some anisotropic orange spots are differentiated. The vermiform soft ferricrete is crossed by numerous tubular voids of centimetric size that are filled by a gray–white crypto–crystalline clayey plasma in which many ferri–argilans are differentiated, which may indicate clay illuviation processes. Goethite dominates over the hematite, and its Al substitution ranges from 1 to 7 mol% Al₂O₃ (Fig. 11A). Hematitic nodules are rare and only located higher in the vermiform ferricrete at the transition with the soft nodular layer. They are isolated within the goethitic plasma and often surrounded by secondary goethite whose the unit-cell dimensions are \( a = 4.62 \pm 0.002 \text{ Å}, \ b = 9.95 \pm 0.004 \text{ Å}, \) and \( c = 3.04 \pm 0.001 \text{ Å}. \) Hematite is substituted by 6 mol% Al₂O₃ whereas secondary goethite is substituted by about 12 mol% AlOOH (Fig. 11B).

The soft nodular layer consists of nodules whose the edges are jagged. As in the high plateau profile they exhibit an hematitic core outlined by a goethitic rim. No microprobe analyses have been done on weathering plasmas and minerals composing the matrix and nodules of this layer. On average, it is made up of 40% kaolinite, 35% goethite substituted by 12 mol% Al₂O₃, 15% hematite substituted by 4 mol% Al₂O₃, and 10% gibbsite (Beauvais, 1991).

The protonodular and protopisolitic ferricretes of the hill-slope profiles consist of hematitic nodules surrounded by goethitic rims embedded in an indurated clay ferruginous matrix whose the porosity is filled by secondary gibbsite crystals larger than 10 μm (Fig. 12A and B). The matrix of the protopisolitic ferricrete of the downslope profile indeed corresponds to a plasma made up of only 6% kaolinite, 42% goethite, and 52% gibbsite (Fig. 13A) and it also contains 2.53% TiO₂, 0.15% La₂O₃, and 0.29% P₂O₅. The primary goethite of the matrix is substituted by 15 mol% Al₂O₃, whereas the secondary goethite developing around the nodules is substituted by approximately 8 mol% AlOOH (Fig. 13B). It also contains 0.23% P₂O₅ and 0.1% CuO. The hematite exhibits two different morphologies: it is either associated with kaolinite or it develops across the primary structure as secondary crystallizations exhibiting "cauliflower" habits (Fig. 12C). This hematite is less aluminous than that associated with the kaolinite of the protonodular ferricrete in the upslope profiles (1 mol% Al₂O₃ instead of 4.4) (Figs. 10 and 13B); its unit-cell dimensions are \( a = 5.098 \pm 0.003 \text{ Å}, \) and \( c = 13.922 \pm 0.007 \text{ Å}. \) The kaolinite "booklets" of the protonodular ferricrete of the upslope profile...
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Fig. 8. SEM photomicrographs in the ferricrete of the high plateau profile: (A) and (B) Intertwinned hematite crystals with a “cauliflower” habit coating kaolinite with an inherited primary structure or the edge of voids in a clayey plasma made up of small size kaolinite respectively (He, hematite crystals; K, kaolinite). (C) Gibbsite and goethite secondary development in the matrix of a round polyhedral nodular domain (G, gibbsite; Go, goethite). (D) Intertwinned flakes of secondary goethite (Go) developing around the void edges and the primary structures (he, hematitic matrix; mk, inherited kaolinitized mica).

are barely ferruginous, substituted on average by 2 mol% Fe$_2$O$_3$ (Fig. 10). The ferruginization leads to an increase of TiO$_2$ (0.32% against 0.09%), P$_2$O$_5$ (0.71% against 0.13%), and CuO (0.13% against 0.09%). The unit-cell dimensions of the hematite associated with the kaolinite “booklets” are $a = 5.046 \pm 0.001$ and $c = 13.777 \pm 0.004$.

In summary, the kaolinitic lower part of the saprolite of the upslope profile preserves the parent rock textures while the gibbsitic upper part deletes it. The downslope profile is characterized by a ongoing ferrugination process from the kaolinitic gray-white plasma of the mottled clay layer to the goethitic or hematitic plasmas of the vermiform soft ferricrete (Fig. 11A and B), which reflects the absolute iron accumulation within the porosity filled by illuviated clayey matrices, leading to less Al substituted iron oxyhydroxides with a dominance of the goethite over the hematite. The protopisolitic ferricrete of the downslope profile is characterized by aluminous plasmas and by automorphous gibbsite crystallizations, that tends to increase the Al substitution of the goethite rather than that of the hematite (Fig. 13B).

3.3. Geochemical Balance of Lateritization Processes

Two lateritization processes thus control the petrological differentiation patterns of the profiles, weathering in the saprolite and ferruginization in the rest of the profiles. As the weathering in the saprolite preserves the original parent rock textures, one has estimated the isovolumetric chemical balance
Fig. 9. SEM photomicrographs in the saprolite of the upslope profile: (A) Pseudomorphic replacement of primary minerals by kaolinite and goethite. (B) Transformation of kaolinite into halloysite and gibbsite. (C) Incongruent transformation of kaolinite into gibbsite. (D) Secondary gibbsite development in voids affecting the goethitic ferruginous plasma. (E) Finely crystallized gibbsite from the incongruent dissolution of kaolinite within the clay ferruginous plasma (Km, kaolinite from micas; Ka, kaolinite from amphibole; ox, iron oxyhydroxide; K, kaolinite; ha, halloysite; G, gibbsite; m, relic micas; Go, goethite; kGo, kaolinite–goethite plasma).
in a way similar to that proposed by Millot (1970), Gardner et al. (1978), and Ambrosi and Nahon (1986). Therefore, the bulk and grain density (\( \rho_b \) and \( \rho_g \)) the porosity (\( \rho \)) the mineralogical and bulk chemical compositions of each weathering and ferri-


gization layer (Beauvais, 1991) were used with the norma-

tive calculations derived from the microprobe analyses of

weathering minerals and plasmas to assess a geochemical bal-

ance for bulk samples of 1000 cm\(^3\). The Fe–Al substitution

rates were also taken into account in the geochemical balance

calculations.

3.3.1. Geochemical balance of weathering processes

The isovolumetric weathering process as stressed in the

upslope profile leads to the development of 1000 cm\(^3\) of sap-

rolite characterized by \( \rho_b = 1.47 \text{ g/cm}^3 \), \( \rho_g = 2.32 \text{ g/cm}^3 \), and \( p = 0.35 \) at the expenses of 1000 cm\(^3\) of amphibole–schist, composed of 30% amphibole, 25% albite, 10% phengite, 5% chlorite, 5% epidote, and 5% garnet with \( \rho_b = 2.94 \text{ g/cm}^3 \), \( \rho_g = 3 \text{ g/cm}^3 \), and \( p = 0.02 \). This transformation implies the partial leaching of silica, that allows the formation of 65% kaolinite substituted by 2 mol% Fe\(_2\)O\(_3\), while iron and alum-

num are relatively enriched to form 30% goethite substituted by 15 mol% Al\(_2\)O\(_3\) and 5% gibbsite. The respective mean bulk chemical composition of the parent minerals were estimated from the different formulas previously reported. The isovolu-

metric weathering of the rock by the saprolite is thus described by

\[
\begin{align*}
1.75 \text{ amphibole} &+ 2.45 \text{ albite} + 0.69 \text{ phengite} \\
+ 0.22 \text{ chlorite} &+ 0.33 \text{ epidote} + 0.39 \text{ garnet} + 36.1 \text{ H}_2\text{O} \\
+ 1.78 \text{ O}_2 &+ 21.89 \text{ H}^+ \\
+ 2.79 \text{ Fe}^{2+} &\Rightarrow 4.26(\text{Si}_{1.95}\text{Al}_{0.05}\text{Fe}_{0.90})\text{O}_5(\text{OH})_4 \\
+ 9.2(\text{Fe}_{0.83}\text{Al}_{0.17})\text{O(OH)} &+ 0.96 \text{ gibbsite} + 18.77 \text{ H}_2\text{SiO}_4 \\
+ 1.22 \text{ Al}^{3+} &+ 5.51 \text{ Mg}^{2+} + 4.02 \text{ Ca}^{2+} + 3.42 \text{ Na}^+ \\
+ 1.33 \text{ K}^+ &,
\end{align*}
\]

meaning that 100% (Mg, Ca, Na, K), 69% silica, and 10% Al are released, whereas 35% Fe is relatively accumulated. The saproliti-

zation of the parent rock likely happened under humid and hot conditions, such as those created by a tropical humid climate, implying high soil water fluxes and organic carbon. Such conditions may have effectively favored the co-formation of Al–goethite and gibbsite with kaolinite at the expense of the parent silicate minerals.

Upwards to the transition with the mottled clay layer, the former kaolinitic saprolite is transformed into a more gibbositic layer composed of 48% gibbsite, 36% goethite substituted by 20 mol% AlOOH, and 16% Fe–kaolinite with \( \rho_b = 1.5 \text{ g/cm}^3 \), \( \rho_g = 2.3 \text{ g/cm}^3 \), and \( p = 0.35 \). This part of the profile is characterized at once by pedoturbated structures changing the geometry of the porosity and thus deleting the parent rock textures and by the hydration–oxidization of the organic matter reflected by gaseous emanations composed of CO\(_2\) and CH\(_4\) as previously mentioned. Under those more reducing and hydrated conditions the kaolinite effectively transforms into gibbsite according to the geochemical reaction,

\[
4.26 \text{ Fe–Kaolinite} + 9.2 \text{ Al–goethite} + 0.96 \text{ gibbsite} \\
+ 25.19 \text{ H}_2\text{O} + 0.88 \text{ Fe}^{3+} + 2.78 \text{ Al}^{3+} \Rightarrow 1.05 \text{ Fe–Kaolinite} \\
+ 11.04[(\text{Fe}_{0.85}\text{Al}_{0.15})\text{O(OH)}] + 9.2 \text{ gibbsite} + 6.42 \text{ H}_2\text{SiO}_4 \\
+ 10.98 \text{ H}^+.
\]

It follows from Eqn. 5 that 75% silica is released, while 21% Al and 10% Fe are gained. This confirms that the transformation of kaolinite into gibbsite is primarily a desilication process under relatively acid pH conditions. The aluminum is also enriched from absolute accumulations as proved by the secondary gibbsite crystallizations within the voids where the water ac-


tivity is high. Conditions of low pH and high water and Al activities also allow goethite with a relatively high Al substi-

tution to be preserved along with the gibbsite (Fitzpatrick and Schwertmann, 1982).

3.3.2. Geochemical balance of ferruginization processes

The ferruginization process stimulates the formation of he-

matite and goethite. Assuming that it is an ongoing process, it concerns the formation of mottled clay layers, soft nodular layers and/or soft ferricretes, and finally the actual ferricrete (Nahon, 1991; Tardy, 1993). It was also defined as the epigene replacement of kaolinite by hematite, a general process gov-

erning the formation of ferruginous nodules and ferricretes (Nahon et al., 1977; Tardy and Nahon, 1985; Ambrosi et al., 1986; Nahon, 1986).

The ferruginization process in the mottled clay layer is commonly characterized by the hematite formation in mottles made up of kaolinite and goethite inherited from the underlying saprolite (Tardy and Nahon, 1985; Ambrosi and Nahon, 1986). In the upslope profile, the hematitic ferruginization starts modestly since the mottled clays are composed of 50% kaolinite, 35% goethite substituted by 12 mol% AlOOH, 5% hematite, and 10% gibbsite with \( \rho_b = 1.54 \text{ g/cm}^3 \), \( \rho_g = 2.57 \text{ g/cm}^3 \), and \( p = 0.40 \). The formation of the mottled clays at the expense of the saprolite can be described by

\[
\begin{align*}
4.26 \text{ Fe–kaolinite} &+ 9.2 \text{ Al–goethite} + 0.96 \text{ gibbsite} \\
+ 5.49 \text{ H}_2\text{O} &+ 2.65 \text{ Fe}^{3+} \Rightarrow 3.02 \text{ kaolinite} \\
+ 9.91 [(\text{Fe}_{0.85}\text{Al}_{0.15})\text{O(OH)}] &+ 0.96 \text{ hematite} + 1.77 \text{ gibbsite} \\
+ 2.48 \text{ H}_2\text{SiO}_4 &+ 2.88 \text{ H}^+ + 1.69 \text{ Al}^{3+},
\end{align*}
\]

implying that 29% silica and 16% Al are released while 25% Fe is gained. The loss of Al is limited because the kaolinite is slightly dissolved whereas gibbsite forms.

The ferruginization process under the ferricretes of high plateau and upslope profiles is also characterized by further iron accumulations in the clay–ferruginous material of the mottled clay layer leading to the development of the soft nodular layer. In the upslope profile, this layer contains, on average, 40% kaolinite substituted by 2 mol%, 35% goethite substituted by 12mol% AlOOH, 15% hematite substituted by 4 mol% Al\(_2\)O\(_3\) and 10% gibbsite, with \( \rho_b = 1.95 \text{ g/cm}^3 \), \( \rho_g = 3.01 \text{ g/cm}^3 \), and \( p = 0.35 \). It may develop according to the geochemical reaction,
Fig. 10. Geochemical composition of weathering mineral and plasmas in different layers of the upslope profile of hillside in SiO₂-Al₂O₃-Fe₂O₃ ternary diagram (black circles, kaolinitic plasma of saprolite; black and white diamonds, goethitic plasma of saprolite and mottled clays, respectively; white triangles and crossed squares, primary and secondary gibbsite, respectively in saprolite; white circles and black squares, kaolinite and hematite of “booklets” respectively in ferricrete).

3.02 kaolinite + 9.91 Al-goethite + 0.96 hematite
+ 1.77 gibbsite + 6.3 H₂O + 3.59 Fe³⁺ → 2.62 kaolinite
+ 10.74 [(Fe₀.₈₈Al₀.₁₂)O₆(OH)] + 2.49 [(Fe₁.₄₅Al₀.₅₆)O₆]
+ 1.92 gibbsite + 0.8 H₂SiO₄ + 9.72 H⁺ + 0.35 Al³⁺, (7)
showing that 13% silica and 4% Al are released while 25% Fe is gained. Reactions in Eqs. 6 and 7 indicate that the increase in iron due to the formation of hematite is low. The pedogenic environment prevailing in the mottled clay and the soft nodular layers of the forested upslope profile is characterized by hydrated and reducing conditions that favor the development of Al-goethite over the hematite.

In the high plateau profile the soft nodular layer richer in purple reddish hematitic nodules is composed of about 28% kaolinite, 23% goethite substituted by 12 mol% AlOOH, 34% hematite substituted by 5 mol% Al₂O₃, and 15% gibbsite with ρb = 2.48 g/cm³, ρg = 2.97 g/cm³, and p = 0.16. The development of the soft nodular layer from a mottled clay layer presumed to have a composition similar to that of the upslope profile can thus be described by,

3.02 kaolinite + 9.91 Al-goethite + 0.96 hematite
+ 1.77 gibbsite + 29.04 H₂O + 1.46 Al³⁺
+ 14.68 Fe³⁺ → 2.37 kaolinite + 9.12 [(Fe₀.₈₈Al₀.₁₂)O₆(OH)]
+ 9.10 [(Fe₁.₄₅Al₀.₅₆)O₆] + 3.72 gibbsite + 1.3 H₂SiO₄
+ 48.42 H⁺, (8)
meaning that 22% silica is released while 14% Al and 58% Fe are gained. The hematitic ferruginization is so pronounced here, relative to the upslope profile, that the secondary Al-goethite and gibbsite are still well preserved, implying that the gains of Al and a part of Fe may result from absolute accumulation processes. Even though the mottles of the mottled clay layer truly transform into elongated nodules according to an aggrading hematitic ferruginization process (Tardy and Nahon, 1985), the occurrence of round polyhedral nodules and iron-depleted clayey pockets in the upper part of the soft nodular layer also suggest that this part of the profile could originate from the chemical degradation of the overlying ferricrete likely because of a change of climatic conditions (Beauvais and Tardy, 1991). This degradation facies is on average composed of 64% kaolinite, 20% of goethite substituted by 16 mol% AlOOH and 16% hematite substituted by 9 mol% Al₂O₃ with ρb = 2.35 g/cm³, ρg = 2.85 g/cm³, and p = 0.17. The local degradation of the soft nodular layer can thus be described by the following geochemical reaction

2.37 kaolinite + 9.12 [(Fe₀.₈₈Al₀.₁₂)O₆(OH)]
+ 9.10 [(Fe₁.₄₅Al₀.₅₆)O₆] + 3.72 gibbsite + 5.96 H₂SiO₄
+ 2.25 Al³⁺ + 26.37 H⁺ → 5.35 kaolinite
+ 7.83 [(Fe₀.₈₄Al₀.₁₆)O₆(OH)] + 4.23 [(Fe₁.₄₂Al₀.₅₆)O₆]
+ 25.37 H₂O + 11.04 Fe³⁺, (9)
meaning that 56% silica and 18% Al are relatively concentrated.
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while 44% Fe is released. This result combined with the petrological observations indicate that the released iron probably migrates downwards and precipitates at the bottom of the soft nodular layer or the top of the mottled clay layer to form a goethitic nodular soft ferricrete (Beauvais, 1991). This facies is on average made up of 30% kaolinite, 60% goethite substituted by about 27 mol% AlOOH, only 5% hematite substituted by 2 mol% Al₂O₃ and 5% gibbsite with \( \rho_b = 2.65 \text{ g/cm}^3, \rho_g = 3.13 \text{ g/cm}^3, \text{ and } p = 0.15 \). The geochemical reaction for this secondary ferruginization process at the top of the mottled clay layer can be written as,

\[
3.02 \text{ kaolinite} + 9.91 \text{ Fe--goethite} + 0.96 \text{ hematite} \\
+ 1.77 \text{ gibbsite} + 24.52 \text{ H}_2\text{O} + 3.94 \text{ Al}^{3+} \\
+ 9.61 \text{ Fe}^{3+} \Rightarrow 2.57 \text{ kaolinite} + 24.07 \left[\text{Fe}_{0.72}\text{Al}_{0.27}\right]\text{OOH} \\
+ 1.35 \left[\text{Fe}_{1.96}\text{Al}_{0.04}\right]\text{O}_3 + 1.25 \text{ gibbsite} + 0.9 \text{ H}_2\text{SiO}_4 \\
+ 40.65 \text{ H}^+ , \quad (10)
\]

implying the release of 15% silica and a gain of 30% Al and 47% Fe. The resulting nodular soft ferricrete is formed in part by Fe and Al absolute accumulations that leads to the formation of Al--goethite associated to gibbsite instead of hematite under conditions of high water and Al activity. The reactions shown in Eqns. 8 to 10 describe the superimposition of two opposite mechanisms reflecting different pedoclimatic environments. First the hematitic nodules have been formed by an aggrading ferruginization process under contrasted climatic conditions, i.e., characterized by alternating wet and dry seasons. Second, those nodules were degraded under more humid conditions as those prevailing today, and the resulting loss of iron accumulated at the base of the soft nodular layer to form a goethitic nodular soft ferricrete. During that evolution, the Al substitution of the different generations of goethite varied according to the variations of pH and activities of silica and aluminum (Fitzpatrick and Schwertmann, 1982; Schwertmann and Kämpf, 1985; Tardy and Nahon, 1985).

The ferruginization process under the ferricretes of downslope profiles is dominated by the goethite development over the hematite. The mottled clay layer and the vermiform soft ferricrete may appear like a nodular facies under way to forming as described by Tardy and Nahon (1985), but the comple-
Fig. 13. Geochemical composition of weathering minerals and plasmas in different layers of the upper part (soft nodular and proto- pisolitic ferricrete layers) of the downslope profile of hillslope in SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-Fe\textsubscript{2}O\textsubscript{3} ternary diagrams (white triangles, matrix embedding nodules; black circles, kaolinite of “booklets”; white circles, brown–orange plasma; white squares, hematite of kaolinite “booklets”; black diamonds, primary goethitic plasma; black squares, secondary hematite; white diamonds, secondary goethite).

...
features reported above as the kaolinite–hematite paragenesis suggest that the massive ferricrete of the high plateau could directly derive from the ferruginization of a saprolitic material, once located upper in the regolith (Tardy, 1993). In that case, the geochemical reaction can be written as,

\[ 4.26 \text{Fe–kaolinite} + 9.2 \text{Al–goethite} + 0.96 \text{gibbsite} \]
\[ + 28.77 \text{H}_2\text{O} + 17.26 \text{Fe}^{3+} \rightarrow 2.56 \text{Fe–kaolinite} \]
\[ + 7.35 \text{Al–goethite} + 9.93 \text{Al–hematite} + 2.42 \text{gibbsite} \]
\[ + 3.4 \text{H}_2\text{SiO}_4 + 48.21 \text{H}^+ + 1.19 \text{Al}^{3+}, \quad (14) \]

meaning that 40% silica and 11% Al are released whereas 68% Fe is gained. Although the ferricrete is rich in hematite it remains ~60% kaolinite. A small proportion of Al is released by 1 mol% AlOOH and 23% gibbsite for implying that 71% silica and 13% Al are released while 53% Fe is gained. This protosolitic ferricrete is the poorest in kaolinite and the richest in hematite. Gibbsite likely formed from hydration and desilication processes of the kaolinite. Although an aggregating ferruginization process according to the model proposed by Nahon (1976, 1986) and Ambrosi and Nahon (1986) cannot be disproven, one can also consider that a part of Fe could have been imported according to a process similar to that described above for the ferricrete of the upslope profile (Fig. 2).

In the downslope profile the protosolitic ferricrete is made up of 16% kaolinite substituted by 2 mol% Fe$_2$O$_3$, 18% goethite substituted by 12 mol% AlOOH, 44% hematite substituted by 1 mol% Al$_2$O$_3$, and 23% gibbsite with $\rho_d = 2.59$ g/cm$^3$, $\rho_g = 3.14$ g/cm$^3$, and $p = 0.17$. The geochemical balance accounting for the development of that ferricrete facies from the aggrading ferruginization of the underlying soft nodular layer can be expressed as,

\[ 2.62 \text{kaolinite} + 10.74 \text{goethite} + 2.49 \text{hematite} \]
\[ + 1.92 \text{gibbsite} + 24.43 \text{H}_2\text{O} + 2.18 \text{Al}^{3+} \]
\[ + 11.11 \text{Fe}^{3+} \rightarrow 1.84 [(\text{Si}_2\text{Al}_{1.5}\text{Fe}_{0.04})\text{O}_5(\text{OH})_3] \]
\[ + 11.36 [(\text{Fe}_{0.88}\text{Al}_{0.12})\text{OOH}] + 8.73 [(\text{Fe}_{0.97}\text{Al}_{0.03})\text{O}_3] \]
\[ + 3.67 \text{gibbsite} + 1.56 \text{H}_2\text{SiO}_4 + 39.87 \text{H}^+, \quad (15) \]

3.4. Geochemical Patterns of Ferruginization Processes

The results obtained from the geochemical reactions in Eqs. 6 to 16 allow (1) to analyse the effect of the ferruginization processes on the behavior of different geochemical and mineralogical quantities as a function of the consumption or release of $\text{H}^+$, that traduces an increase or a decrease of pH (Figs. 14 and 15), and (2) to discuss the way the kaolinite is dissolved during the ferruginization processes (Fig. 16). The stronger the release of $\text{H}^+$, the lower is the pH, the higher the quantity of water consumed, the better are the drainage conditions and the highest is the iron gain (Fig. 14A). This characterizes the aggregating ferruginization processes governing the development of the hematite with a low Al substitution in the upper well oxidized parts of the profiles or the neoformation of the goethite with a high Al substitution in the lower more
hydrated parts where the Al activity is high (Figs. 14B and 15A and D). When the system loses iron as in the reactions Eqns. 9 and 11, both H⁺ and dissolved silica are consumed (Figs. 14A and 15C). This effectively happens when the degradation driven by iron dissolution–precipitation mechanisms operates, stimulating the neoformation of kaolinite and goethite with minor Al substitution instead of hematite and gibbsite (Fig. 15A–C). When the silica balance ≥ 0 with increasing pH, the hematite is more aluminous in the degradation facies (Fig. 15C and D), while the less aluminous hematite is developed in layers, which are also the poorest in kaolinite (Fig. 15B and D), that could appear contradictory with the idea of an epigene replacement of the kaolinite by the hematite (Nahon et al., 1977; Tardy and Nahon, 1985; Nahon, 1986). The aluminum balance of the hillslope profiles is contrasted because it depends on the dissolution rate of kaolinite and on the ability of gibbsite to crystallize. In the upslope profile, the aluminum increases as the pH lowers whereas it decreases in the downslope profile (Fig. 14B), where the dissolution of kaolinite goes faster than in the upslope profile (Fig. 15B and C). In this profile gibbsite continuously increases from the mottled clays to the ferricrete (Fig. 16A). In fact, kaolinite is better correlated to gibbsite rather than to hematite (Fig. 16A and B) suggesting that it was less ferruginized by hematite according to an epigene process than it underwent an incongruent dissolution wherever the gibbsite formed.

3.5. Climatic Evolution Patterns of the Lateritic Weathering Mantle

It was proposed that mineralogical variations of bauxites and ferricretes could reflect climate and palaeoclimate changes driven by the continental drift in Africa and Brazil (Tardy et al., 1988, 1991; Tardy and Roquin, 1998). For instance, a bauxite mainly composed of gibbsite and goethite should be formed under humid conditions while a ferricrete rich in hematite and kaolinite should reflect drier climatic conditions. This study’s observations and results suggest that the lateritic weathering mantle of the Haut–Mbomou area in Central Africa could have undergone the effects of chemical and mechanical erosion processes according to climatic changes. Under the effect of a climatic change from humid to drier conditions a presumably thick saprolite layer made up of kaolinite and goethite could have been oxidized and ferruginized to form a massive ferricrete, i.e., the parent ferricrete, since this latter is mainly composed of bundles of kaolinite booklets similar to those of the actual underlying saprolite but shrouded in an hematitic cement, instead of being dissolved and replaced by hematite according to epigene processes. As those climatic conditions persisted, the weathering rate of the parent material decreased while the ferruginization front went down into the saprolite favoring the development of mottled clay and soft nodular layers between the saprolite and the ferricrete, with a dominance of the hematite over the goethite. This initial lateritic
weathering mantle overlain by the parent massive ferricrete is actually only preserved on the high plateau and its edges suggesting that it could then have undergone further weathering and erosion processes on the hillslopes under the influence of alternating humid and drier climates. A return to more humid conditions could have set off the degradation of the parent ferricrete under the combined effects of the humidity and the organic matter oxidation (Beauvais and Tardy, 1991; Tardy, 1993). This mechanism is likely reflected (1) by the Fe-depleted clayey pockets and the numerous round polyhedral nodules occurring at the base of this ferricrete and the top of the underlying soft nodular layer in the high plateau profile, and (2) the occurrences of Al–goethite and gibbsite with hematite and kaolinite in the ferricrete and in the nodules of the soft nodular layer. Degradation of the parent ferricrete resulted in Fe and Al release that led to intraprofile migrations and absolute accumulations of secondary Al–goethite with relatively high Al substitution and associated gibbsite lower in the profiles, in particular at the top of the saprolite of the upslope profile and at the base of the soft nodular layer of the high plateau profile where a nodular soft ferricrete rich in Al–goethite neoforms. A new evolution towards drier climatic conditions first stimulated mechanical erosion processes of the parent ferricrete degradation products that is reflected by geomorphic patterns as, (1) the two discrete scarps incising the hillslope topography and (2) the numerous blocks of parent ferricrete spread around. Those climatic conditions should have gone on to allow the aggregation–ferruginization of the remaining lateritic products on hillslopes that form the actual protopisolitic ferricrete embedding parent ferricrete relics. Today the actual subhumid conditions further stimulate the inner chemical degradation of the ferricretes around the high plateaus where a ring of forest develops. Those conditions also maintain an hydromorphic environment in the downslope profiles making the mottled clays and the vermiciform soft ferricrete to look like a pseudo-gley. The clayey matrices are bleached, the iron dissolution–precipitation processes are stimulated, Al substitution of the Fe–oxyhydroxides increase and goethite dominates over hematite.

4. CONCLUSION

In the Haut–Mbomou area, a simple geochemical balance of lateritization processes based on petrological observations indicates that the ferruginization of the weathering materials of amphibole–schist rocks does not appear as a simple on-going process from the bottom to the top of the profiles. Instead, the actual lateritic weathering mantle could result from different stages of weathering–erosion process according to climatic changes, which determine the aggrading ferruginization or degradation processes of ferricretes. The aggrading ferruginization leads either to the formation of hematite with low Al substitution under dehydration, oxidization and low pH conditions, or to the neoformation of goethite with high Al substitution in which the water and aluminum activities are high and the redox potential is lowered. The degradation processes favor the development of goethite at the expenses of hematite, and they are traced by relatively high Al substitution, in particular for relic hematite. The massive ferricretes of the high plateaus are the oldest, appearing to be relics of past drier climates. These ferricretes could result from the ferruginization of previous saprolites because they still contain numerous kaolinite booklets, which are not clearly ferruginized by the hematite according to epigenic processes but simply embedded in an hematitic ferruginous cement. The relatively low Al substitution of the hematite could also preclude the hypothesis of the epigenic replacement. The ferricretes of the hillslopes could derive at least pro parte from the degradation and the erosion of the previous massive ferricretes during the downward reduction of the regolith under the effects of climatic changes from dry to humid. They are, however, richer in goethite and gibbsite, whereas hematite and kaolinite could be relics of past drier climates. The geomorphological patterns of the landforms and the petrological features of the underlying lateritic weathering mantle could be in that way good signatures of climatic changes.

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