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Developments in Earth Surface Processes 2

# WEATHERING, SOILS & PALEOSOLS

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*Chapitre 16*

*Chapter 16*

# Geochemistry and evolution of lateritic landscapes

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## Introduction

Laterites are widespread in Australia, India, Burma, Brazil and in intertropical Africa. In these regions, bedrocks are generally weathered to depths of over 10 to 150 m, depending on age of laterization, regional tectonic activity, climate and nature of the parent materials. Despite a certain homogeneity in mineralogical and chemical composition, they offer a large variety of colors, textures and petrographic facies which may not obviously reflect the parent rock from which they derive. Over most of the areas of the Brazilian and the African shields, a very thick lateritic mantle has been continuously formed over more than 100 Myr (King, 1957, 1962; Michel, 1973). Laterites are mostly old formations which are not necessarily fossils but have been evolving and continue to evolve under various tropical climates, changing or fluctuating from equatorial, humid tropical to semi-arid. As a consequence of the complexity of climatic history, formation and destruction mechanisms of lateritic profiles and landscapes are generally somewhat difficult to decipher.

Despite a considerable amount of work and a large bibliography (d'Hoore, 1954; Maignien, 1958, 1966; Leneuf, 1959; Millot, 1964; Tardy, 1969; Mohr et al., 1972; McFarlane, 1976, 1983; Tardy and Nahon, 1985), several questions remain unresolved, new observations are being established, new data are being produced and new ideas and theories are now emerging.

The purpose of this chapter is to present some of the recent results of research into the evolution of profiles and landscapes, of laterites, associated bauxites, ferricretes or soft kaolinitic nodular horizons. Their geochemistry and paleoclimatology will be stressed.

## Autochthony, allochthony and lithodependence of ferricretes

In western and central Africa, the lateritic weathering mantle is very thick, widespread, and, in many cases, capped by old and widely developed ferricretes

(King, 1948; Maignien, 1958; Michel, 1973; Nahon, 1976; McFarlane, 1976; Leprun, 1979).

Ferricretes consist of relative accumulations of poorly mobile major elements such as iron, aluminum and silicon, minor or trace elements such as vanadium, chromium, phosphorus, and insoluble minerals such as quartz, ilmenite, tourmaline, zircon. These elements and minerals may concentrate *in situ* or may be transported over short distances either in solution in the percolating waters or mechanically in bioturbation products. Most of them are autochthonous. The most soluble minerals are dissolved, and moderately or highly mobile elements are leached in solution and removed from lateritic landscapes. Beside the resistant primary minerals (mainly quartz), ferricretes are generally composed of a fairly constant secondary assemblage made of hematite, goethite, kaolinite and sometimes gibbsite.

Despite their apparent homogeneity, ferricretes show a large diversity of mineralogical and chemical compositions, related to their age, their degree of evolution and the nature of the parent rock from which they derive. Some very immature and recent ferricretes retain the mineralogical and the chemical signature of their parent rock. They are called "lithodependent". In others, older and more mature, mineralogical and chemical compositions are homogenized and the composition of the parent rock is almost totally modified. These can be called "lithoindependent".

The terminology used here is explained in detail in Tardy (this book).

### Mineralogical and geochemical diversity of the lateritic patchworks

At different scales of observation, from regional to local, laterites outcrop as patchworks of a high degree of mineralogical and chemical diversity.

### Age of lateritic surfaces

On a continental scale as shown by King (1957, 1962), Michel (1973), McFarlane (1973), Boulet (1978) and Grandin (1976) in western and central Africa, units of laterites, different in their degree of evolution, as well as in their mineralogical and chemical composition, cover surfaces of different ages. Michel (1973) has recognized three bauxitic surfaces (Jurassic, Cretaceous, Eocene) followed by four levels capped by ferricretes at different stages of evolution: *relief intermediaire* (Pliocene), *haut glacis* (early Quarternary) and *moyen glacis* (middle Quaternary; Figure 16.1). This regional sequence of peneplanation surfaces has been interpreted as resulting from the alteration of humid and arid periods which supposedly succeeded since the Jurassic. Ages of the Jurassic, Cretaceous and Eocene bauxitic surfaces are probably correct while the ages of ferricretes associated with what is called *haut glacis* and *moyen glacis* are certainly older than Quarternary. In fact, calculated or evaluated ages of profiles (Leneuf, 1959; Tardy, 1969; Gac, 1980; Gac and Tardy, 1980; Fritz, 1975; Nahon and Lappartient, 1977; Nahon, 1986) suggest that ferricretes a few metres thick, overlying lithomarges of several tens of metres in thickness need
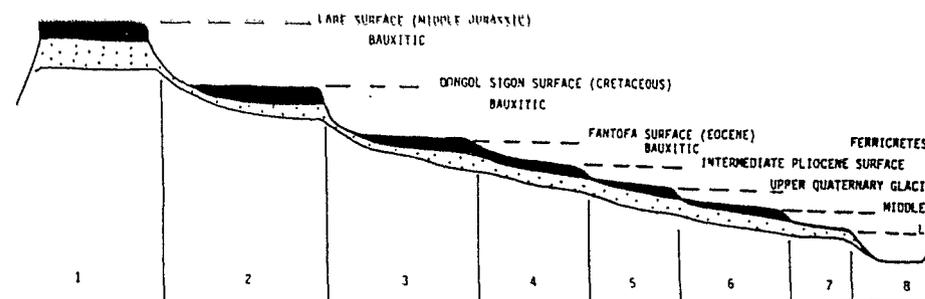
Fig. 16.1. The seven peneplanation surfaces of Michel (1973) capped by laterites of different kinds (bauxites or ferricretes) and of different degree of evolution, observable from the Fouta Djalon in Guinea to the Niger alluvial plain in Mali.

several million years to form. In other words it is proposed here that, in Western Africa, from the Jurassic to the present time, laterites were continuously formed. Bauxites have been covered since the Oligocene by ferricretes. Ages of ferricrete overlying morphological surfaces may range from about 1 to 40 million years and consequently, at a continental scale, degrees of evolution of outcropping ferricretes may be very diverse.

At a regional scale (20 km) a ferricrete lateritic landscape consists generally of a myriad of plateaus capped by iron duricrusts (carapaces, cuirasses, gritty layers) and separated by depressions or thalwegs, in which there are outcrops of the lower horizons such as mottled zones, lithomarges, saprolites and sometimes parent rocks (Figure 16.2). In a given system, for example the *haut glacis* of Michel (1973), all plateaus were supposed to lie on the same morphological level and were supposed
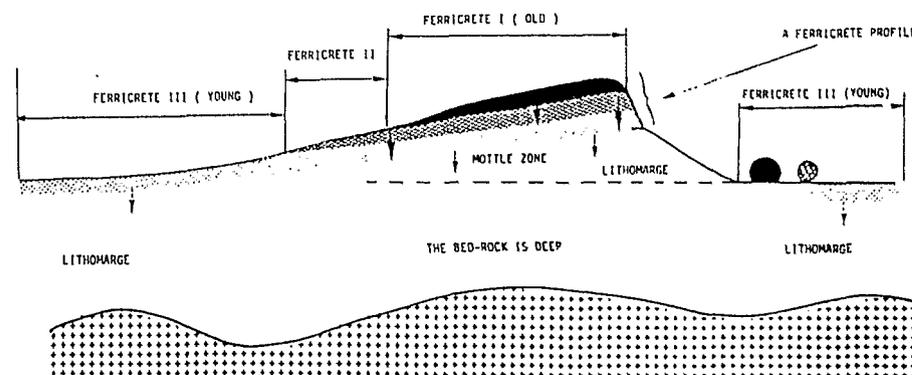


Fig. 16.2. Lateral distribution of lateritic facies in a tropical landscape shaped by erosion and subsequent alteration.

to exhibit the same characteristics. In fact, they do not show the same mineralogical and chemical composition and consequently the same degree of evolution (Mazaltarim, 1989; Boeglin, 1990).

The same kind of heterogeneity is also observable on a local scale in a set of ferricrete samples collected at the surface of a given morphological unit of a plateau system, covered by a continuous ferricrete (Figure 16.3; Mazaltarim, 1989; Roquin et al., 1989; Boeglin, 1990; Freyssinet, 1990).

At each scale of observation, the heterogeneity of outcropping facies has received different interpretations (Figure 16.4). Some authors invoke climatic differences (Michel, 1973). Others claim that tectonics plays an important part in differentiating the altitudes of peneplanation (McFarlane, 1973). Yet others have looked at the heterogeneity as being due to variations in chemical compositions of parent rock (Leprun, 1979), or to lateral variations of facies due to lateral migration of elements (Fe, Al, Si) within profiles (Nahon, 1976). A systematic mapping of ferricrete plateaus located in Mali (Kangaba) in Burkina Faso (Gaoua) and Central Africa (Zemio) (Mazaltarim, 1989; Beauvais, 1990; Boeglin, 1990; Freyssinet, 1990) shows that the surficial heterogeneity can be explained by a differential surface erosion process. The erosion leads in different places and at different times to an exposure of subsurface horizons younger and less evolved than other ones, located close-by and not eroded. After erosion, all the outcropping young and old facies are submitted to continuous weathering under similar conditions (Figures 16.2 and 16.3).

A continuous ferricrete covering a given morphological surface appears in fact as a patchwork of petrographical, mineralogical and chemical facies differing in age and degree of evolution. This can be regarded as a consequence of the differential erosion which finally involves all the ferricrete surfaces.

## Allochthony or autochthony of ferricretes

The diversity of the petrographic facies or of the mineralogical and chemical compositions of the outcropping ferricrete samples make the interpretation of the surficial geochemistry difficult. For many years the question of the allochthony or autochthony of ferricretes has been debated. Are they the result of lateral transportation of iron in solution precipitating in a lithodependent host saprolite (Maignien, 1958; Michel, 1973; McFarlane, 1976) or are they formed from long distance mechanically transported materials, so that they are entirely independent of the surrounding rocks (Lamotte and Rougerie, 1962; Vogt, 1967; Seret, 1978)? Should we consider the lateritic mantles as masks without any relationship with the underlying rocks or as skins developed from the underlying parent materials (Millot et al., 1976)?

During these last ten years, evidence of ferricrete autochthony has accumulated (Wackermann, 1975; Blot et al., 1976, 1978; Boulet, 1978; Pion, 1979; Schellmann,
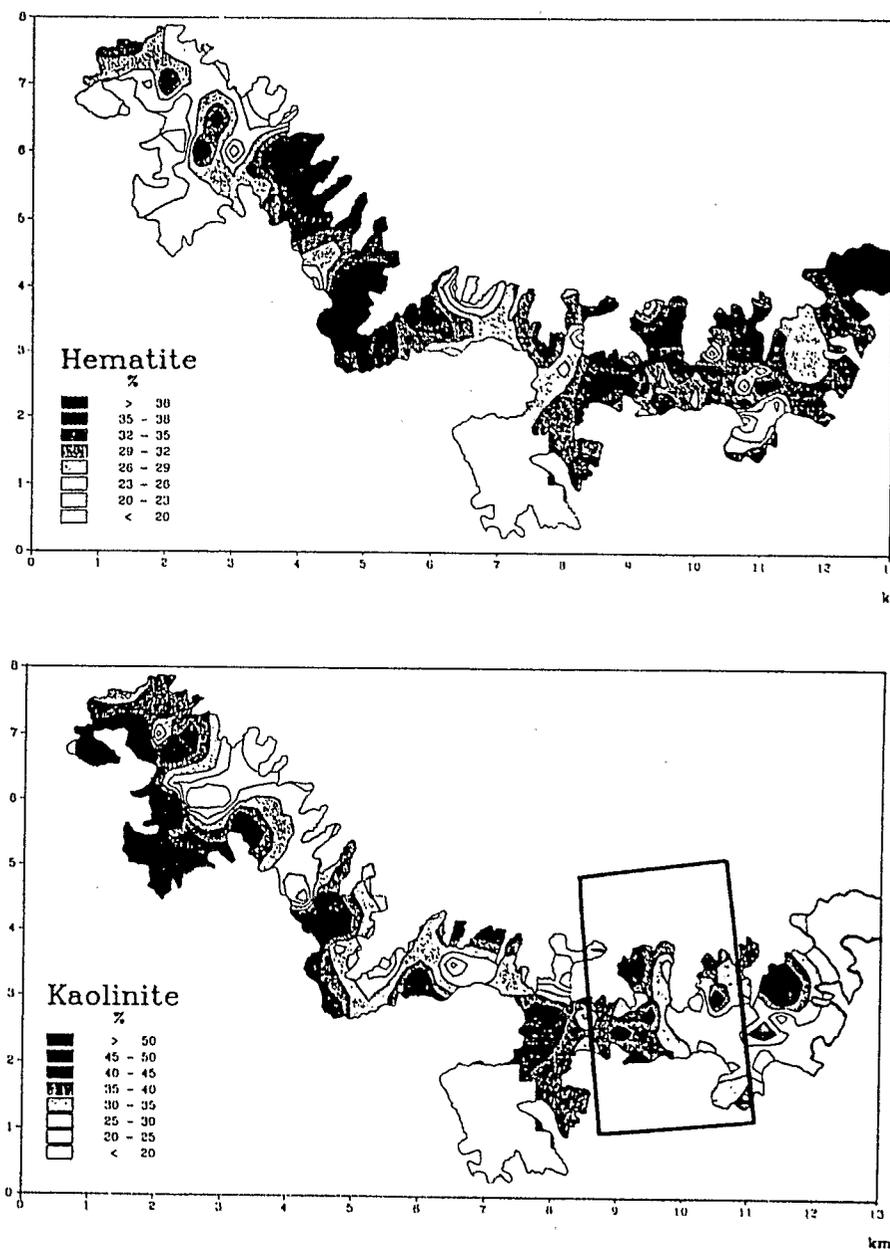


Fig. 16.3. Patchworks of different petrographical, mineralogical and geochemical facies of ferricrete, due to differential erosion over a given morphological surface. The soil surface was permanently submitted to a contrasted tropical climate and outcropping ferricretes are of different ages and degrees of evolution (Mazaltarim, 1989; Boeglin, 1990; Freyssinet, 1990).

1986; Leprun, 1979). In most cases, quartz and resistant minerals as well as iron and some trace elements reflect the composition of the underlying rocks. The lithodependence of ferricretes is now generally admitted.

### Lithodependence of young duricrusts and chemical homogenization of old ferricretes

Ferricretes of different degrees of evolution and age, overlying parent rocks of different compositions are clearly lithodependent in young and poorly evolved systems while they are lithoindependent in old and highly evolved facies, which are chemically homogenized. In Table 16.1 several analyses of ferricretes collected in the region of Gaoua (Burkina Faso) include parent rocks (acid PRA or basic PRB) and their associated ferricretes classified as a function of their iron content ($Fe_2O_3$ %) (FYA: young on granitic rocks; FMA and FMB: mid-evolved on acid and basic rocks, respectively; FOA and FOB: highly evolved on acid and basic rocks, respectively). Some evolutionary trends are shown in Figure 16.5.



Fig. 16.4. Five interpretations for lateral differentiations of lateritic landscapes; a. surfaces of different ages formed under different climatic conditions (Michel, 1973); b. a single surface dissected at different topographical levels (Beaudet, 1978); c. a single surface of ferricretes differing because of their parent-rock composition (Leprun, 1979); d. a lateral differential evolution (Nahon, 1976); e. a differential erosion which induces the outcropping of ferricrete facies of different ages and degrees of evolution.



Fig. 16.5. An example of the mineralogical and chemical composition of ferricretes of Gaoua (Burkina Faso), located on different basic or granitic parent rocks (PR). For low $Fe_2O_3$ contents, compositions are distinct: ferricretes are lithodependent. For high $Fe_2O_3$ contents, compositions are homogenized: ferricretes seem to be lithoindependent. (From Tardy et al., 1988.)

TABLE 16.1

Average mineralogical and chemical composition of granitic rocks (PRA) and basic rocks (PRB) and of their associated ferricretes (37 samples): moderately evolved (FYA, on granites), midi-evolved (FMA, on granites and FMB, on basic rocks) and highly evolved (FOA, on granites and FOB, on basic rocks; MEN: average FOA and FOB)

| | PRA (n = 6)[a] | PRB (n = 7) | FYA (n = 2) | FMA (n = 18) | FMB (n = 10) | FOA (n = 5) | FOB (n = 2) | MEN (n = 7) |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 70.75 | 55.76 | 52.20 | 30.81 | 25.81 | 16.49 | 17.55 | 16.80 |
| $Al_2O_3$ | 14.56 | 15.12 | 10.52 | 14.87 | 18.70 | 14.53 | 12.94 | 14.07 |
| $Fe_2O_3$ | 2.01 | 9.17 | 27.59 | 42.67 | 42.90 | 57.54 | 56.27 | 57.18 |
| $MgO$ | 0.68 | 4.95 | 0.09 | 0.10 | 0.11 | 0.04 | 0.11 | 0.06 |
| $CaO$ | 2.39 | 7.60 | 0.20 | 0.21 | 0.21 | 0.20 | 0.20 | 0.20 |
| $Na_2O$ | 4.88 | 3.19 | 0.05 | 0.07 | 0.09 | 0.08 | 0.09 | 0.08 |
| $K_2O$ | 2.14 | 0.64 | 0.26 | 0.11 | 0.20 | 0.06 | 0.15 | 0.09 |
| $Mn_3O_4$ | 0.03 | 0.17 | 0.04 | 0.20 | 0.15 | 0.10 | 0.15 | 0.12 |
| $P_2O_5$ | 0.11 | 0.16 | 0.15 | 0.27 | 0.23 | 0.27 | 0.31 | 0.28 |
| $TiO_2$ | 0.27 | 0.67 | 0.53 | 0.83 | 0.75 | 0.89 | 0.73 | 0.84 |
| $H_2O$ | 1.27 | 3.17 | 7.23 | 9.45 | 10.79 | 9.32 | 11.48 | 9.94 |
| Sum | 99.17 | 100.66 | 98.68 | 99.45 | 99.80 | 99.31 | 99.89 | 99.47 |
| Sr | 449 | 317 | 12 | 14 | 20 | 5 | 22 | 10 |
| Ba | 656 | 314 | 46 | 206 | 101 | 34 | 120 | 59 |
| V | 34 | 191 | 387 | 846 | 794 | 1194 | 1073 | 1160 |
| Ni | 9 | 55 | 48 | 54 | 49 | 69 | 72 | 70 |
| Co | 8 | 35 | 21 | 44 | 61 | 26 | 48 | 32 |
| Cr | 11 | 187 | 160 | 358 | 485 | 416 | 540 | 451 |
| Zn | 45 | 123 | 23 | 57 | 67 | 84 | 219 | 122 |
| Cu | 13 | 57 | 61 | 109 | 131 | 132 | 162 | 141 |
| Sc | 4 | 25 | 12 | 28 | 37 | 57 | 32 | 50 |
| Y | 5 | 15 | 11 | 11 | 11 | 11 | 18 | 13 |
| Zr | 127 | 75 | 224 | 214 | 210 | 147 | 119 | 139 |
| La | 26 | 9 | 8 | 14 | 11 | 8 | 11 | 9 |
| Ce | 44 | 27 | 36 | 80 | 62 | 33 | 43 | 37 |
| Eu | 1.1 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Yb | 0.3 | 1.2 | 1.4 | 0.8 | 1.2 | 1.4 | 1.7 | 1.5 |
| Lu | 0.3 | 0.3 | 1.0 | 0.3 | 0.6 | 0.7 | 0.6 | 0.6 |
| Nb | 4 | 3 | 16 | 12 | 12 | 13 | 11 | 13 |
| Qtz | 28 | 8 | 43 | 17 | 9 | 3 | 5 | 4 |
| Kaol | | | 23 | 31 | 41 | 32 | 29 | 30 |
| Goet | | | 27 | 32 | 33 | 29 | 52 | 35 |
| Hema | | | 6 | 17 | 16 | 37 | 15 | 31 |
| Gib | | | 0 | 2 | 2 | 0 | 0 | 0 |
| RPHG[b] | | | 18 | 35 | 32 | 56 | 23 | 47 |

Note: there are no samples in the group FYB, the moderately evolved ferricretes on basic rocks.

[a] n = number of samples

[b] RPHG = 100 × hematite/(goethite + hematite).

Quartz and P, Ba, Cr, Sc, Ni, Zn, Cu, Ce and La are characteristic of the nature of the parent rock. In carapaces and in poorly or mid-evolved ferricretes (FYA, FMA, FMB), which are relatively poor in iron (30–40%, $Fe_2O_3$), the nature of the parent rock still can be detected, while in ferricretes rich in iron (55–60%) mineralogical and chemical compositions are almost totally homogenized. In old and highly evolved ferricretes, the nature of parent rocks is not recognizable and there is no way to separate those which are formed either on granites, gneiss, schists, amphibolites, gabbros, sedimentary or volcanic rocks. Independently of the nature of parent rocks from which they derive, the final composition is the same: poor in quartz (5%) and mostly made of kaolinite (30%), goethite (35%) and hematite (30%). When aging, ferricretes become richer in iron and in hematite relatively to goethite and poorer in quartz. Kaolinite content remains almost constant. Trace elements which are originally located in heavy and resistant primary minerals such as zircon, ilmenite, cassiterite for example, are progressively redistributed: they are either leached out, incorporated into or adsorbed on to, goethite, hematite and kaolinite (Tardy et al., 1988a; Mazaltarim, 1989; Boeglin, 1990; Freyssinet, 1990).

### Conclusion

Most of the ferricretes develop through a downward vertical movement of iron and resistant minerals (such as quartz and zircon) accompanying the lowering of the landscape surface. They occur as lithodependent autochthonous relicts; at a landscape scale they are autochthonous and do not result from a large lateral transport. Therefore, the lithodependence principle refers only to the column of parent rock previously located above, which is in most cases similar to the unweathered material located below. The degree of lithodependence diminishes with age and degree of evolution. Along the progress of alteration a chemical homogenization takes place and all the ferricretes of different origin become similar with time. The homogenization can also be partly due to lateral movements.

### Remobilization of surficial material by termite activity

Erhardt (1951) was probably the first to suggest that termites play an important role in ferricrete formation. The subject was discussed at length by McFarlane (1976). Some researchers such as Russell (1962) believe that what are called vesicular, vacuolar or tubular structures are formed by termite activity, while others like Griffith (1953), de Swardt (1964) and Millot (1964) deny that termites could be responsible for lateritic structures and iron accumulation.

After the work of Watson (1972), Weber (1966), Yakushev (1968), Lee and Wood (1971), Boyer (1973), Lepage et al. (1974), Wood and Sands (1978), Cloud et al. (1980), Lavelle (1983), Grassé (1984, 1986) and others, Eschenbrenner (1986, 1987) has shown how the structure of lateritic profiles and particularly the structure of glaebular horizons depend on termite activity. The observations can be summarized as follows (Figure 16.6).
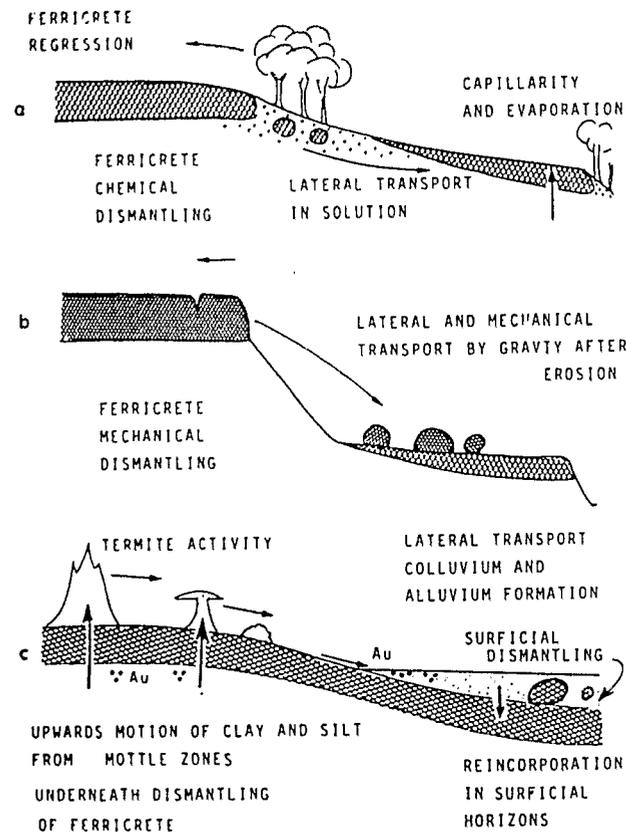
Fig. 16.6. Lateral movements of material in landscapes: a. lateral migration of iron in solution; b. lateral mechanical movements of disaggregated blocs of ferricretes; c. lateral transport of material reworked by termite activity.

(a) Termite mounds are commonly very abundant on ferricrete plateaus. Termite activity consists mainly of mechanical remobilization within the whole profile and within the mottle zone in particular.

(b) Termite activity also results in an upward motion of clay, silt or even sand particles, which are deposited on the soil surface and then submitted to mechanical erosion. The depth of uptake [up to 12 or 13 m, according to Boyer, (1973)] is important in determining what materials are transported. Commonly the uptake source corresponds mainly to the mottle zone or at least to the top of the lithomarge of the typical lateritic profile.

For this reason, the surficial silty materials accumulated in lateritic landscapes show a chemical and mineralogical composition similar to that of the mottle zone. For instance, the shape and the surface of the gold grains that are commonly found,

in silty surficial materials, are almost identical to those of the mottle zone but differ from those of both ferricrete or lithomarge (Figure 16.6; Freyssinet, 1990).

(c) Termite activity may also lead to downward movements of particulate materials in the vacuolar voids and channels of the profiles. Normal weathering leads to a decrease in quartz, zircon, tourmaline, cassiterite and other resistant minerals from the lithomarge to the top of the massive ferricrete horizons. By contrast, termite activity and incorporation of surficial material into deeper horizons, yield an increase in resistant minerals from the bottom to the top and from the massive ferricrete to the surficial gritty horizon. Consequently most of the chemical properties of the surface horizons are modified by bioturbation (Figure 16.6).

(d) Because of lateral transport of clay and silt material by mechanical erosion of the soil surface, termite activity is also responsible for lateral movements of lateritic material along the slopes. Consequently, it may be responsible for the lateral dispersion of elements and the formation of aureoles and halos well identified in geochemical prospection.

(e) Termite activity is also most probably responsible for the formation of the soft clay-silt horizon which in many situations overlies either a bauxite or a ferricrete or a nodular horizon or a stone line. The soft horizon can even be very thick and, being clay-rich, can temporarily retain water and induce ferricrete dismantling and the formation of a stone line (Tardy, this book).

## Vertical lowering of lateritic landscapes

Despite lateral movements of iron in solution (Maignien, 1964; Millot, 1964; McFarlane, 1973) and despite lateral transport of fine materials reworked by termite activity, one can consider that at a landscape scale and at a regional scale most of the movements are vertical (Tardy et al., 1988b). Landscapes evolve with time by a vertical lowering of soil surface and of weathering fronts.

### Gold distribution in laterites

Gold is one of the most valuable of metals which concentrate in laterites. Furthermore native gold, reputed to be very stable and almost insoluble, appears as a significant marker of the vertical lowering of lateritic landscapes (Freyssinet et al., 1989). It accumulates in ferricretes together with quartz and other resistant minerals. In mineralized districts, lateritic weathering profiles can be very thick (50 to 100 m) and quartz veins or fine stockworks bearing the gold mineralization, may intersect the whole profiles; they remain almost unaltered in the saprolites and lithomarges. Quartz grains become disaggregated and corroded in the mottled zone and quartz veins are, as a rule, entirely dismantled when crossing the ferricrete. Quartz particles may sometimes remain at the surface in the gritty horizon.
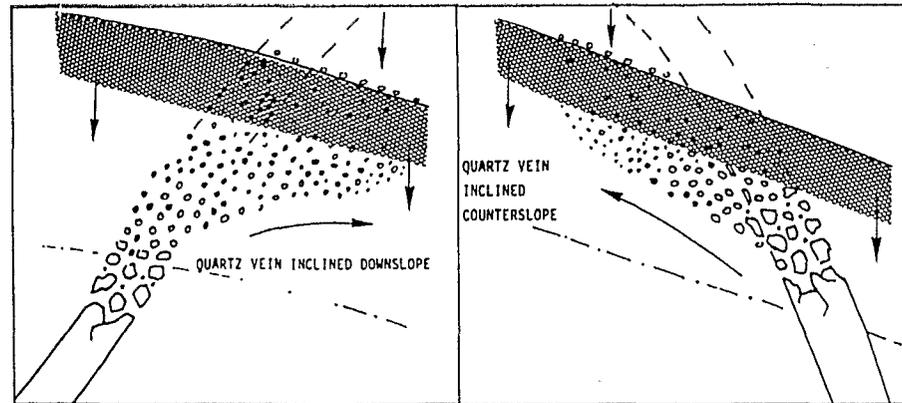
Fig. 16.7. Formation of geochemical halos around mineralized quartz veins. Vertical lowering of the soil surface, deepening of the weathering front and apparent lateral motion of material upslope or downslope. (Adapted from Leprun, 1979.)

The gold mineralization remains relatively concentrated around the quartz veins in saprolites and lithomarges, but becomes concentrated and scattered in the mottled zone and highly dispersed in the ferricrete. Ferricrete develops together with a relative accumulation of gold and resistant minerals and with apparent mechanical dispersion of these materials. The apparent mechanical dispersions around quartz veins are evidences for a vertical lowering of the lateritic landscapes through time (weathering fronts and soil surface; Figure 16.7).

The mechanical dispersion is also associated with a chemical remobilization. Despite its reputation as an immobile element, several authors have shown that gold may be mobilised in supergene conditions (Krauskopf, 1951; Cloke and Kelly, 1964; Koroleva and Pogregnyak, 1984; Webster, 1986; Machairas, 1970; Evans, 1981; Herail, 1984; Mann, 1984; Webster and Mann, 1984; Wilson, 1984; Stoffregen, 1986). Morphological and geochemical evidence of chemical migrations and neoformations of gold in laterites has been found in the mineralized district of Kangaba, South Mali (Freyssinet et al., 1987). In lateritic profiles, the primary gold flakes associated with quartz structures are mechanically liberated, chemically dispersed and concentrated in the residual ferricrete. The chemical dispersion and concentration include phases of corrosion, dissolution of primary gold and precipitation of secondary gold. In the weathering profile and towards the top, the gold grains are progressively corroded, their size decreases and shapes characteristic of chemical rounding appear. At the same time, secondary gold can be formed in pores of weathered materials, in etch-pits of gold flakes or at the surface of goethite and hematite. Microspherulites of flexuous membranes (0.25 $\mu$m wide), including weathering ferruginous matrix and dendrites, also develop. Secondary gold can also crystallize around the primary etched nuggets and is easily distinguished from pri-

mary gold by its fineness and chemical purity. In fact, primary gold yields between 5 to 9% silver, as well as traces of copper (900 ppm), nickel (300 ppm) and sulfur (200 ppm), while secondary gold is very pure but may include traces of iron, probably inlayed during the secondary crystallization. The chemical dispersion by dissolution-precipitation is evidence that ferricretes require a long time to form.

### Rates of chemical erosion and weathering and of landscape lowering

By taking into account the composition of waters and of hydrological balances, the weathering rates, that is, the lengths of time required to form, for example, 1 m of kaolinite lithomarge and all the associated horizons can be estimated. Results given in Table 16.2 show that 1000 mm of water percolating each year through a profile allows the formation of 1 m of kaolinite lithomarge and consequently allows a lowering of the weathering fronts of 10 m per Myr or 1000 m per 100 Myr. Thus lowering of the landscape since the Cretaceous (100 Myr) may be of the order of several hundreds of metres and at least 1 km (Tardy, 1969, in press; Gac, 1980; Gac and Tardy, 1980).

### Schematic evolution of a ferricrete and bauxite covered landscape

At a landscape scale or at a regional scale, iron or aluminum accumulations as well as soil surfaces and weathering fronts move downwards and mostly vertically. Ferricretes and bauxites are thus lithodependent. However, the lithodependence is not on the rocks presently located below but on the rocks previously located above. Ferricretes and bauxites as well as most lateritic profiles, are relicts or residuals of large amounts of parent rock which has been altered and dissolved over large thickness. Some undissolved resistant minerals (gold or quartz, for example) remaining at the soil surface and later reincorporated in profiles can produce geochemical halos with apparent lateral dispersion of the same order of magnitude as the vertical lowering of the landscape (Figure 16.8).

TABLE 16.2

Rates of chemical weathering of granitic rocks under various climates

| | $HCO_3^-$ (mmoles/kg) | $SiO_2$ $H_2O$ | Rainfall (mm/yr) | Drainage (mm/yr) | $T$ (°C) | Weathering rates | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | (m/Myr) | (km/100 Myr) | (yr/m) |
| Norway | 0.08 | 0.05 | 1200 | 600 | 5 | 3 | 0.3 | 350,000 |
| France | 0.13 | 0.15 | 1200 | 600 | 10 | 8 | 0.8 | 126,000 |
| Chad | 0.89 | 1.42 | 700 | 0 | 32 | 1 | 0.1 | 1,000,000 |
| Centrafica | 0.62 | 0.33 | 1200 | 200 | 26 | 5 | 0.5 | 190,000 |
| Ivory Coast | 0.09 | 0.33 | 1500 | 550 | 25 | 14 | 1.4 | 70,000 |
| Malagasy | 0.10 | 0.16 | 2500 | 1500 | 28 | 33 | 3.3 | 30,000 |

Source: Tardy (1969; in press).
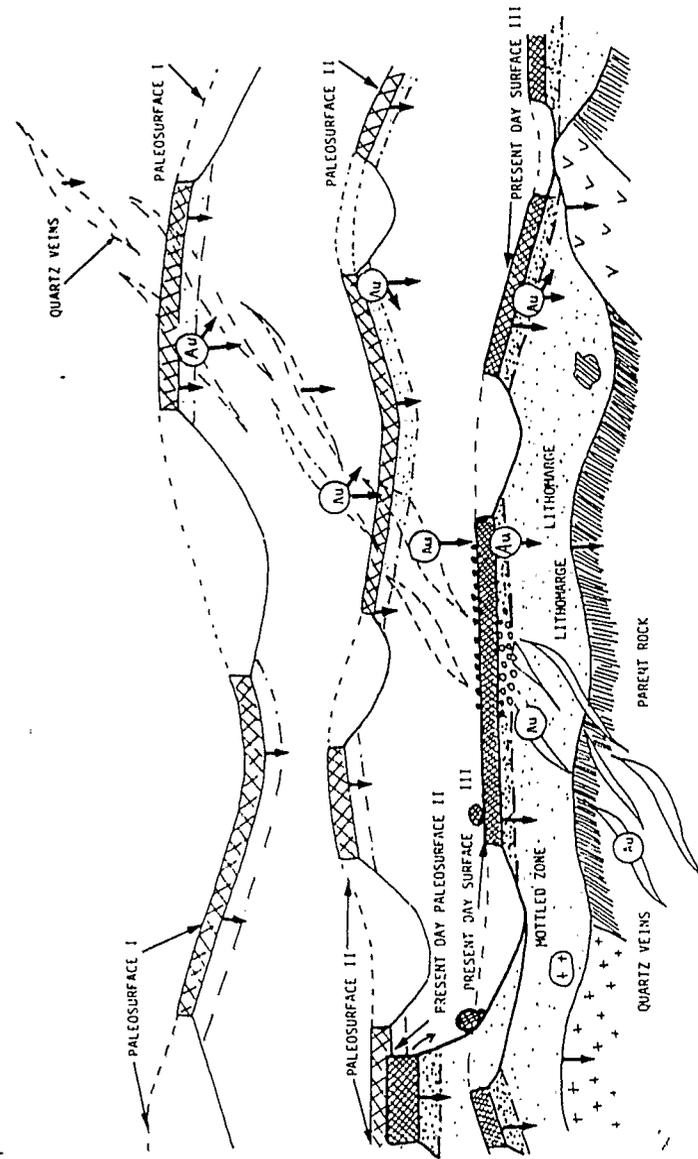
Fig. 16.8. A schematic vertical lowering of a lateritic landscape, as a function of time. As an example, a gold bearing quartz vein crosses the ferricrete surface at 45° so that the lateral superficial dispersion is of the same order of magnitude as the vertical distance, covered by the weathering front.

## Successions of hydrated and dehydrated minerals in lateritic profiles

### Dehydration reactions in Al, Fe and Mn-systems

Lateritic profiles and particularly bauxites, ferricretes and kaolinitic mantles, show successions of horizons more or less indurated and sequences of minerals which are in different hydration states. In the unsaturated zone located above the ground water table, the less hydrated phases are interstratified between two horizons containing more hydrated minerals. This general distribution is explained by seasonal fluctuations of the thermodynamic activity of water within the profiles. Such fluctuations also explains how duricrusts such as ferricretes for example, are formed, conserved or destroyed (Tardy and Novikoff, 1988; Tardy et al., 1988a, b).

In lateritic profiles several sequences of hydrated–dehydrated–hydrated minerals have been observed: gibbsite–kaolinite–gibbsite in Oxisols (Bourgeat, 1972, Delvigne, 1965); goethite–hematite–goethite in ferricretes (Nahon, 1976; Tardy and Nahon, 1985); gibbsite–boehmite–gibbsite in lateritic bauxites (Valeton, 1972; Boulangé, 1984); or even kaolinite—diaspore (boehmite)–gibbsite in karst bauxites (Combes, 1969; Bardossy, 1982). These mineral sequences are not always complete, as given (for example in bauxites). However, the maxima of boehmite, diaspore and sometimes corundum (Medvedev, 1971) always correspond to the maxima of hematite and to the optimal development of ooids and pisoids (Bardossy, 1982). A similar process occurs in manganese duricrusts in which the sequence manganite–pyrolusite–cryptomelane is observed (Weber et al., 1979; Nahon et al., 1984). In ferricretes in which the mechanism of hydration–dehydration–rehydration was demonstrated (Nahon, 1976; Tardy and Nahon, 1985), the optimal induration and accumulation of iron correspond to the zone of nodule formation and to the maximum value of the ratio hematite/goethite. The secondary goethite which appears at the top of the profiles corresponds to a rehydration process which is thought to be responsible for the destruction of the original nodules and for ferricrete dismantling (Nahon, 1976).

Our designation of the label hydrated or dehydrated to a mineral is based on the reactions:

$$2\,FeOOH \ (goethite) = Fe_2O_3 \ (hematite) + H_2O \tag{1}$$

$$MnOOH \ (manganite) + 0.25\,O_2 = MnO_2 \ (pyrolusite) + 0.5\,H_2O \tag{2}$$

$$Al(OH)_3 \ (gibbsite) = AlOOH \ (boehmite) + H_2O \tag{3}$$

$$Al(OH)_3 \ (gibbsite) + H_4SiO_4(aq) = 0.5\,Al_2Si_2O_5(OH)_4 \ (kaolinite) + 2.5\,H_2O \tag{4}$$
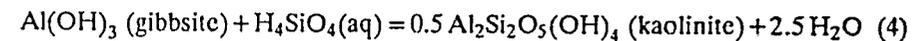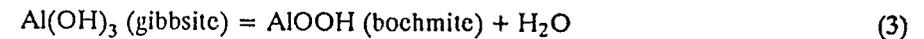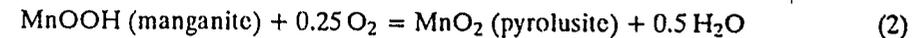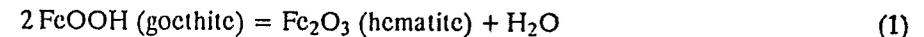
Goethite, manganite and gibbsite are hydrated minerals while hematite, pyrolusite, boehmite and kaolinite are dehydrated minerals. Hydrated minerals appear at the bottoms of profiles close to the ground water table or downslope where the unsatu-

rated domain is reduced in size. They also appear again close to the surface of thick profiles, at the edges of large channels, temporarily hydrated during the wet season. Dehydrated minerals appear in the intermediate part of the unsaturated zone (permanently dryer). They form concretions, almost always accompany induration, and contribute to duricrust-formation. The dehydrated minerals are typically minerals of laterites *sensu stricto* (subject to hardening).

### Gibbsite and kaolinite successions in lateritic profiles

Both weathering of primary minerals and secondary mineral transformation occuring in soils, commonly lead to the exchange of $H_2O$ molecules. For the gibbsite–kaolinite reaction (4) the expression of the equilibrium constant is the following:

$$\log[H_4SiO_4] - 2.5\log[H_2O] = \log K_R \qquad (5)$$

Few studies have dealt with the importance of the thermodynamic activity of water in low $P$–$T$ reactions (Chesworth, 1972, 1975; Bourrié and Pedro, 1979; Mattigod and Kittrick, 1980; Tardy, 1982; Trolard et al., 1986; Trolard and Tardy, 1987, in press), and normally it is taken to be equal to 1. This is equivalent to considering $H_2O$ to be pure liquid water in its standard state. Thus in equation (5) log $[H_2O] = 0$.

In fact both the thermodynamic activities of silica and of water are important in defining equilibrium in reaction (4). When the activity of silica, in solution, decreases, gibbsite may be stabilised relative to kaolinite (Garrels and Christ, 1965; Gardner, 1970). If the activity of water decreases, the stability field of kaolinite enlarges while the gibbsite field is reduced, (Tardy, 1982; Tardy and Novikoff, 1988).

The value which has to be chosen for the equilibrium constant depends on several factors, particularly on the crystal size and the cristallinity of both gibbsite and kaolinite. Fritz and Tardy (1973) chose log $[H_4SiO_4] = -4.5$, at 25°C, in order to take into consideration that in most African soils gibbsite currently forms on basic bedrocks, from which quartz is absent, and rarely develops on granitic or sandstone bedrocks, in which quartz is abundant.

The distribution of gibbsite and kaolinite in lateritic profiles is in fact more complex than usually described in textbooks. Gibbsite, for example, not only forms in the near surface horizon, located above the kaolinitic layer, or in the high parts of the landscapes, but also in the coarse saprolite at the contact with the parent rock, located below a soft kaolinitic layer, and also in the mid-slopes of the landscape relief, downslope from kaolinitic profiles (Figure 16.9). Bauxitic deposits of Amazonia, constantly submitted to an equatorial climate and overlying quartz-rich sandstones, clearly show that gibbsite and quartz can be closely associated without
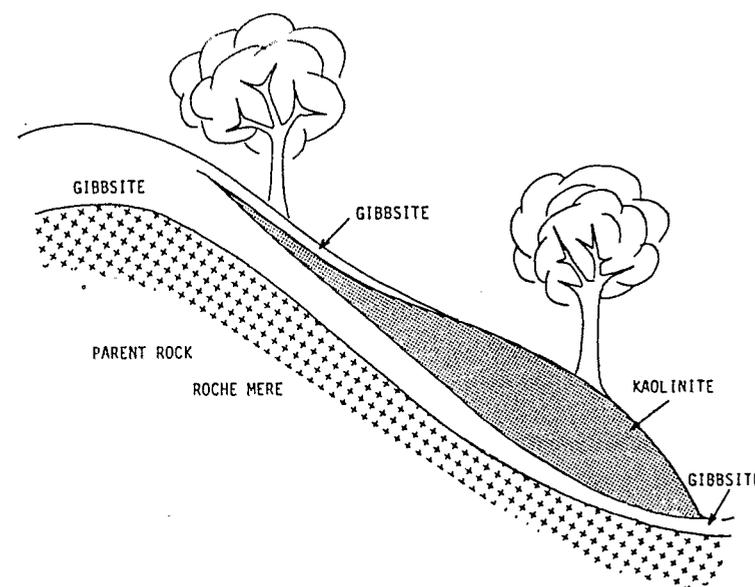
Fig. 16.9. Distribution of gibbsite and kaolinite in lateritic profiles of the Ivory Coast, showing: a. only gibbsite; b. a succession of gibbsite–kaolinite–gibbsite; and c. a succession of kaolinite–gibbsite from top to bottom of the profiles and from upslope to downslope on the landscapes (after Delvigne, 1965).

forming kaolinite (Lucas, 1989). From this, we suppose that, under permanently humid conditions, gibbsite and quartz may be more stable than kaolinite, while under a dryer climate kaolinite is more stable than the gibbsite-quartz association. If log $[H_4SiO_4] - 2.5$ log $[H_2O] = -3.952$, at 25°C, and if the activity of water $[H_2O] = 1$, quartz and gibbsite are stable together. When the activity of water decreases and becomes lower than $[H_2O] < 0.8$, kaolinite is more stable than gibbsite and quartz.

### Climatic and hydrostatic factors governing the thermodynamic activity of water in lateritic profiles

The activity of water, written as $a_w$ or $[H_2O]$, is a dimensionless number which express how much a given state of capillary water ($a_w < 1$) is different from the standard state of the pure liquid and free water ($a_w = [H_2O] = 1$). By convention water in its standard state is a pure water at the pressure of 1 bar.

The difference between energies of water located in a pore either behind a planar interface ($P = 1$ bar in both sides, in air and in water; $a_w = 1$) or a curved interface ($P = 1$ bar, in air; $P < 1$ bar, in water; $a_w < 1$) is also equal to the difference of the chemical potentials characterizing water in the two situations (at $P = 1$ bar and at $P < 1$ bar). Furthermore, the difference of the two chemical potentials is,

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by a definition, a function of the activity of water; the activity of water is also equal to $p/p°$, the ratio of the partial water pressures in the dry air and in the saturated air, respectively (Hillel, 1971). This energy difference of water trapped behind a meniscus, the radius of which is equal to $r$, is also equal to that required to elevate one mole of water to a capillary height $h_c$, so that:

$$\mu_w - \mu°_w = RT \ln a_w = RT \ln p/p° = V\Delta P = -2\sigma\frac{V}{r} = -\rho g V h_c$$

in which $V$ stands for the molar volume of water, $\sigma$ for the interfacial tension, $\rho$ for the water density and $g$ for the gravitational field.

In a porous medium in which hydration and dehydration processes take place, the activity of water is controlled by capillarity. At the equilibrium between humid air and capillary water: the lower the ground water level, the higher the capillary height, the smaller the radius of the menisci, the smaller the radius of pores in which water is trapped, the smaller the relative humidity of the air, the smaller the chemical potential of water, the smaller the water activity and the more the capillary water environment leads to dehydration of the minerals.

Hydrological factors play an important role in determining mineralogical sequences in the deep and thick lateritic profiles (Lelong and Lemoine, 1968; Degallier, 1975; Toulemont, 1984; Valles, 1986). In the unsaturated zone of such profiles, water activity fluctuates during the year as a function of depth, between the ground water level ($[H_2O] = 1$) and the soil surface where activity is most of the time lower than one ($[H_2O] < 1$). Remarkably, a minimum in water activity at about 1 to 5 m depth, is possible, where prevailing conditions are drier than in the lower horizons (close to the water table) throughout the year, and also drier than in the surface horizon during the wet season (Vachaud et al., 1978; Vauclin and Vachaud, 1981; Imbernon, 1981; Vauclin, 1982; Figure 16.10). During the dry season dehydration takes place at the surface and in this hydric hollow. During the wet season the quasi-saturation of the surface horizons acts in favour of rehydration of the minerals previously dehydrated during the dry season. This rehydration takes place only in pores and voids of large size where the thermodynamic activity of water was previously high. In the small-size pores the activity of water remains small. The hydric hollow region in which dehydration takes place almost permanently is the most probable location for induration and nodule formation and therefore for the production of ferricretes or other duricusts. Its depth and its thickness is primarily dependant on the dryness of the climate and on the depth of the ground water table.

The thermodynamic activity of water is closely correlated with climatic and hydrostatic factors which both characterize the physical state of water in the unsaturated zone located above the ground water table. At the piezometric level, water activity is by definition equal to one ($[H_2O] = 1$). Above the piezometric water level, water activity is smaller than one ($[H_2O] < 1$) and dehydration reactions take place
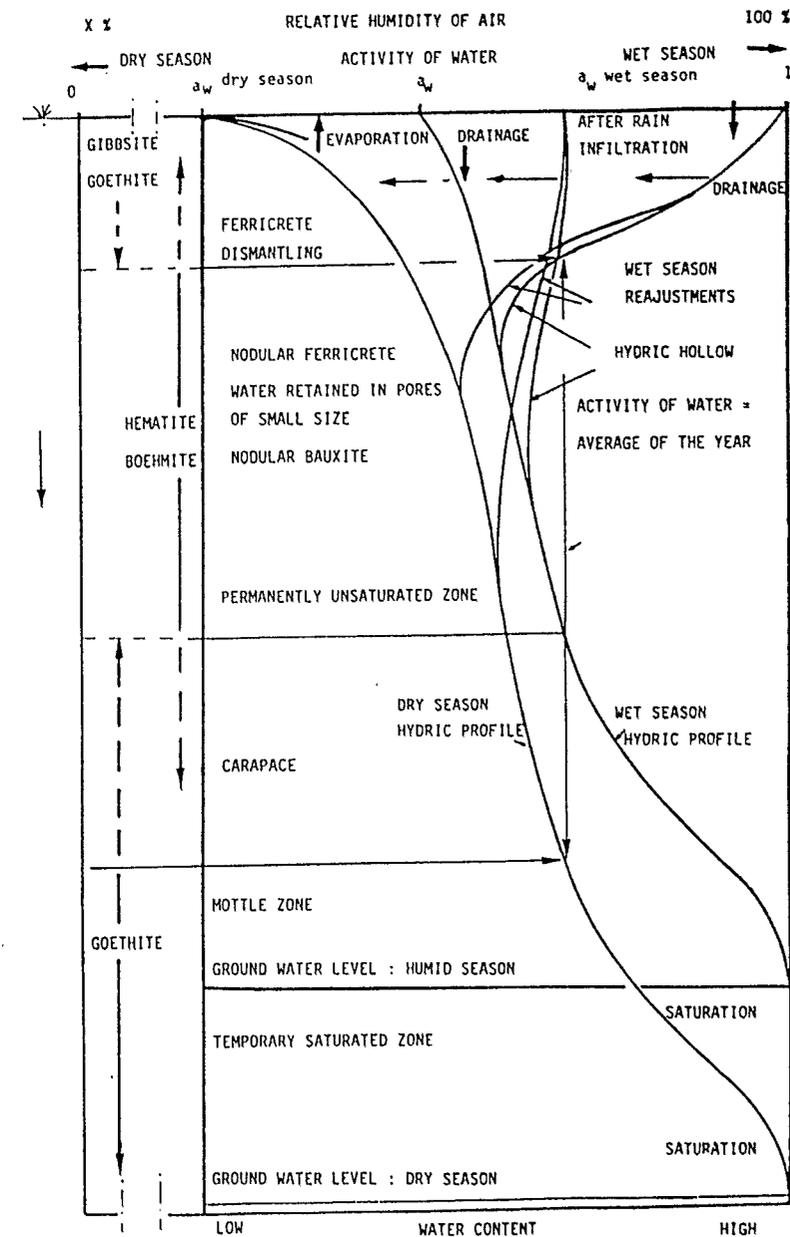
Fig. 16.10. Seasonal distribution of water activity across a weathering profile, in a non-equilibrium situation, above a deep ground water level (10 m) (after Tardy et al., 1988a).

(Hillel, 1971; Tardy and Nahon, 1985; Trolard and Tardy, 1987; Tardy and Novikoff, 1988; Tardy et al., 1988a).

## Chemical composition and climatic distribution of goethite and hematite in soil profiles and landscapes

Schwertmann (1988) analyzed occurence and formation of iron oxides in various pedoenvironments. In weathering profiles, the ratio of hematite to hematite plus goethite [Hm/(Hm + Go)] is controlled by temperature, humidity of the soil atmosphere, pH, organic matter content, altitude and latitude.

### Temperature

The ratio Hm/(Hm + Go) formed from ferrihydrite increases with temperature (from 4° to 25°C) at which the system is aging. Besides temperature, pH also has a strong effect (Schwertmann, 1988). In Oxisols, Ultisols and Inceptisols of Brazil, the proportion of hematite (Hm) compared to goethite increases with increasing mean annual air temperature (Kämpf and Schwertmann, 1983). In the northern hemisphere, a line drawn at approximately 40°N latitude separates soils without hematite (North) from soils with hematite (South) (Figure 16.1; Schwertmann, 1988).

### Relative humidity of the soil atmosphere

The relative humidity of the soil atmosphere at the contact of which hematite and goethite form is controlled by soil moisture at a profile scale or at a landscape scale, and by the difference between rainfall and evaporation. The effect of relative humidity (RH) on the crystallization of hematite and goethite from synthetic ferrihydrite is shown by Torrent et al. (1982). Amounts of hematite and goethite both decrease, but Hm/(Hm + Go) increases when the relative humidity of the air decreases.

On a landscape scale, soils have generally less hematite, yield more goethite and become yellower and less red with increasing wetness downslope (Curi and Franzmeier, 1984; Adams and Kassim, 1984; Schwertmann, 1988). Red ferrallitic soils, rich in hematite and formed of kaolinite–hematite micronodules are generally located upslope, in well drained conditions, while yellow ferrallitic soils rich in goethite are located downslope where the water table is higher in the profile (Chauvel, 1977; Chauvel and Pedro, 1978; Muller, 1987).

On a regional scale, in Southern Brazil for example, goethite is more abundant in soils subjected to an excess of rainfall over evapotranspiration (Kämpf and Schwertmann, 1983).

### pH and organic carbon content

With regards to hematite–goethite formation, pH and organic carbon content of soils are typical kinetic factors. A decrease of pH below 8, and an increase of organic carbon both act in favour of goethite instead of hematite (Schwertmann, 1965; 1988).

Correlating the ratio Hm/(Hm + Go) with such factors as temperature, relative humidity, latitude, elevation, pH and organic matter content yields interesting results. Some of these factors, for example altitude (elevation) or latitude, include the effect of temperature and moisture. Furthermore, on a regional scale, some parameters such as soil pH and organic matter content are closely related to rainfall. Therefore, it is difficult to separate their specific influence. Soil temperature is regulated by climatic factors such as latitude, altitude and continentality. The relative humidity of the soil atmosphere, that is, the thermodynamic activity of water, is controlled by rainfall, evaporation, permeability, pore size, and depth to the ground water table.

If pH and organic matter are typically kinetic parameters, temperature and activity of water are both thermodynamic factors which have to be taken into account as well. In fact, the mass action law applied to the equilibrium hematite–goethite, yields:

$$FeO_{1.5}(\text{hematite}) + 0.5\,H_2O\,(\text{water}) = FeOOH\,(\text{goethite})$$
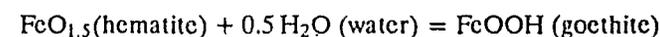
$$K(T) = \frac{[FeOOH]}{[FeO_{1.5}]\,[H_2O]^{0.5}}$$

The mass action law constant, $K(T)$, is a function of temperature, and the equilibrium conditions are chiefly dependent on the activity of water ($a_w = [H_2O]$). However, hematite–goethite equilibria are also regulated by the activity of the two solid phases: [FeOOH] for goethite and [FeO_{1.5}] for hematite. Solid phase activities are determined by three conditions which have to be taken into consideration separately: purity, chemical composition (aluminum content) and grain size. Thus solid phase activities are dependent on both thermodynamic and kinetic parameters.

Berner (1969), reviewing the stability conditions of hematite in water, has pointed out that although hematite is more stable than goethite, kinetic phenomena may be the reason for the non-spontaneous formation of hematite. Langmuir (1969) is in agreement with Berner's view (1969) that fine-grained goethite is thermodynamically unstable relative to well crystallized hematite. Later, Schwertmann and Taylor (1977) and Kämpf and Schwertmann (1983) also indicated that kinetics is the major factor that governs the rate of dissolution or precipitation of the iron oxides and oxyhydroxides. However, natural observations made on ferricretes suggest that beside the kinetic interpretation, the distribution of goethite and hematite and their Al-content variations can be understood in terms of thermodynamically metastable

equilibria, in which not only the size of the grains but also the temperature and the chemical potential of water are involved.

### Distribution of Al-hematite and Al-goethite in laterites

Tardy and Nahon (1985) and Trolard and Tardy (1987, in press) have reviewed the abundant litterature devoted to Al-goethite, Al-hematite and $Fe^{3+}$-kaolinite distribution in laterites.

The aluminum contents of goethite and hematite should be regarded as a function of the nature of other minerals with which they are associated. In goethites of red soils, the substitution rates diminish when the climate becomes less humid and percolating solutions are richer in silica (Tardy, 1971). This is probably due to the presence of kaolinite which controls the chemical composition of the solution (Trolard and Tardy, in press).

Compositions range from 2 to 20 mole percent of AlO(OH) in goethites of ferricretes and other soils in which kaolinite is present. Compositions range from 18 to 27 mole percent in goethites associated with gibbsite in bauxites. Thus, the substitution rate of AlO(OH) into FeO(OH) is lower in ferricretes than in bauxites, as generally admitted by Nahon (1976), Nahon et al. (1977) and Leprun (1979), in laterites of Senegal and Ivory Coast. Hematite generally has less substitution than goethite and both are less aluminous when kaolinite and quartz are present than when gibbsite forms.

Obviously, the aluminum contents of goethites and hematites are controlled by the activity of aluminum in solution which in turn is determined by the solubility of aluminous minerals, that is gibbsite and kaolinite. It turns out that the relative stability fields of goethite and hematite may depend on their degree of Al-substitution which is dependent on the stability of the other aluminous minerals with which they are associated. The conditions of formation of goethite and hematite may be ultimately determined by the activity of silica in solution and by the activity of water in pores in which these minerals form.

### Thermodynamic stability field of Al-goethite and Al-hematite

Stability fields of Al-goethite and Al-hematite, gibbsite, boehmite and kaolinite can be considered to be a function of particle size, temperature and the thermodynamic activity of water (Trolard, 1988; Trolard and Tardy, 1987, 1989).

In ferricretes or in synthetic samples, the particle sizes of Al-goethite crystals commonly range from 100 to 400 Å, while those of Al-hematite range from 40 to 400 Å (Schwertmann, 1965; Langmuir, 1969, 1971; Langmuir and Whittemore, 1971; Amouric et al., 1986; Koch et al., 1986).

### Stability diagrams

For a given temperature, $T$, and according to the equilibrium conditions expressed earlier, stability diagrams are constructed as a function of the aluminum content and water activity. Five simplified diagrams are given in Figure 16.11 for 5°, 15°, 40°, 55° and 80°C. When temperature decreases, several modifications are observed. The stability field of the association of Al-hematite and boehmite is reduced. The stability field of the association of the Al-goethite and gibbsite becomes larger. For a given composition and a given water activity, the Al-substitution in Al-goethite associated with gibbsite decreases. When temperature increases the contrary is observed. The stability field of Al-goethite is reduced, gibbsite disappears near 40°C and is replaced by boehmite; the stability field of Al-hematite is enhanced; at about 75°C, Al-goethite disappears.

For a constant water activity ([$H_2O$] = 1, for example) and for a given composition [$Al_2O_3/(Fe_2O_3 + Al_2O_3)$] the degree of substitution of diaspore in Al-goethite, when Al-goethite is associated with gibbsite, increases with temperature. The degree of substitution of corundum in Al-hematite also increases with temperature. These variations are represented in Figure 16.12.
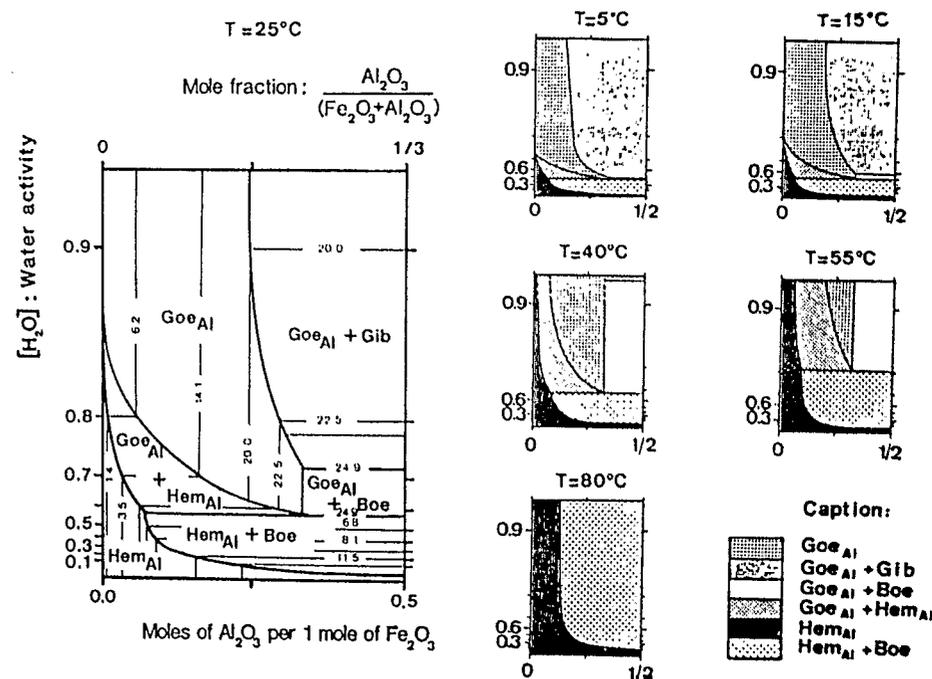


Fig. 16.11. Stability diagrams for Al-goethite, Al-hematite, gibbsite and boehmite at 25°C and at different temperatures as a function of water activity (from Trolard and Tardy, 1987).
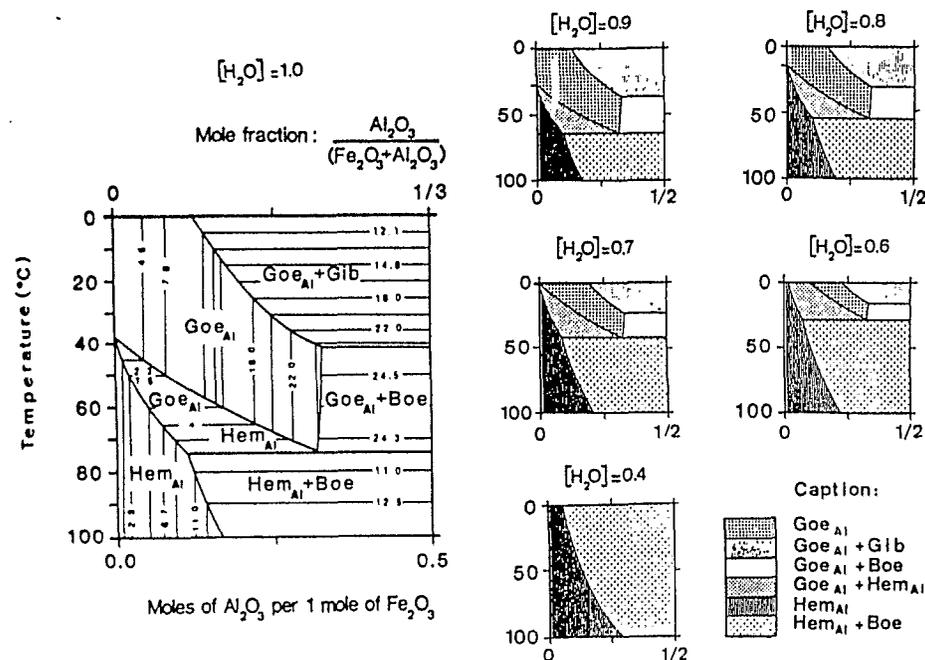
Fig. 16.12. Stability diagrams for Al-goethite, Al-hematite, gibbsite and boehmite at [H₂O] = 1 and at different activity of water, as function of temperature (from Trolard and Tardy, 1987).

Figures 16.11 and 16.12 show that an increase in temperature and a decrease in water activity, have qualitatively similar effects on the stability fields. This is because the entropy and the heat capacity of water in gibbsite ($Al_2O_3.3\ H_2O$), goethite ($Fe_2O_3.H_2O$) and boehmite ($Al_2O_3.H_2O$) are smaller than those characterizing liquid water.

## Conclusions

It is clear that the chemical potential of water plays a major role in the transformation of gibbsite into boehmite, as already pointed out by Chesworth (1972), for the transformation of boehmite into corundum at low temperature (Bardossy, 1982) and for the transformation of goethite into hematite (Tardy and Nahon, 1985).

Equilibrium diagrams show the conditions of formation of Al-goethites, Al-hematites, gibbsite and boehmite in laterites, bauxites and ferricretes. The stability fields of the various associations are presented in terms of the thermodynamic activity of water, temperature and particle size. The diagrams allow for substitutions of Al for Fe in goethite and hematite and we have regarded these solid solutions as ideal.

The fact that an ideal solid solution must extend continuously from one member to the other is masked in the diagram by the appearance of other stability fields which partly overlap the solid solution fields of AlOOH–FeOOH and $Al_2O_3$–$Fe_2O_3$. The assumptions of ideal solid solutions leads to the prediction of composition limits for Al-goethites (<30%, mole fraction of diaspore) and Al-hematites (<15%, mole fraction of corundum) which agree very well with Al-contents of natural associations as reviewed by Tardy and Nahon (1985).

In summary, the stability diagrams based on activity of water and temperature permit the following conclusions.

(a) Dehydration transformations of the type: goethite → hematite; gibbsite → boehmite → corundum; or gibbsite → kaolinite, can be promoted by a decrease in the thermodynamic activity of water (at constant $T$), by an increase in temperature (at constant $a_w$) or by $a_w$ decreasing and $T$ increasing simultaneously.

(b) A decrease in water activity has a similar effect to an increase in temperature. The successions of mineral phases and parageneses are similar in both cases: (1) Al-goethite → Al-goethite + Al-hematite → Al-hematite, for systems of low aluminum content, and (2) Al-goethite + gibbsite → Al-goethite + boehmite → Al-hematite → (Fe-corundum), for systems of high aluminum content.

(c) When minerals are in association such as (Al-goethite + gibbsite) or (Al-goethite + Al-hematite), the Al-goethite or Al-hematite compositions do not depend on the composition of the system but only on water activity or temperature. The aluminum contents increase as water activity decreases or temperature increases.

(d) When Al-goethite and boehmite are stable together, the Al-goethite composition does not depend on the composition of the system nor on temperature and water activity. It is remarkable that, in this case, the aluminum content of goethite is almost fixed [for example, $(Al_{0.25}\ Fe_{0.755})OOH$ at 25°C]. The same considerations are valid for the association of hematite and corundum.

(e) When only Al-goethite or Al-hematite are stable, their aluminum content depends neither on water activity nor on temperature. The Al-goethite and Al-hematite compositions depend only on the ratio of $Al_2O_3/(Al_2O_3 + Fe_2O_3)$ in the system.

(f) The stability field of kaolinite in the presence of gibbsite or boehmite is dependent both on activity of water and activity of silica. At 25°C and 100 kPa total pressure, if the silica activity is lower than $10^{-4.57}$, kaolinite is not stable whatever the activity of water. In the dissolved silica activity interval [$10^{-4.57}$ to $10^{-4.50}$] gibbsite, then kaolinite and finally boehmite can be stabilized, successively, when the water activity decreases. In the interval [$10^{-4.5}$ to $10^{-4.0}$] only kaolinite and boehmite are stable. For a decreasing water activity, the stability field of boehmite progressively overlaps the kaolinite domain (Trolard and Tardy, 1989).

(g) The presence of kaolinite instead of gibbsite and boehmite in soils or weathering profiles should promote changes in the Al-content of aluminous goethite, as the

equilibrium with kaolinite decreases when water activity or silica activity increases. This may explain why, in general, goethites are poorer in aluminum downslope, in lowlands and in hydromorphic soils compared to Ultisols or Oxisols located at the top of profiles or in high landscape situations where the aqueous pore solutions are depleted in silica.

(h) The iron content in kaolinite is shown to be dependent on the water activity and on dissolved silica activity. An increase of water activity at a fixed silica activity or an increase of silica activity at a fixed water activity should induce an increase of iron relative to aluminum in the ferruginous kaolinite. However, the dominant factor which probably controls the iron content in ferruginous kaolinite is its solubility related to its crystallinity which generally decreases from the bottom to the top of the profiles: the lower the crystallinity, the higher the solubility and consequently the higher the iron-content in ferruginous kaolinite.

Clearly the chemical composition of goethite, hematite and kaolinite are controlled by equilibrium with other phases present in the system, by silica activity regulated by the rate of percolating waters, by temperature and by the activity of water which is a function of climatic and regional drainage conditions.

## Periatlantic climates and paleoclimates; the role of temperature and water activity in the distribution and mineralogical composition of bauxites and ferricretes

Since the Jurassic, parts of the Brazilian and the African shields have been subjected to either equatorial, humid tropical, or arid tropical climates. Both are covered by a thick and widely distributed lateritic mantle, the age, the nature and the mineralogical composition of which varies from one region to another. Bauxites form under hot and humid equatorial climates (25°C and rainfall > 1800 mm per year), while ferricretes develop under seasonally contrasted tropical climates (30°C and rainfall between 1300 and 1700 mm per year). Since the Jurassic and the opening of the Atlantic ocean, Africa and America have been moving northwards and equator and tropics have been shifted southwards. Consequently the surface of the periatlantic continents were covered by laterites of different kinds and of different ages (Figures 16.13 and 16.14).

In the southern hemisphere, and particularly in Brazil and in South- and South-East Africa, ferricretes are not widely distributed, but bauxites are abundant and widely developed.

Ferricretes are not widely distributed, either because they were previously formed under contrasted tropical climates and later dismantled under equatorial climates or because paleoclimates were never sufficiently hot and contrasted or because contrasted paleoclimates did not operate during a long enough time (Tardy et al., 1988b). In Brazil for example, scattered hematitic ferricretes were described in the
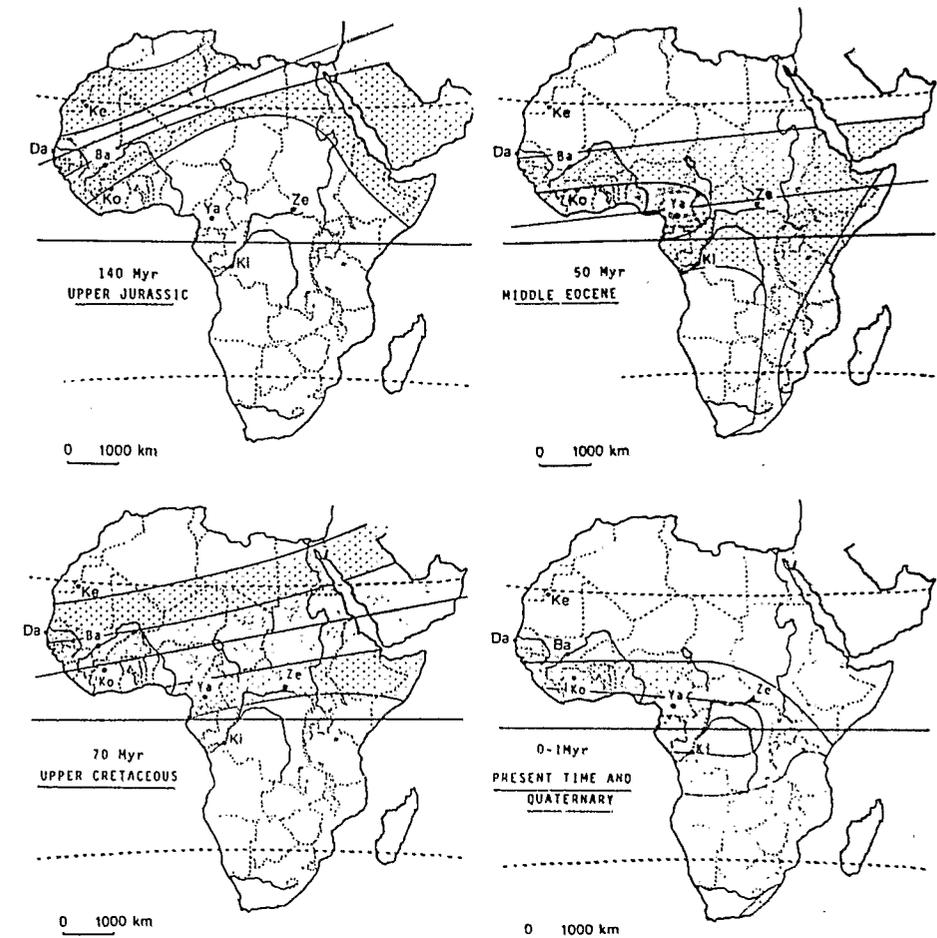
Fig. 16.13. Paleoclimatic potential distribution of bauxites (dark shadowed) in equatorial domains of ferricretes (light shadowed) in contrasted tropical zones of Africa (from Parrish et al., 1982, and after Kobilsek, 1989).

Nordeste, Goias and Matto Grosso and seem to be preserved in these semi-humid regions. Ferricretes also outcrop in several parts of Amazonia but appear to have been dismantled under the rain forest equatorial climate (Melfi et al., 1979; Tardy et al., 1988b; Nahon et al., 1989).

Ferricretes are also present in South Africa (Milnes et al., 1987; Milnes and Fitzpatrick, 1987; Fitzpatrick, 1988). However, they have not the same extent and the same development as in the northern hemisphere. Particularly in western and central Africa, hematitic nodular or pisolitic ferricretes are widely developed (Maignien, 1958; Michel, 1973; Nahon, 1976; McFarlane, 1976; Leprun, 1979; Petit,
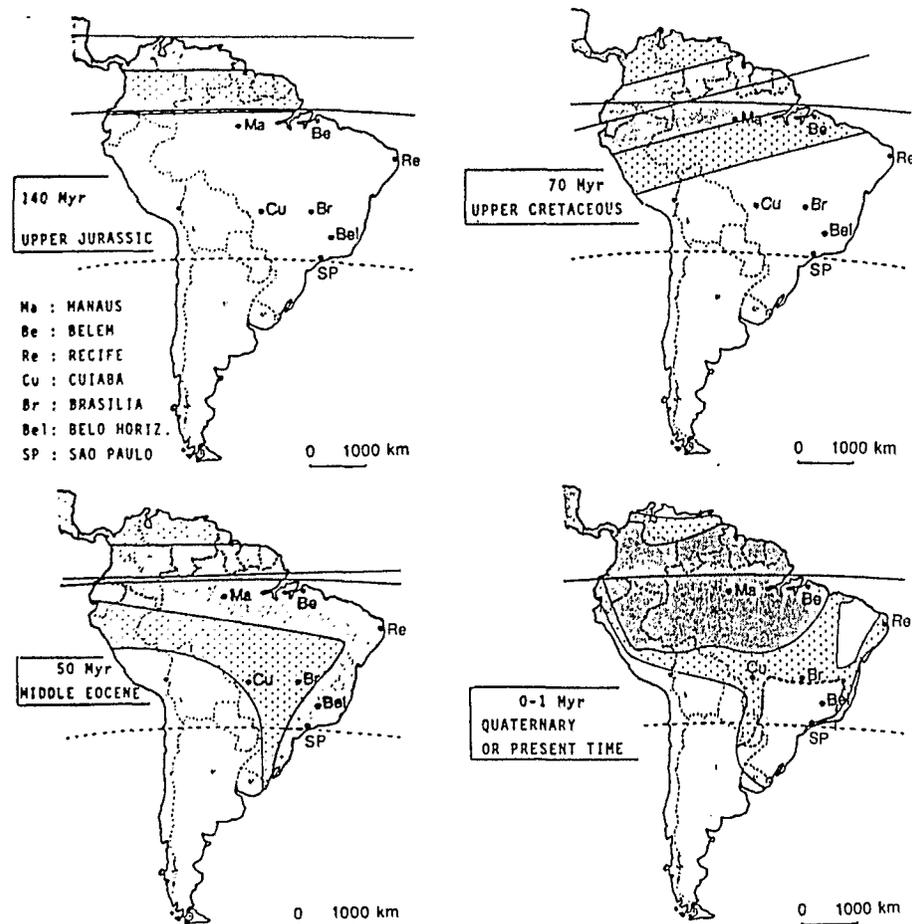
Fig. 16.14. Paleoclimatic potential distribution of bauxites (dark shadowed) in equatorial domains of ferricretes (light shadowed) in contrasted tropical zones of South-America (from Parrish et al., 1982, and after Kobilsek, 1989).

1985). Bauxites are widespread in Guinea, Ivory Coast, Nigeria and Cameroon. Some bauxites are very old and seem to have been formed since the Jurassic and through the Cretaceous and the Eocene in near equatorial conditions (Michel, 1973; Boulangé et al., 1973; Hieronymus, 1973; Boulangé, 1984; Valeton and Beissner, 1986; Figures 16.13 and 16.14). In South America bauxites may be very old (Jurassic) or younger (Miocene) (Weber, 1959; Dennen and Norton, 1977; Aleva, 1981; Truckenbrodt and Kotschoubey, 1981; Kronberg et al., 1982; Groke et al., 1982; Melfi and Carvalho, 1983; Lemos and Villas, 1983; Trescases and Melfi, 1985); in South-East Africa, they are reported to be essentially Eocene (Grubb, 1973, 1979;

Parrish and Curtis, 1982; Parrish et al., 1982; Fitzpatrick, 1983, 1988; Patterson et al., 1986). In both cases, for a million years climates have been continuously humid and paleoclimates have been evolving from arid to humid (Figure 16.15; Tardy et al., 1988b). In both cases, bauxites are dominantly gibbsitic and generally show massive structures with no pisolite development nor boehmite formation.

The remaining old bauxitic laterites which are abundant in Mali and in Burkina Faso located at the edges of Sahara yield mainly gibbsite but also some boehmite (Balkay and Bardossy, 1967), formed later together with a secondary development of pisolites. In these regions, probably at the end of the Eocene or since the Miocene, under contrasted tropical climates, gibbsitic bauxites ceased to form and hematitic and kaolinitic ferricretes began to develop. The secondary formation of boehmite and pisolites in bauxite is probably contemporaneous with the extension of the ferricrete, occuring when equatorial climates were replaced by tropical, as the Sahara progressively moves southwards (Tardy et al., 1988b). Thus on a continental scale, regions in which gibbsitic bauxites were formed continuously or over a long period of time do not show a wide development of ferricretes, while those which exhibit boehmitic and pisolitic bauxites are covered by a large mantle of surficial iron accumulation. This is particularly the case in western and central Africa, where ferricrete may have been formed since the end of the Cretaceous (McFarlane, 1976; Tardy et al, 1988).

In the present-day equatorial regions covered by rain forest, gibbsitic and goethitic soils are now forming. However, ferricretes that are being dismantled also outcrop (Novikoff, 1974; Volkoff, 1985). It is clear that some, if not all, of the hematitic nodular red soils or nodular stone lines may result from a secondary transformation of ancient ferricretes formed earlier under seasonally contrasted climates and presently submitted to humid equatorial conditions. This is clearly the case in a large part of the Congo and the Amazon basins (Nahon et al., 1989).

Earlier it was demonstrated that the relative stability of goethite compared to hematite, and gibbsite compared to boehmite, is controlled by two thermodynamic and climatic factors, that is, temperature ($T$) and water activity ($a_w$). Thermodynamic activity of water is a parameter equivalent to the relative humidity of the air [$a_w = p/p° = 100HR$ (%)] which characterizes the dryness or the humidity of the climates. Both an increase of temperature and a decrease of the water activity, can lead to the formation in laterites, of dehydrated minerals instead of gibbsite [$Al(OH)_3$] (Tardy and Nahon, 1985; Trolard and Tardy, 1987). Consequently, tropical climates such as those prevailing south of the Sahara, and characterized by a mean annual temperature of about 30°C and by a dry season of several months during which the relative humidity of the air becomes lower than 70%, encourage the formation of hematite and kaolinite in iron accumulations and of secondary boehmite in gibbsitic bauxites, previously formed.

During the last 100 Myr and due to the slow drift of continents, climatic zones have progressively shifted. During the Jurassic, the equator was located in what is
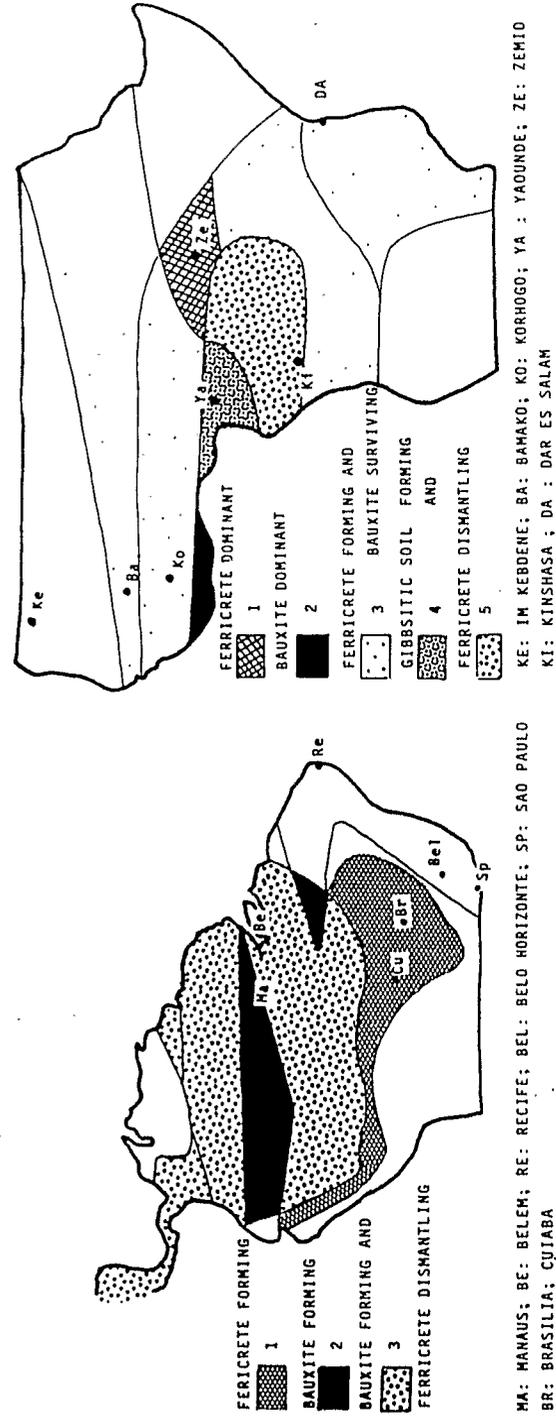
Fig. 16.15. Paleoclimates and succession of potential lateritic domains in Brazil and in Africa. 1: Domain submitted to contrasted tropical climate and probably continuously covered by ferricretes since Cretaceous (100 Myr) or Eocene (50 Myr). 2: Exclusively bauxites: equatorial domain covered by bauxites since Cretaceous (100 Myr). 3: Bauxite transformation and ferricrete formation domain previously submitted to equatorial climate and later exposed to contrasted tropical climates; previously covered by bauxites and later by ferricretes. 4: Ferricrete dismantling and bauxite formation, in domains previously covered by ferricretes and currently evolving under the rainforest equatorial climates.

MA: MANAUS; BE: BELEM; RE: RECIFE; BEL: BELO HORIZONTE; SP: SAO PAULO
BR: BRASILIA; CUIABA

FERRICRETE FORMING — 1
BAUXITE FORMING — 2
BAUXITE FORMING AND FERRICRETE DISMANTLING — 3

KE: IM KEBDENE; BA: BAMAKO; KO: KORHOGO; YA : YAOUNDE; ZE: ZEMIO
KI: KINSHASA; DA : DAR ES SALAM

FERRICRETE DOMINANT — 1
BAUXITE DOMINANT — 2
FERRICRETE FORMING AND BAUXITE SURVIVING — 3
GIBBSITIC SOIL FORMING AND FERRICRETE DISMANTLING — 4
FERRICRETE DISMANTLING — 5

now Mauretania and Northern Venezuela. Then Africa rotated and the two continents were displaced northwards, shifting the equator southwards (Parrish et al., 1982). Both Brazil and southeast Africa, initially more arid, have become progressively more humid. By contrast, west and central Africa, more humid to begin with, later became dryer and less humid. Western and central Africa on one hand, and southeast Africa and central Brazil on the other, during the Cretaceous and the Tertiary, were subjected to climates which, independently of global fluctuations, have been changing in an opposite way. Consequently, some climatic contrasts, which today separate the first from the second group of continental regions, might have also operated in the past.

Finally, the spatial and temporal distribution as well as the observed mineralogical composition of bauxites and ferricretes, in Brazil and in Africa, not only result from the diversity of the present-day climates but also reflect the paleoclimatic evolution which took place since the latest Jurassic and the opening of the Atlantic.

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