Structural characteristics of hematite and goethite and their relationships with kaolinite in a laterite from Cameroon. A TEM study.

by Micheline BOUDEULLE* and Jean-Pierre MULLER**

* Laboratoire de Minéralogie-Cristallographie, UA C.N.R.S. 805, Université Claude Bernard - Lyon I
43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.

** ORSTOM, UR Pétrologie de la Surface and Laboratoire de Minéralogie-Cristallographie, UA C.N.R.S. 09,
Universités Paris VI et VII, 4, place Jussieu, 75252 Paris Cedex 05, France.

Abstract. — TEM investigations on goethite and hematite associated with kaolinite in lateritic weathering profiles (Cameroon) have shown : (1) the variability of goethite habit, in contrast to hematite, according to sampling locality, (2) the occurrence of intermediate phases, primary or resulting from a topotactic transformation of hematite into goethite, (3) intergrowths of hematite and goethite, and (4) epitaxy of goethite upon kaolinite.

These data are discussed in terms of growth and genetic relationships between minerals (mineral development and relative stability). Petrological implications are considered.

Key-words : hematite, goethite, kaolinite, TEM, growth.

Caractérisation structurale des hématites et goethites d'une latérite (Cameroun) et étude de leurs relations avec la kaolinite. (Microscopie et diffraction électroniques).

Résumé. — Une étude en microscopie et diffraction électroniques a été réalisée sur des échantillons de goethite et d'hématite, associées aux kaolinites, prélevés le long de profils d'altération latéritique (Cameroun). La morphologie de la goethite varie suivant le site de développement, au contraire de celle de l'hématite. Des phases intermédiaires entre ces deux minéraux, soit natives, soit résultant d'une transformation topotactique hématite-goethite ont été identifiées. Des surcroissances de goethite sur hématite et l'épitaxie de la goethite sur la kaolinite ont été observées.

Ces résultats sont discutés en termes de mode de développement, de stabilité et de relations génétiques entre les minéraux. Des implications pétrologiques en sont tirées.

Mots-clés : hématite, goethite, kaolinite, microscopie et diffraction électroniques, croissance.

I. INTRODUCTION

Iron oxy-hydroxides, hematite and goethite, are with kaolinite the main mineral components of laterite. A better understanding of lateritisation processes implies a reconstitution of secondary mineral nucleation and growth conditions and the determination of their stability fields.

Various morphologies, texture and spatial arrangements of hematitic and goethitic materials have been described in numerous field and petrographic studies of metric profiles (see references in Bocquier *et al.*, 1984). Thermodynamic and kinetic modelling, together with laboratory experiments, have attempted to afford global valuable interpretations of the facts (Schwertmann and Taylor, 1977 ; Tardy and Nahon, 1985).

However, at the same time, independent data on the crystallinity (and/or particle sizes) (Kühnel *et al.*, 1975) and Al/Fe substitutions in natural samples, obtained by X-Ray diffractometry (Schulze and Schwertmann, 1984 ; Schwertmann and Latham, 1986), I.R. (Cambier, 1986), ESR (Pinnavaia, 1981) and Mössbauer (Coey, 1980) spectroscopies, emphasized the variability of their structural characters. These characters reflect the initial weathering conditions, but depend also on the subsequent and continuing processes of dissolution and crystallization which have affected the materials (Muller, 1987*a*).

Deciphering the part of each phenomenon implies combined studies at different scales : Transmission electron microscopy (CTEM and HRTM) and diffraction, coupled with *in situ*

chemical analyses (EDS), allows morphological and crystal chemical characterizations of particles and aggregates at the micrometre scale (Greenland *et al.*, 1968 ; Felipe-Morales and Russel, 1972 ; Jones *et al.*, 1982 ; Fordham *et al.*, 1984 ; Amouric *et al.*, 1986).

The present paper reports results of investigations carried out on petrographically well defined samples from Cameroon (Muller, 1987*a*), in order to get more informations about hematite and goethite geneses and their interrelationships with kaolinite.

II. GENERAL LITHOLOGY AND MATERIALS

The studied samples come from a soil toposequence in the Central East Cameroon (Muller, 1987*b*). In the upper zone of the toposequence, the vertical profiles exhibit, from the bottom to the top, three main zones (Figure 1A) :

(1) A *lower weathering zone or saprolite*. The weathering products preserve the original texture and structure of the rock (gneiss). The mineralogical heterogeneity of the rock is evidenced on the centimetre scale through the alternating whitish layers, with dominant kaolinites and quartz, and iron-coloured red layers. This horizon has a loose consistency.

(2) An *intermediate nodular zone*, in which two great types of indurated nodules are distinguished : (i) large and red lithorelictual ferruginous nodules with a more or less preserved rock structure and texture, and (ii) small and red argillomorphous nodules, with a soil texture, becoming more abundant from the bottom to the top of the zone. The internodular matrices have the same general characters as the ferruginous matrices of the upper zone.

(3) An *upper loose clayey zone* with a soil texture, showing upwards a gradual transition from red (mainly hematitic) to yellow (goethitic) matrices, the red one often appearing as non-indurated nodules within the yellow one.

Seven great types of representative materials have been sampled along weathering profiles (Figure 1A) and characterized.

III. METHODS

The studied samples have been drilled from optically selected materials. Parts were powdered by gentle grinding in agate mortar, in order to record XRD patterns (Figure 1B) using a Philips PW 1730 vertical goniometer with a back monochromator and CuKα radiation. Drops of powder suspensions in methanol were air dried on carbon coated grids. Other parts have been embedded in resin and thin-cut, to preserve the original spatial relations.

A standard Philips EM 300 electron microscope (100 kV) was used for low magnification. A JEOL 1200 EX equipped with a TRACOR EDS system, for high magnification and chemical analyses. Results of HRTEM observations, made on a JEOL 200 CX, will be used briefly in this paper, and published in details in a next paper.

IV. RESULTS

1. Goethite

Goethite undergoes some destabilization under extended exposition to the electron beam, which likely modifies the crystal aspect. That has to be taken into account when studying the crystal surfaces. Goethitic materials present a global variability according to the sampling place in lateritic profiles and local evolution in a very place, in terms of morphology, particle size, crystal association and mineral interrelationships. However, these characters lead to the distinction of three types of materials :

a. From yellow and white zones of the saprolite

When associated with fresh neoformed kaolinites and halloysites, goethite forms multidomainic almond or netting-needle like crystals with irregular and pitted edges, non symmetrical terminations, and length up to the micrometre (Figure 2A). Single goethite particles (Figure 2C) developed parallel to the (100) plane, and are elongated along c ([001]), as shown by selected area electron diffraction (SAD) patterns (Figures 2D and 2E). Normal SAD patterns, representing the (100)* reciprocal lattice plane of goethite, often present anomalous intense 001 reflexions.
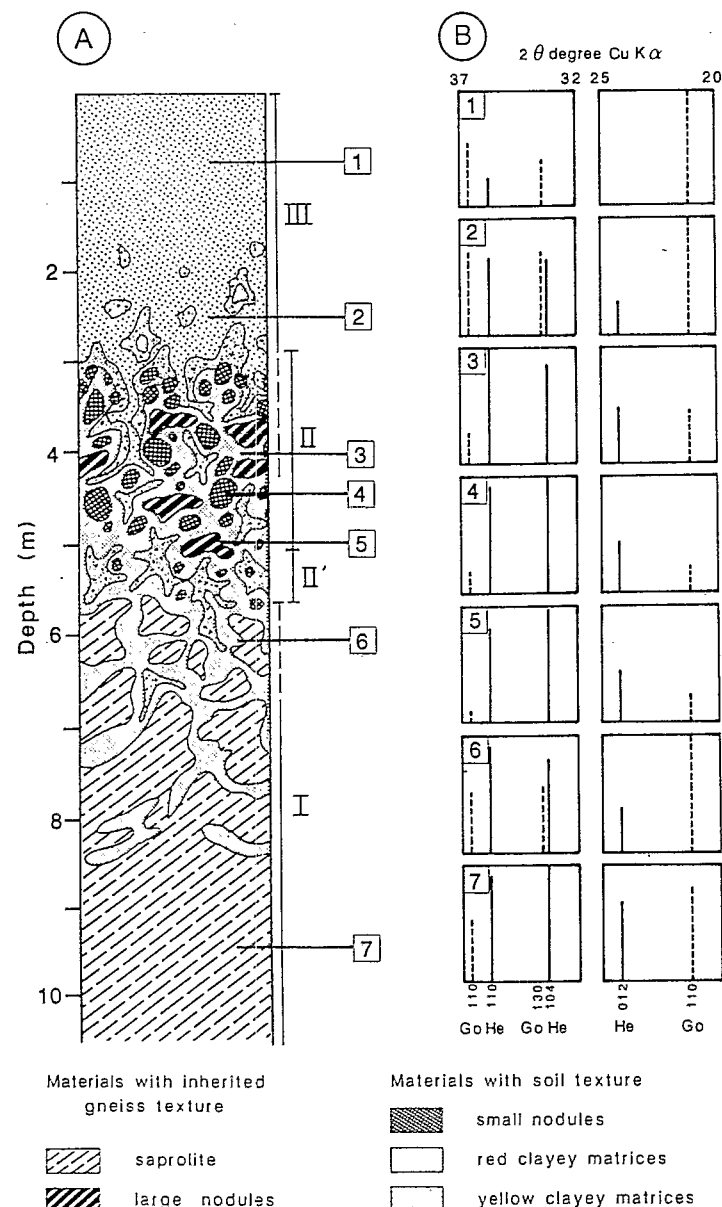
FIG. 1. — [A] *Synthetic sketch map of a lateritic profile (Muller, 1987a), showing the sampling zones.* [B] *Schematic simplified representation of X-Ray diagrams for hematite and goethite from reference samples.*

[A] *Schéma synthétique d'un profil latéritique (Muller, 1987a), montrant les zones de prélèvement.* [B] *Représentation schématique simplifiée d'un diagramme de diffraction RX de l'hématite et de la goethite dans les échantillons de référence.*
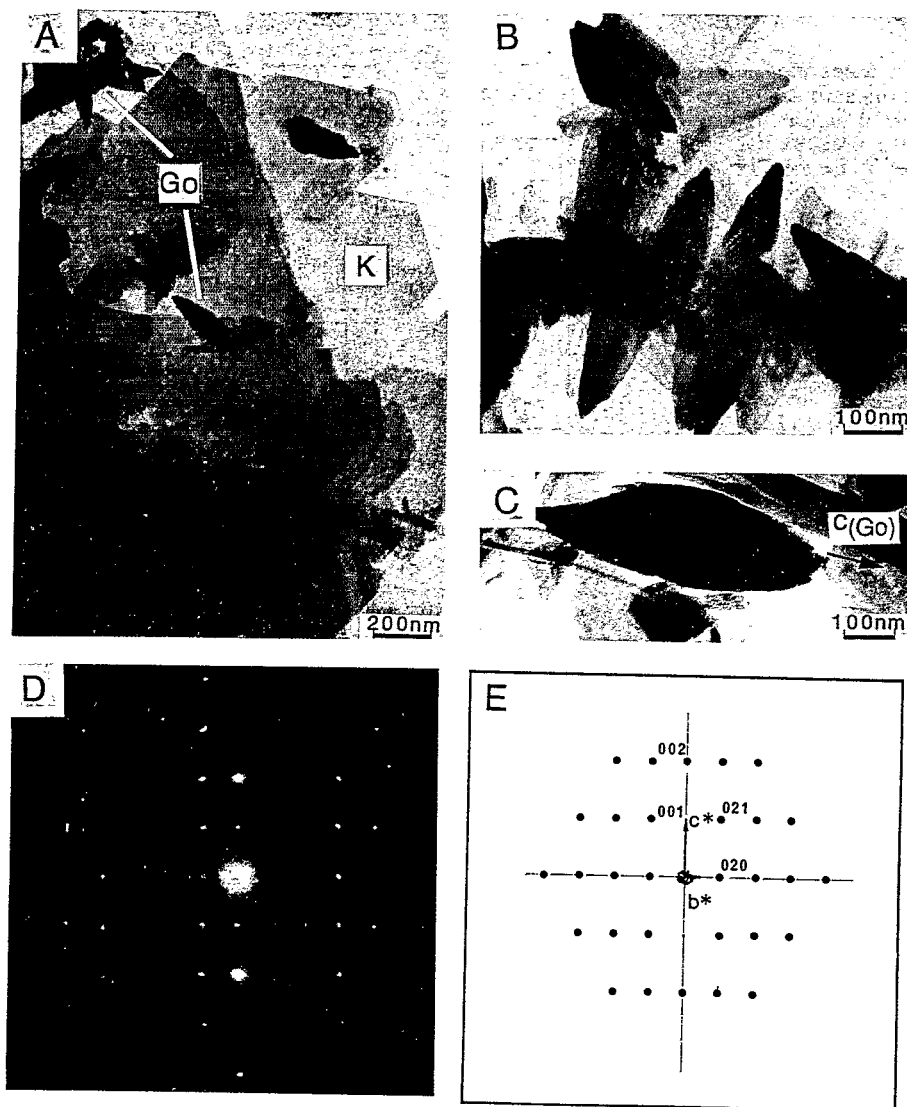
FIG. 2. — [A] *Goethite (Go) crystals upon a large kaolinite (K) flake from a yellow patch in saprolite.*
[B] *Complex tridimensional aggregate of goethite crystals.* [C] *Individual from the same sample.*
[D] *Electron diffraction pattern (SAD) of a goethite crystal parallel to (100).* [E] *Corresponding representation
of (100)*_Go reciprocal lattice plane.*

[A] *Cristaux de goethite reposant sur une plaquette de kaolinite (K) provenant d'une zone jaune de la
saprolite.* [B] *Agrégat tridimensionnel complexe de cristaux de goethite.* [C] *Cristal isolé provenant du même
échantillon.* [D] *Diagramme de microdiffraction électronique d'un cristal de goethite développé parallèlement
à (100).* [E] *Représentation du plan correspondant du réseau réciproque de la goethite ((100)*).*

The reflexions, forbidden on account of goethite space group (*Pbnm*), could appear through multiple diffraction. However, after careful observations, it seems more likely to invoke some structural disorder. The same effect, for example, is noticeable on patterns of Al-substituted synthetic goethites (Mann *et al.*, 1985).

Complex tridimensional star-shaped aggregates are frequent (Figure 2B). Six armed stars with pseudo-hexagonal symmetry result from multiple twinning with rotation about [100], as previously described on natural and synthetic goethites (Cornell *et al.*, 1983 ; Cornell and Giovanoli, 1986). No particular relationships between kaolinite and goethite have been observed in these samples.

b. From red materials (red saprolite, ferruginous nodules, red clayey matrices) :

Different morphologies are evidenced in samples from red materials, where goethite is intimately associated or tied to residual micas, kaolinite and hematite.

(1) *Large multidomains platelets* (Figure 3A), showing pronounced intragranular porosity, with irregular outlines, developed parallel to the (100) plane in form of leaf. Twin diffraction patterns (Figure 3B) are frequent, with (021) as twin plane (Figure 3C). Patterns do not show the spot splitting which would be expected, according to lattice parameters (Sampson, 1969). That indicates a quite perfect lattice match accross the boundaries, which has been confirmed by HRTEM as shown on synthetic crystals by Cornell *et al.* (1983).

(2) Smaller, *anhedral dumpy crystals*, still developed parallel to the (100) plane, with irregular and festooned outlines like oak-leaves (Figure 14). They generally form confuse aggregates or coatings, often associated with hematite.

(3) *Laths* or *acicular crystals*, filling voids and cracks (Figure 4), with irregular outlines and terminations.

In some cases, *kaolinite coating* is observed (Figures 5A and 6A). On figure 5A, a parallel array of goethite crystals, with some starshaped twins, gives a characteristic texture pattern (Figure 5B), with arced 0kl reflexions from goethite, indicative of some relative desorientation. Texture axis **c** ([001]) is parallel to the

(001) plane of kaolinite. Figure 6A displays a more complex organisation with three different directions (120") of goethite development, inducing a twin-like diffraction pattern, with again some misorientation, superimposed on a kaolinite single crystal pattern (Figure 6B).

This oriented growth is interpreted in terms of epitaxy of goethite crystals upon kaolinite (Figure 6), although the hypothesis of endotaxy could not be ruled out definitively.

The epitaxial relationships (Boudeulle and Muller, 1986) are given by :

	Goethite	Kaolinite	
	(100)	(001)	
b_{Go}=9.95 Å	[010]	[200]	$2a_K$=10.32 Å
$3c_{Go}$=9.06 Å	[003]	[010]	b_K=8.93 Å

It should be noted that the theoretical discrepancies between the corresponding lattice periods (Figure 7) are not clearly expressed by diffraction patterns (Figure 6B). That could be indicative of some lattice accommodations at the interface, suggesting a semi-coherent or coherent contact between the two phases instead of an incoherent one.

The kaolinite sheet presents a ternary symmetry, while goethite structure parallel to (100) just displays a binary symmetry. As a matter of consequence, three equivalent directions of positioning for goethite upon kaolinite are possible. That corresponds to the setting in figure 6A and would favour goethite twin formation (Figure 5A). Similar SEM images have been published by Triat (1983).

c. From loose yellow materials with a soil texture (Figure 1A, zone I) :

X-Ray diffraction identifies goethite as the dominant iron phase (Figure 1B, sample 1). Goethite appears as rod-shaped particles or minute rounded crystallites, less than 100 Å in diameter, forming lenticular to framboïdal aggregates (Figure 8). Similar observations have been frequently reported on materials from soils (Jones *et al.*, 1982). The type or degree of interaction within goethite aggregates and between the two phases (Go-K) cannot be assessed : goethite is strongly tied to kaolinite platelets, as their separation can hardly be achieved even after long ultrasonic shaking of suspensions with a
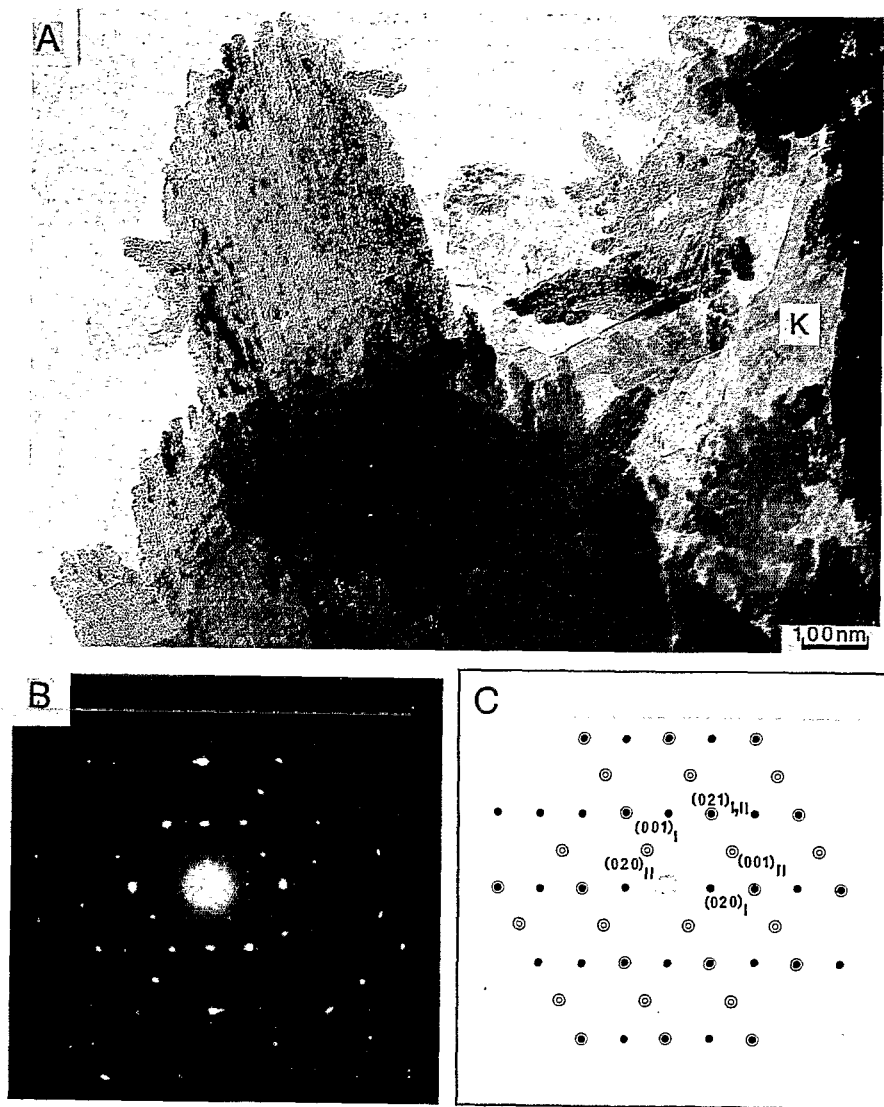
Fig. 3. — [A] Leaves of multidomainic goethite crystals from upper red zone of saprolite with kaolinite (K). [B] Electron diffraction pattern (SAD) of (021) twin association. [C] Corresponding representation of (100)*Go reciprocal lattice plane with 2 individuals, I and II.

[A] Cristaux multidomaines en feuilles de goethite provenant de la partie supérieure de la saprolite (zone rouge). [B] Diagramme de microdiffraction produit par un cristal maclé (plan de macle, (021)). [C] Représentation correspondante des plans (100)* des réseaux réciproques des deux individus.

Fig. 4. — Goethite laths coating and crack filling.

Recouvrement et remplissage de fente par des lattes de goethite.

disperser or even with a chemical treatment (Muller and Calas, 1987), precluding good high resolution examination.

2. Hematite

Whatever the sampling place (red and loose saprolite, indurated nodules or even red clayey matrices in the top zone), hematitic materials do not display major or significant differences.

Large hematite crystals are not easily characterized, owing to the sample preparation methods : they are either too thick for TEM observation or have been pulled of because of their hardness during cuting. When imaged along [0001] they show sharp edges, with subhexagonal outlines.

Smaller crystallites, in the micrometre size range or less, have a typical and reproducible appearance : the anhedral platelets present a

granular aspect, with some moire-like contrasts, and serrated or stair-like edges (Figure 9A and 9B). The SAD pattern (Figure 9C) is a typical (0001)* reciprocal net of hematite single crystals (Figure 9D).

Weathering, posterior to growth, seems to be responsible for their aspect, as illustrated by figure 10, which shows the effects of partial dissolution on a characteristic hexagonal crystal. However, as dissolution processes affect primarily the zones of weakness of crystals, either in terms of lattice defects or growth features, weathering could emphasize an initial subgrained texture.

Crystals of hematite are readily synthesized by ageing precipitates from aqueous Fe(III) solutions (Feitknecht and Michaelis, 1962 ; Atkinson et al., 1968 ; Schwertmann, 1969). TEM examinations of the reaction products (Fischer and Schwertmann, 1975 ; Johnston and Lewis, 1983) show that the original ferrihydrite particles coalesce to form hexagonal hematite platelets, which increase to 300-400 Å with ageing. The same process, with a layer-by-layer tridimensional development, would readily explain the observed microstructures of the natural crystals.

Typical rounded residual hematite crystals are imaged in soil materials (Figure 8), generally without interactions with kaolinites. Apart from the only observed case of oriented growth of hematite upon a kaolinite platelet (Figure 14), direct interrelationships between the two minerals have not been found. In contrast to hematite, kaolinites of the zones where hematite is present do not display any sign of dissolution or destabilization effects.

3. Intermediate phases

Some granuleous particles present features like pock-marks or craters, up to a fifty Angstroms in diameter, quite evenly distributed (Figure 11), which give them a different look, when compared with hematite and goethite crystals. No evolution of this aspect during beam exposure is noticed, indicating that these features are not radiation-induced damages, like in kaolinites, but intrinsic weathering effects. These particles are found in samples from red
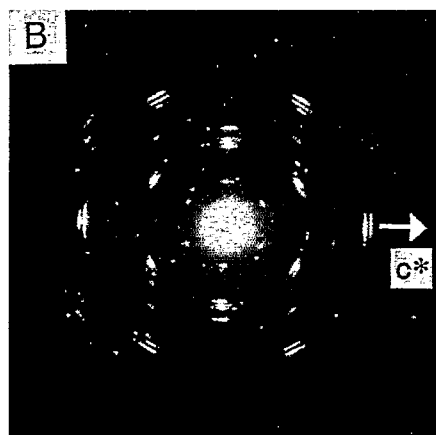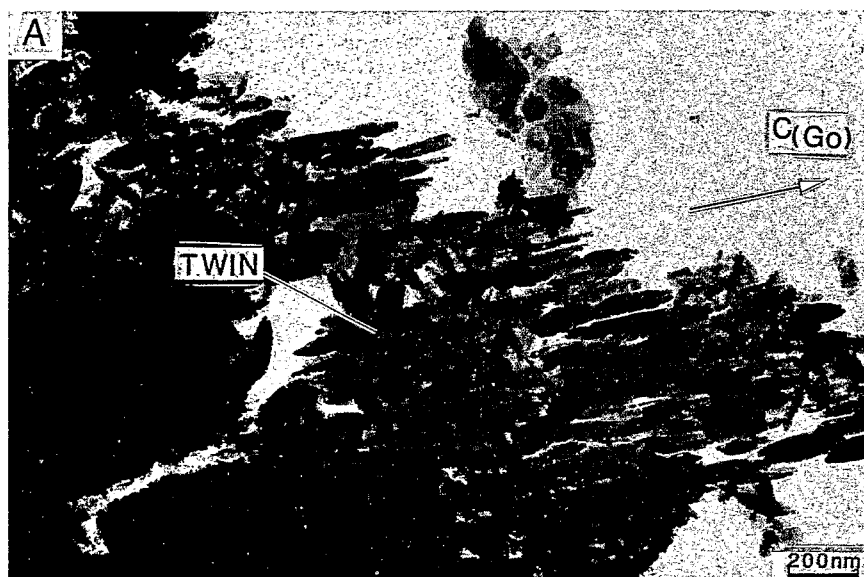
FIG. 5. — [A] *Oriented growth of goethite upon kao-linite : parallel texture with twins.* Texture axis c_{Go} ([001]) [B] *Corresponding electron diffraction texture pattern.* (Inner spots are 020 reflexions from twins).

[A] *Croissance orientée de la goethite sur la kaolinite.* Texture parallèle avec macles. [B] *Diagramme de diffraction associé.*

FIG. 6. — [A] *Epitaxial growth of goethite upon kaolinite* : ternary network of goethite crystals (Go) ; K1 = original kaolinite flake, K2 = parallel growth. [B] *Electron diffraction pattern (SAD) showing the twin-like pattern* [(100)*$_{Go}$ reciprocal lattice plane ; inner spots : 110 and 020 type spots from kaolinite].

[A] *Croissance épitactique de la goethite sur la kaolinite* : réseau ternaire de cristaux de goethite (Go). K1, plaquette de kaolinite support ; K2, croissance parallèle de kaolinite. [B] *Diagramme de diffraction associé, montrant la répartition des réflexions 0kl de la goethite analogue à celle d'une macle (021).* Les spots proches du centre sont des réflexions de type 110 et 020 de la kaolinite.

layers of saprolite and red internodular matrices of the nodular zone.

Different SAD patterns, of single-crystal type, have been recorded from that kind of particles (Figure 12), which contain only iron and a few aluminum, as shown by X-Ray EDS.

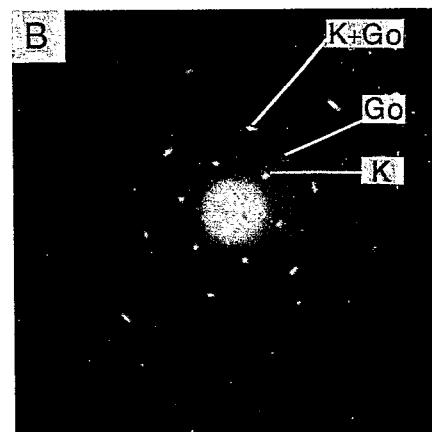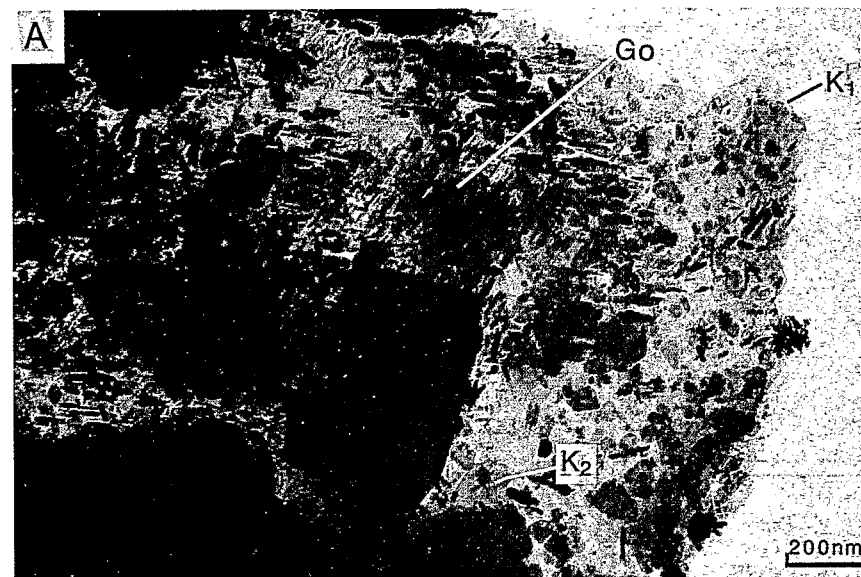The simplest pattern (Figure 12A) exhibits, in addition to the strong reflexions of hematite

(0001)* reciprocal plane (Figure 12B, a), a second weak hexagonal net with a 30" rotation with respect to the other and $d_{hkl} \approx 2.9$ Å for central spots (Figure 12B, b) : they fall midway between two equivalent ($11\bar{2}0$) type hematite reflexions ($d_{hkl} = 2.5$ Å). A similar pattern with 2.9-3 Å additional reflexions has been described by Amouric *et al.* (1986), for hematite from iron-crust pisolites, and interpreted as topotactic maghemite upon hematite. However, a distinct arcing of the spots, and a radial net contraction, with respect to the hematite net, were noted, which are not obviously seen in the present case. A more complex diagram (Figure 12B, c) shows additional spots with $d_{hkl} \approx 5$ Å, which can be compared to d_{020} (4.98 Å) for goethite.

As a matter of fact, the observed patterns represent a logical series from (0001)* reciprocal net of hematite single crystal to (100)* reciprocal net of (021) twinned goethite as shown by figure 3C.

As the diagrams are different from those describing the dehydration process of goethite into hematite published by Watari *et al.*, (1983), a
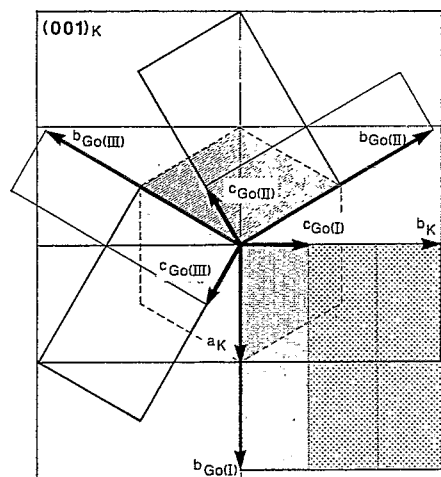
topotactic and pseudomorphic transformation of hematite into goethite can be considered. Nevertheless, this process implies a complete reconstruction and expansion of the lattice, and it seems doubtful that such a transformation would preserve quite perfectly the lattice orientations.

An other interpretation is proposed in parallel : Atkinson *et al.* (1968), studying the effect of pH on crystal nucleation in Fe(III) solutions, noted that "Intermediate types occur and were difficult to distinguish, since the diffraction patterns for goethite twin crystals and

FIG. 7. — *Epitaxial lattice relationships between kaolinite and goethite*. The hexagonal cell refers to kaolinite octahedral layer.

Orientation relative des réseaux de la kaolinite et de la goethite épitaxiée. La maille hexagonale hachurée décrit le feuillet octaédrique de la kaolinite.

hematite crystal, on [100] and [0001] zone axes respectively, are very similar''. The patterns can be indexed as a superstructure of hematite, with a doubling of basal cell parameters (Figure 12B). It should be noted that the same samples, studied by means of XRD (Figure 1B), give anomalous intensities for hematite diagrams, interpreted as resulting from structural disorder by Perinet and Lafont (1972).

Goethite and hematite structures are based upon hexagonal close packed layers of oxygen or/and hydroxyl groups, giving a common sublattice, within which the octahedral vacancy filling scheme differs according to the phase (Goldsztaub, 1931 ; Bernal *et al.*, 1959 ; Francombe and Rooksby, 1959). Yet, the anion net retains similar parameters in two directions.

	Hematite (0001)	**Goethite** (100)	
8.72 Å	[21.0]	[003]	3c_{Go}=9.06 Å
2b_{He}=10.07Å	[02.0]	[010]	b_{Go}=9.95 Å

$[00.1]_{He}$: 3-fold symmetry axis
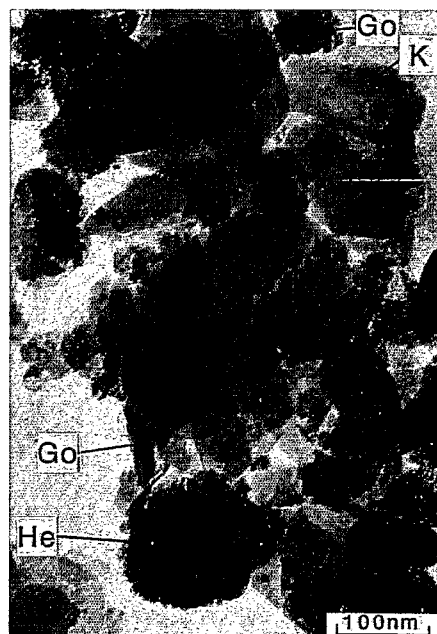$[100]_{Go}$: 2-fold symmetry axis

FIG. 8. — *Typical association of goethite (Go), hematite (He) and kaolinite (K) crystallites forming the upper level with soil texture of the lateritic sequence.*

Association caractéristique de cristaux de goethite (Go), hématite (He) et kaolinite (K) apparaissant dans le niveau supérieur à texture de sol de la séquence latéritique.

On symmetry grounds (as for kaolinite), three equivalent directions of goethite development from a hematitic nucleus are possible, and actually occur, inducing twin formation (Figure 13). Such particles are probably less stable than hematite ones and would undergo alteration more drastically (Cornel *et al.*, 1974).

4. Intergrowths of oxy-hydroxides

As noted above, intergrowths of hematite and goethite have been found. The most significant picture, in terms of crystal growth, is presented on figure 14 which shows at low magnification, upon a large kaolinite platelet, oriented dendrites and a continuous layer of hematite with
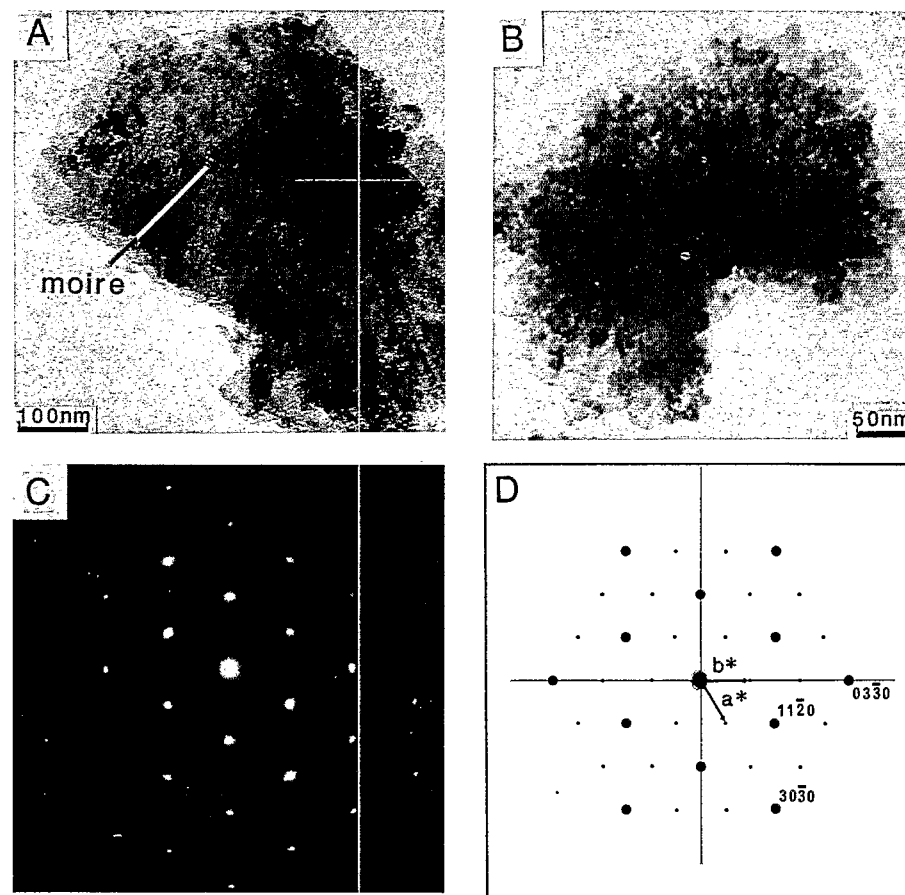

FIG. 9. — *Hematite crystals*. [A] Thin cut : note the moiré effects. [B] Suspension : note the typical edges. [C] Single crystal electron diffraction pattern. [D] Corresponding reciprocal lattice plane (0001)*_{He}.

Monocristaux d'hématite. [A] Coupe ultra-mince : noter les effets de moiré. [B] Suspension : remarquer les bords caractéristiques. [C] Diagramme de microdiffraction associé à [B]. [D] Plan réciproque (0001)* correspondant de l'hématite.

oriented and random intergrowth of goethite. Composite particles, presenting both an intermediate structure and goethite, have been imaged (Figure 15A and 15B).

V. DISCUSSION AND CONCLUSION

1. Mineral development

The reconstitution of lateritisation processes

requires that indicators or references of the different stages, identified as relicts, can be found. Although crystal growth conditions in natural medium differ on many points from experimental ones, some correlations can be drawn. As iron oxy-hydroxides development from aqueous solutions has been extensively studied in laboratories in the very purpose to get correlations with the natural phenomena, hematite and goethite morphological studies afford valuable informations.
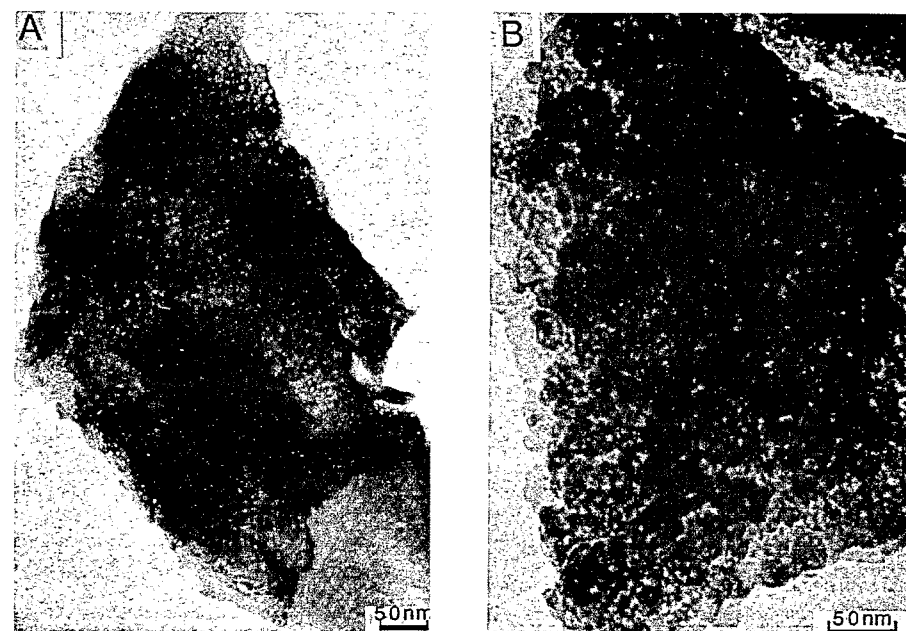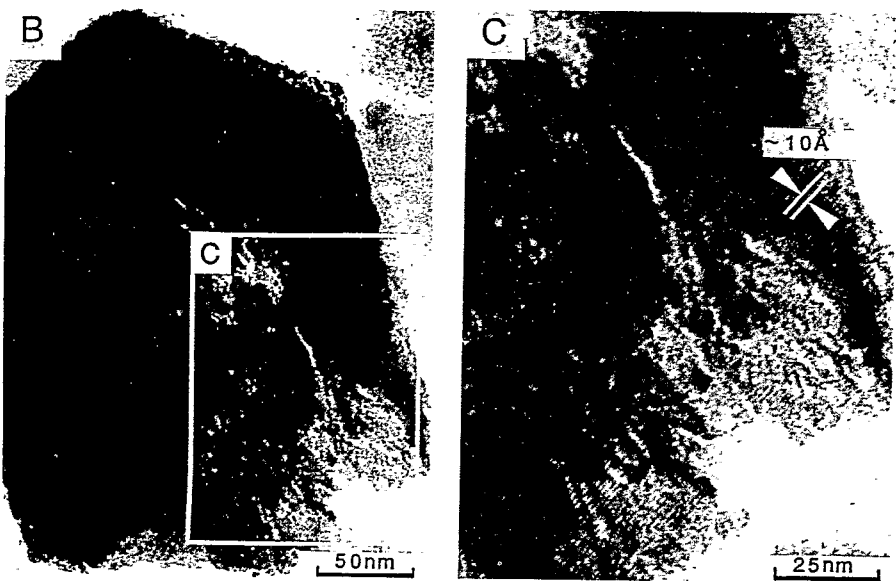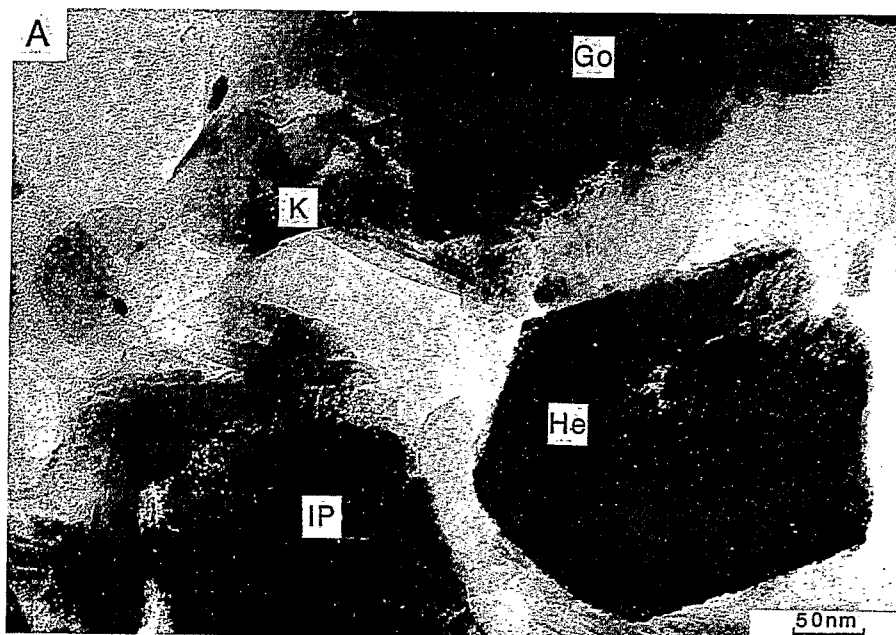
FIG. 11. — *Particles with intermediate structure (see text) showing dissolution indices.* [A] Thin cut, and [B] suspension.

Particules ayant une structure intermédiaire (voir texte) présentant des indices de dissolution. [A] Coupe ultra-mince. [B] Suspension.

Hematite morphological characters support the assumption of formation of hematite after nucleation from amorphous Fe(III) hydroxides in an aqueous system. As these characters seem to be generally observed, whatever the size of the particle and the location of the sample in the lateritic profile, the formation process can be considered as unique.

The diversity of goethite morphologies according to sampling place reveals unambiguously differences in the environmental growth conditions. Unfortunately, the local variability, at a

very high scale, precludes realistic correlations with the complex experimental data. Nevertheless, some comments can be made.

According to the experiments (Atkinson *et al.*, 1968 ; Cornell and Giovanoli, 1985), goethite development in solutions or gels proceeds either (i) with a true nucleation and associated elongated crystals, or (ii) with a dissolution and reprecipitation growth mechanism or "reconstructive transformation", as first proposed by MacKay (1960), inducing more equant habits or twins : the precursors are ferrihydrite germs or hematite nuclei.

FIG. 10. — [A] *Hematite (He), goethite (Go), intermediate phase (IP) and kaolinite in a thin section.* [B] *Hematite crystal, viewed along [0001], with the corresponding typical hexagonal outline, affected by partial dissolution.* [C] *Detail of B (rectangle) showing the preserved hematite lattice (lattice or wedge fringes) in the dissolution area.*

[A] *Hématite (He), goethite (Go), phase intermédiaire (IP) et kaolinite (coupe ultra-mince).* [B] *Le cristal d'hématite, développé parallèlement à (0001), est affecté par une dissolution partielle.* [C] *Ce détail de [B] montre le réseau préservé de l'hématite (franges de coin ou de réseau) dans la zone de dissolution.*
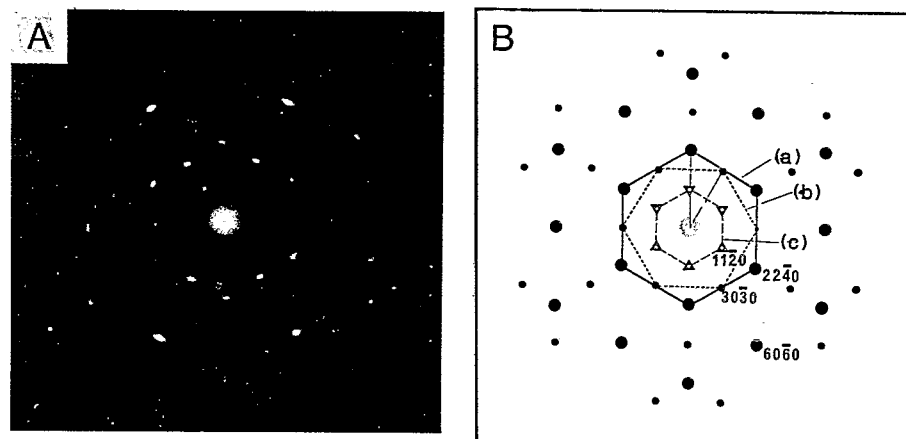
FIG. 12. — [A] *Typical diffraction pattern for intermediate structure.* [B] *Indexation as hematite superstructure, with doubling of the unit cell basal parameters* (Compare with Fig. 9D) ; (a) hematite normal reflexions ; (b) first kind of additional reflexions (d ≈ 2.9 Å) ; (c) second kind (d ≈ 5 Å).

[A] *Diagramme typique d'une phase intermédiaire.* [B] *Indexation comme surstructure de l'hématite avec des paramètres de réseau doubles* (voir Figure 9D) ; a) Réflexions normales de l'hématite ; b) Premier type de réflexions additionnelles (d ≈ 2.9 Å) ; c) Deuxième type (d ≈ 5 Å).
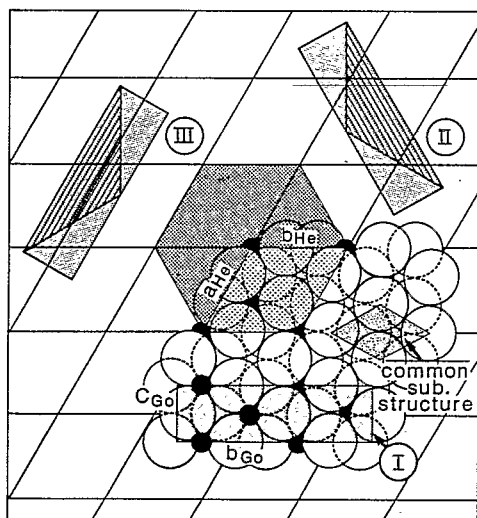

FIG. 13. — *Structural relationships between hematite and goethite* (Bi-dimensional representation). Note the anion common sub-structure and the three equivalent settings for goethite (I, II, III). Ruled areas for goethite unit cells correspond to domains in (021) twin position.

Relations structurales de la goethite et de l'hématite : noter la sous-structure anionique commune et les trois orientations équivalentes de la goethite (I, II, III). Les zones hachurées des mailles de goethite représentent des domaines en position de macle (021).

The observed morphologies and the existence of intermediate forms suggest that the second process has been the more efficient, with probably primary iron compound remnants (micas,
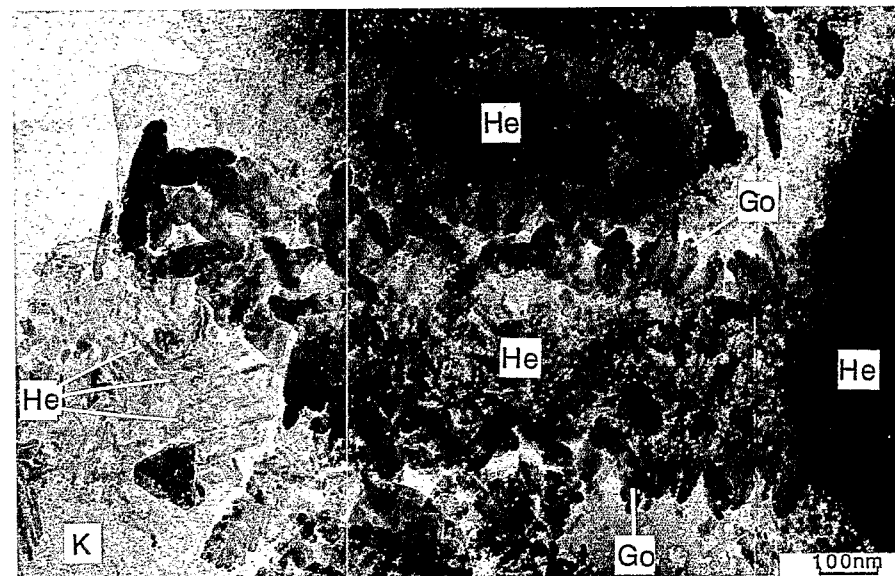
garnets,...) playing the rôle of seeds in the first steps of weathering and goethite development.

Goethite epitaxial growth upon kaolinite would, at first sight, represent another mode of development, with "heterogeneous nucleation". However, the extent of Fe- substitution within kaolinite octahedral layer (and Al in goethite), on one hand, the close structural relations between this layer and hematite layer, on the other hand, lead to consider that the scheme proposed for describing intermediate phase formation (Figures 7 and 13) can be readily transposed : iron substituted domains within kaolinite layer could act like nuclei, inducing definite in-

FIG. 14. — *Intergrowths of hematite (He) and goethite (Go) upon a kaolinite platelet (K) :* oriented dendrites (left) and large crystals of hematite and leaf-like association of goethite crystallites.

Surcroissances d'hématite (He) et de goethite (Go) sur une plaquette de kaolinite (K) : dendrites orientées et larges cristaux d'hématite ; association de cristallites de goethite en forme de feuilles de chêne.

terrelationships (in fact true bonding) between the minerals.

Iron hydroxides precipitation in the presence of well crystallized reference kaolinites has been studied (Greenland and Oades, 1968 ; Saleh and Jones, 1984 ; Jones and Saleh, 1986). Coatings of different types of oxyhydroxides showed only weak association with basal clay surfaces, generally explained in terms of electrostatic interactions. Epitaxial growth depends on the physicochemical parameters of the medium, and among them specially the surface state of the supports. It is believable that this state, for fresh, even still growing kaolinite crystals, in a natural medium, would be drastically different from the experimental one (Schwertmann, 1979 ; Robert *et al.*, 1987).

2. Mineral stability

In contrast to kaolinite which remains preserved in the same zones, hematite crystals

undergo a later weathering and constitute a secondary source of iron. Goethite stability cannot be apprehended directly, no distinctive signs of destabilization being detected.

Besides, because of the close associations of hematite and goethite either in a same and one particle (intermediate phase) or as intergrowths, the problem arises of the stability field jointness or overlapping for the two minerals. Nevertheless, it should be recalled that goethite, when associated to hematite, seems often to postdate it and tends to develop in more open sites. Moreover, goethite, in these cases, is associated with hematite or hematite-like particles which present dissolution marks and are potential precursors for goethite growth, in a hematite-goethite transformation involving a dissolution-crystallization mechanism (Bedarida *et al.*, 1973). Such kinetic processes would explain the failure of classical thermodynamic approaches to describe iron oxyhydroxide behaviour in lateritization.
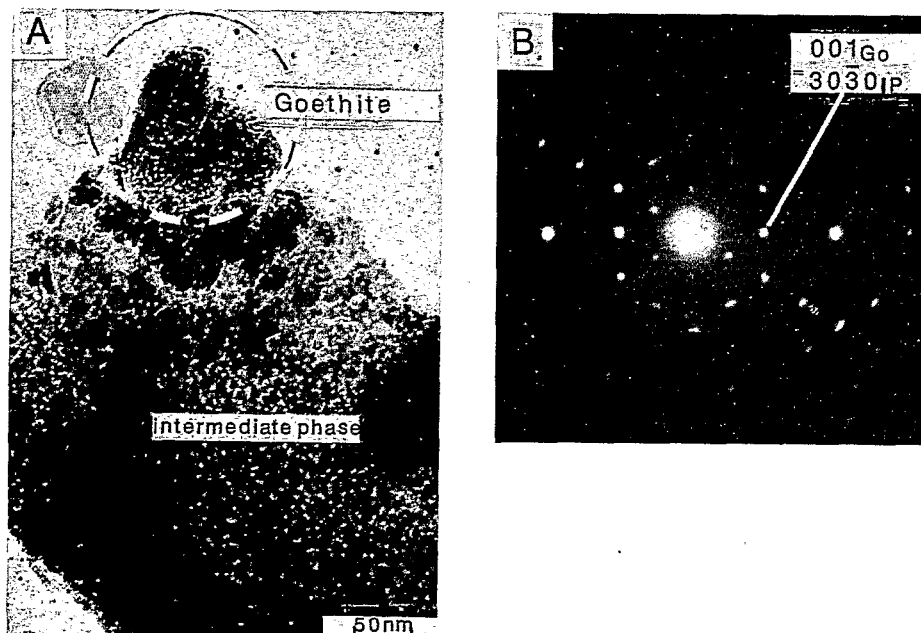
FIG. 15. — [A] *Association of intermediate phase and goethite (Go).* [B] *Complex electron diffraction pattern showing the parallel orientation of the two lattices* (the indexations correspond to figures 2E and 12B).

[A] *Association d'une phase intermédiaire et de goethite (Go).* [B] *Le diagramme de diffraction associé montre l'orientation parallèle des deux réseaux.*

3. Petrological implications

At the scale of lateritic profiles, the above data would imply :

(1) A first generation of goethitic material, resulting from *in situ* direct weathering of iron-bearing rock-forming minerals.

(2) Iron transfers via solutions as soon as the intergranular porosity of the weathered rock would allow it, inducing nucleation and growth, as achieved experimentally, of hematite, hematite-goethite and goethite particles.

(3) Next generations of goethite, resulting from dissolution-crystallization processes affecting hematite and intermediate particles.

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