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DISSOLUTION OF KAOLINITES AND ACCUMULATION OF IRON OXIDES IN LATERITIC-FERRUGINOUS NODULES: MINERALOGICAL AND MICROSTRUCTURAL TRANSFORMATIONS

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ABSTRACT

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In-situ geochemical and structural microanalysis of non-disturbed samples of laterite and mineralogical identifications of microsamples demonstrate an orderly succession of mineralogical and structural transformations. These transformations result in the formation of Fe-nodules. They start from a micaceous phase whose micropores are occupied by hematite. Because the source of iron is external to micas this hematite corresponds to an absolute accumulation (in the meaning of Brewer, 1964). The following transformations constitute a succession of three mineral phases corresponding to relative accumulations with the removal of some components and in-situ reutilization of residual materials.

(1) Phase of Fe-kaolinite accumulation during which the structures inherited from micas are preserved.

(2) Phase of Al-hematite accumulation resulting from a dissolution of Fe-kaolinite, with development of pedoplasma and vesicular porosity.

(3) Phase of accumulation of more or less aluminous goethite which ultimately results in the crystallization of geodes at the borders of voids.

INTRODUCTION

In most of the lateritic formations of Central Africa, under humid tropical climate and forest cover, residual accumulations of iron oxi-hydroxides are discontinuous usually in the form of nodules (Martin, 1967; Stoops, 1968; Ojanuga and Lee, 1973; Bocquier et al., 1984). They form a nodular zone composed of some indurated nodular facies packed in a ferruginous-clay S-matrix. This nodular zone is situated between an underlying weathering zone (or saprolite) and an overlying loose ferruginous-clay zone.

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Many petrographic observations have been made on ferruginous and indurated nodules in such a context, especially on a microstructural point of view (Hamilton, 1964; Stoops, 1968; Schmidt Lorenz, 1964; Eswaran et al., 1979). Moreover, it is well known that the main mineralogical components of these nodules are kaolinite and iron oxides together with resistant primary minerals such as quartz and muscovites (Herbillon, 1980). All these studies essentially deal with the nature and the distribution of the constituents.

The objective of this paper is to assess the structural and historical relations between these constituents or their associations (plasmas; according to Brewer, 1964). So, an attempt is made to define some of the transformations which take place in the course of Fe-nodule formation and the succession of mechanisms responsible for these transformations.

MATERIALS AND METHODS

Materials

The samples analysed come from a soil toposequence in the Central-East Cameroon (Sarazin et al., 1982; Rosello et al., 1982). At the upper part of this toposequence the profiles show an orderly development of three main horizons from the bottom to the top (Fig. 1).

(1) A lower *weathering horizon* (or saprolite) in which the weathering products assume a replica texture and structure of the original rock (gneiss). These secondary products are mainly macrocrystalline kaolinite, hematite and goethite (10% Fe_2O_3) associated with stable primary grains (quartz, muscovite). This horizon has a low consistency and is very porous. In the upper part of the horizon, volumes of saprolite are isolated in a ferruginous clay material characterized by the disappearence of the original rock texture and structure and composed of microcrystalline kaolinite associated with iron oxides ($\simeq$ 10% Fe_2O_3). A gradual transition can be observed between: (a) a discontinuous red and compact matrix generally associated with the saprolite, in which hematite is more abundant than goethite; (b) a continuous and loose yellow matrix in which goethite is the dominant or the only iron oxide.

(2) An intermediate *glaebular horizon* in which two great types of indurated glaebules (Brewer, 1964) can be described.

(a) The coarser (20—80 mm in diameter) are irregular ferruginous lithorelicts characterized by a more or less preserved rock structure and texture. They are mainly composed of macrocrystalline kaolinite associated with hematite (20—40% Fe_2O_3). These glaebules present a gradual transition with the surrounding matrix. They are more abundant in the central part of the horizon.

(b) The finer (less than 20 mm in diameter) are subrounded argillomorphous nodules characterized by the disappearance of the rock structure

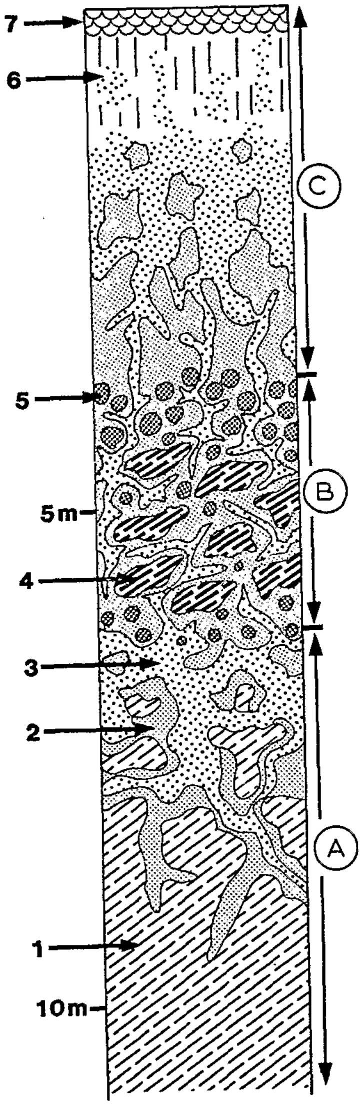


Fig. 1. Schematic representation of a profile: A. weathering horizon; B. glaebular horizon; C. loose ferruginous clay horizon; *1* = saprolite with inherited rock structure and texture; *2* = red and compact matrix; *3* = yellow and friable matrix; *4* = ferruginous lithorelict; *5* = argillomorphous nodules; *6* = yellow and compact matrix; *7* = organic matter accumulation.

(clayey facies). They are mainly composed of microcrystalline kaolinite associated with hematite (40—60% Fe_2O_3). These glaebules are discordant to the surrounding matrices. They are the more abundant, and even exclusive, in the upper part of the horizon.

The interglaebular matrices have the same general characteristics as the ferruginous clay matrices of the underlying horizon. But the red matrix becomes more abundant and very compact. Hematite can be the only iron oxide of this matrix. Inversely the yellow matrix is reduced to a tubular network and becomes very loose.

(3) An upper *loose ferruginous clay horizon*. The matrices present similar characteristics as the interglaebular matrices of the underlying horizon. But from the bottom to the top of the horizon the yellow matrix is again more abundant: the red matrix becomes progressively discontinuous and then disappears at about 1 m depth. At the same time the yellow matrix becomes more compact. The upper part of this horizon is affected by organic matter accumulation.

The constitution of the saprolite and the ferruginous lithorelicts and their relations with the red and yellow matrices have been reported elsewhere (Muller, 1985). The analysis presented here will only deal with the argillomorphous nodules, especially those located in the upper part of the glaebular horizon.

Methods

Undisturbed samples were impregnated with epoxy resin and thin-sectioned for petrographic examination. Fracture surfaces of clods were coated with gold and examined in a JEOL JSM 20 Scanning Electron Microscope (SEM, 20kV).

Two methods of in-situ chemical analysis were performed on the samples: (1) quantitative analyses on thin sections using an electron microprobe (Camebax connected with a EDS ORTEC multiline analyser); and (2) semi-quantitative analyses of clods previously observed by means of SEM.

X-ray powder diffraction (XRD) data were obtained using Co$K\alpha$ radiation (40kV, 40mA) with a Philips PW 1730 goniometer, with a slow-scan of 0.25 or 0.125° 2θ/min. Measurement of the substitution rate in hematite was made, using Mossbauer spectrometry. Information on crystal—chemical characteristics of kaolinites (rate of iron substitution, crystallinity indices) was obtained by combining different methods such as X-ray diffraction, ESR and IR spectrometry.

RESULTS AND DISCUSSION

The matrix of the nodules analyzed is principally composed of ferruginous-clay plasmas, with some skeletal grains and numerous vesicular voids (Fig. 2).

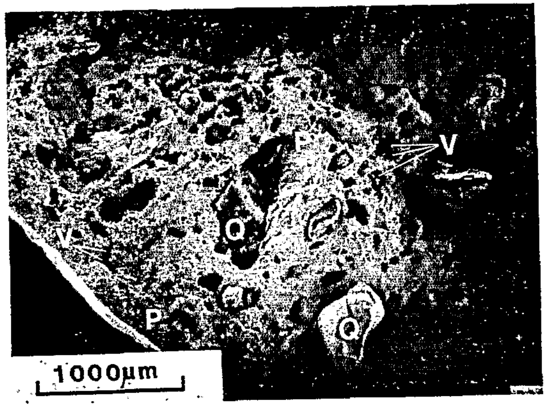


Fig. 2. Lateritic nodule with clayey ("argillomorphous") facies (SEM): P = nodular plasmas bearing kaolinite, hematite and muscovite; Q = quartz grains in their dissolution cavity; V = vesicular porosity.

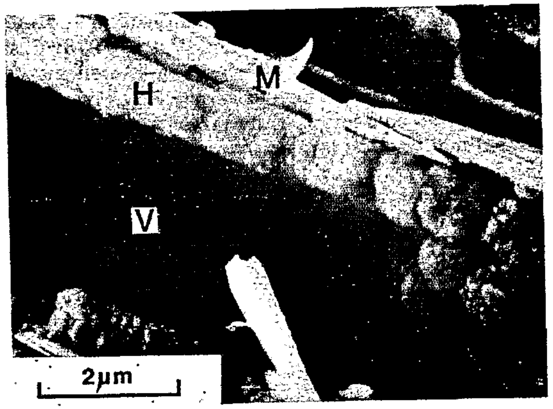


Fig. 3. Absolute accumulation of hematite (H) partially filling the intracrystalline (or interlamellar) pores (V) of muscovite (M) (SEM).

Skeletal grains, which are relics of weathered material, consist of some cracked, strongly-weathered quartz grains within the dissolution cavities (Nahon, 1976; Eswaran and Stoops, 1979; Muller et al., 1981) and of some muscovite that retains polarization colors. The fissural micropores of quartz and the interlamellar pores of muscovite are partially filled by hematite (Fig. 3). Hematite developed before weathering of minerals and thus corresponds to an absolute accumulation in the meaning of Brewer (1964) because origin of iron is external to the minerals.

Cònsitution of nodular plasma

Three types of plasmas in the nodules can be differentiated according to their mineralogy and microstructure.

(A) Well crystallized plasma, composed of Fe-kaolinite related to muscovite weathering and hematite accumulation.

Kaolinite is found as macrocrystallites (10—50 μm, Fig. 4). These crystallites originate from muscovite weathering. In fact, direct relationships are observed under the microscope as the optical continuity of these two minerals in the same crystallite. In addition microchemical analysis identifies residual mica laminae in these macrokaolinites (Fig. 13, a and b). This kaolinite is distinctive *because of its nature*: weakly Fe-rich. ESR spectra have peaks at g = 4.2 and g = 4.9 that are assigned to structural iron in the octahedral position (Meads and Malden, 1975; Angel et al., 1977; Bonnin et al., 1982) (Fig. 5,A.1); the amount of iron substitution is less than 1%; *because of its crystallinity*: relatively well-ordered; on the IR spectra (Fig. 5,A.2), the 3695, 3672, 3655 and 3620 cm^{-1} absorption bands corresponding to the stretching vibrations of the structural OH groups are well resolved; moreover, the 938 cm^{-1} peak, which occurs on the high frequency part of the 915 cm^{-1} band has a marked inflection (Farmer, 1974; Van der Marel and Krhoner, 1969; Giese and Datta, 1973; Cases et al., 1982); only one doublet occurring at 4.35—4.16 Å is well marked between 23 and 25° 2θ (CoKα) on the X-ray patterns (Hinckley, 1963); *because of its crystalline texture*: characterized by arrangement of crystallites according to a three-directional order, thus preserving the phyllitic texture of the original mica.

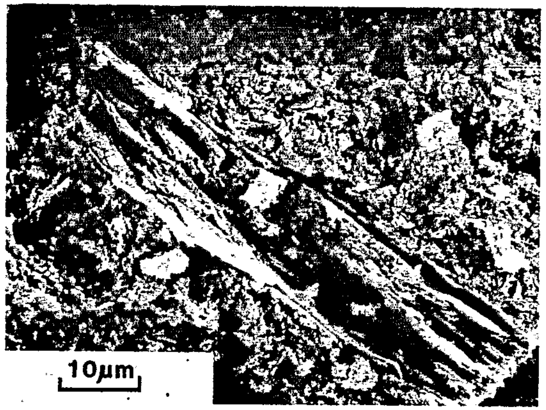


Fig. 4. Macrocrystal of Fe-kaolinite within a red nodular isotic plasma (SEM).

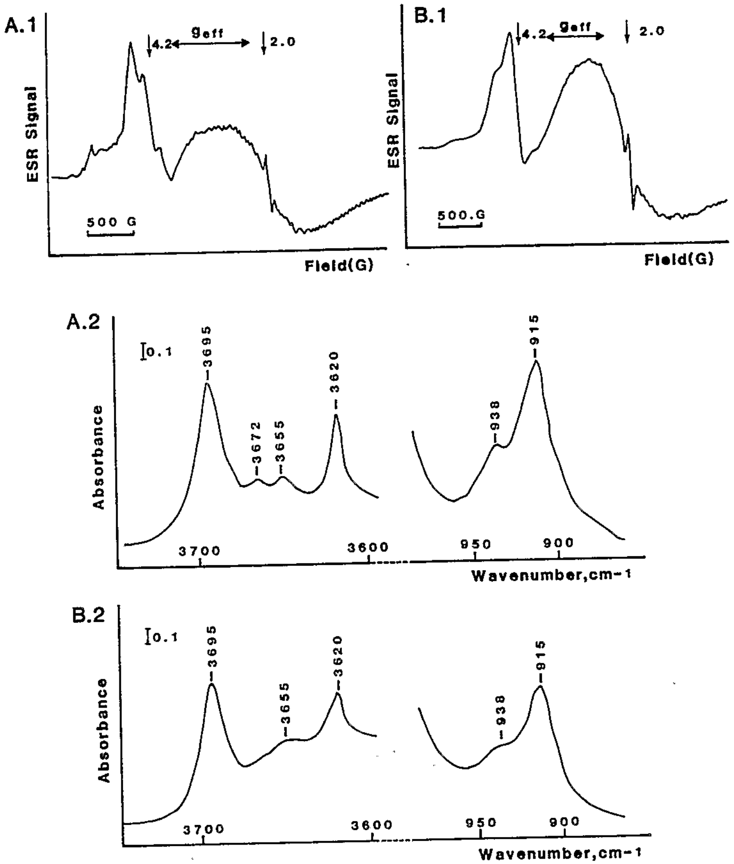


Fig. 5. A. Plasma composed of Fe-macrokaolinites originating from mica weathering and absolute accumulation of hematite. B. Isotic plasma composed of Fe-microkaolinites and of predominant Al-hematite. 1. ESR spectra. 2. IR spectra of kaolinites (in optical density) for high frequencies (3695— 3620 cm^{-1}) and low frequencies (915 cm^{-1}).

Associated *hematite* is microcrystalline. It partially fills the intracrystalline (or interlamellar) micropores of macrokaolinites. Microsampling could not be done corresponding to these interlamellar points, because sufficient material was available only for detailed mineralogical work (such as crystallinity and rate of Al substitution). Nevertheless, observations under the petrographic microscope in natural, polarized and reflected light as well as X-ray analyses of several microsamples could be made on this plasma which is characterized by pinpoint porosity and macrokaolinites. According to Didier et al. (1985), hematite is considered to be a unique crystallized ferruginous phase in these kaolinite clay micro-environments with low porosity.

(B) Poorly crystallized plasma with Fe-richer kaolinite and Al-hematite, the latter being predominant.

This plasma comprises most of the nodular matrix. Under the microscope, it is very dark-red and quasi-isotropic or isotic (Brewer, 1964), its opacity being linked to iron oxide. Observation by scanning electron microscopy shows microfacies which are either compact and glomerular (Fig. 6) or globular at the edges of some voids (Fig. 14). Chemical microanalyses by microprobe indicate that this plasma is composed of 70—90% iron oxide and 10—30% silica and alumina (Fig. 7).

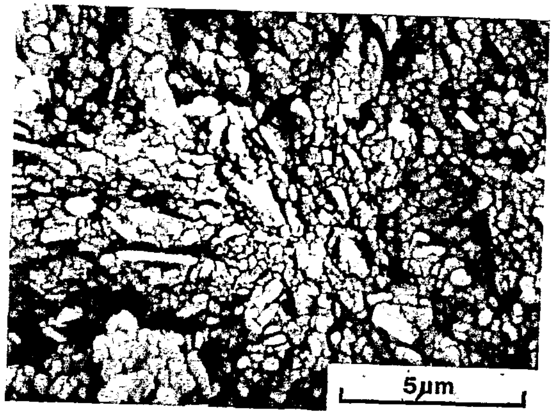


Fig. 6. Isotic plasma with compact glomerular facies (SEM).

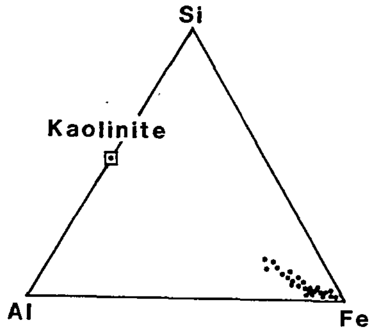


Fig. 7. Chemical microanalyses of the isotic plasma composed of Fe-microkaolinites and Al-hematite.

Kaolinite is present as microcrystallites, generally smaller than 1 μ. This kaolinite can be differentiated from that in macrocrystals *by its nature*: more Fe-rich according to the intensity of peaks at $g = 4.2$ (Fig. 5,B.1) from which the degree of iron substitution may be semi-quantitatively estimated (Herbillon et al., 1976); this is confirmed by some STEM microanalyses on ultra-thin sections that indicate a degree of iron substitution higher than 2%; *by its crystallinity*: very disordered; on IR spectra (Fig. 5,B.2) the disappearance of the 3672 cm^{-1} vibration band is preceded by inversion of the intensities of the 3655 and 3672 cm^{-1} bands and is accompanied by transformation of the 938 cm^{-1} deformation band to a simple shoulder (Cases et al., 1982); on X-ray patterns, the triplet occurring at 4.35, 4.19 and 4.12 Å is not resolved, and on ESR spectra, the surface of the internal peak at $g = 4.2$ is very important (Herbillon et al., 1976; Mestdagh et al., 1980); *by its crystalline texture*: characterized by a disordered and random arrangement of microcrystallites.

Al-hematite is the only crystallized ferruginous phase of this plasma: the d(110) reflection of goethite occurring at 4.18 Å is not present; in contrast, well defined d(hkl) reflections are observed at 3.67, 2.70, 2.51, 2.20, 1.84, 1.69, 1.60, 1.48 and 1.45 Å. Mössbauer spectrometry and microprobe data suggest that the hematite has a low amount of Al substitution (about 5% Al_2O_3).

This isotic plasma corresponds to a new type of arrangement of these two substituted constituents on a microcrystalline scale: its microfacies becomes compact and glomerular or globular when the amounts of Fe-kaolinite decrease and those of Al-hematite increase correspondingly.

(C) Well crystallized plasma with goethite more or less Al-substituted at the edges of voids.

Numerous, irregular and mammillated to regular and subrounded, rarely interconnected voids produce vesicular porosity (Fig. 2). In a majority of them and especially in the large ones, these voids originate from quartz dissolution (as mentioned above). But some of them and particularly the smallest ones do not show any evidence for such dissolution.

Under the binocular microscope, the walls of > 50 μ voids (resolution limit) appear as blackish and bright. Under crossed nicols, these walls are seen as very birefringent, orange-yellow plasma, made of zoned cutans (Brewer, 1964).

Observation by scanning electron microscopy shows that these cutans are composed of superimposed bands with fibrous fabric perpendicular to the walls of voids (Fig. 8). This yellow and birefringent plasma can thus be easily distinguished from the red isotic one under the microscope and by scanning electron microscopy.

X-ray diffraction analyses of microsamples of material from the walls of these voids indicate the occurrence of goethite with various amounts of Al (Norrish and Taylor, 1961; Thiel, 1963).

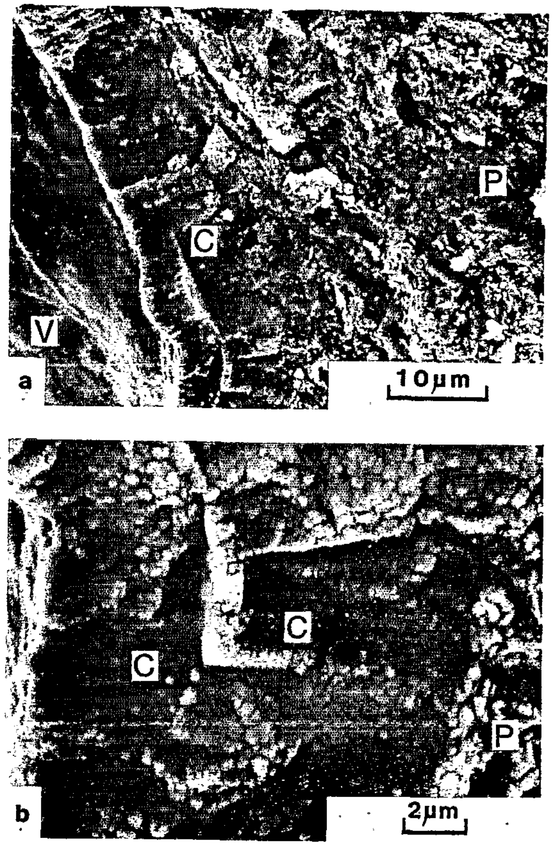


Fig. 8. Zoned cutan of Al-goethite (*C*) at the edge of a vesicular void (*V*) and in direct structural affiliation with the isotic plasma composed of predominant Al-hematite and of Fe-microkaolinites (*P*) (SEM). a. Global view. b. Detail.

These three types of plasmas in which Fe-kaolinite, Al-hematite and variable Al-goethite alternately predominate are always sequentially distributed relative to intranodular voids. In order to specify whether or not this mineralogical succession, beginning with a micaceous mineral and ending with crystallization of goethite geodes (in the meaning of Pettijohn, 1953), correspond to a succession of transformations in situ, it is necessary to point out structural and geochemical relations between these three plasmas and their mineralogical components within the plasmas themselves (what will be called "nodular plasmic mass") and at the edges of intranodular voids.

Mineralogical and microstructural relations within the nodular plasmic mass

(A) Structural relations between nodular plasmas of types 1 and 2.

Observation by scanning electron microscopy brings out progressive transitions between muscovite and macrocrystals of Fe-kaolinites (including residual micaceous laminae, interlamellar pores of which are filled by hematite), on the one hand, and between these macrocrystals of Fe-kaolinite and glomerules of Al-hematite prevailing in the isotic plasma,

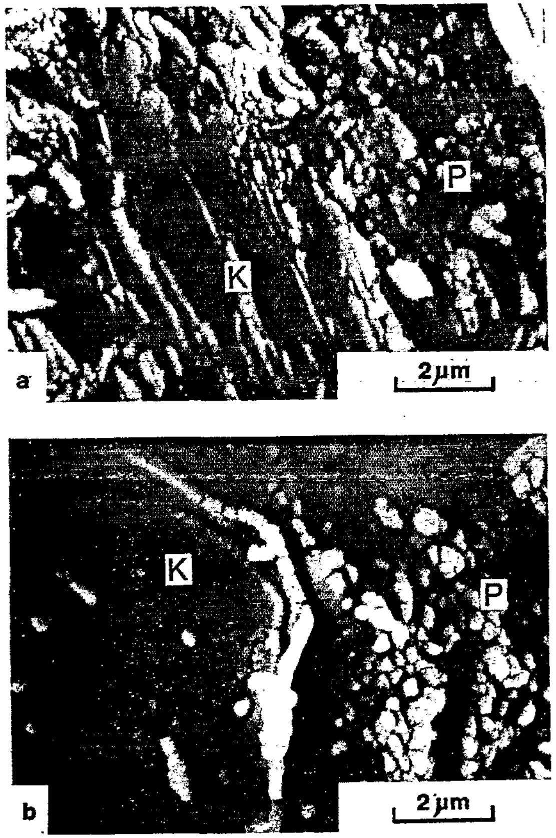


Fig. 9. Progressive transition between Fe-macrokaolinites whose intracrystalline pores are partially filled by hematite (*K*) and plasma with glomerular microstructure and predominant Al-hematite (*P*) (SEM). a. Along the 010 or 100 face of kaolinite. b. Along the 001 face of kaolinite. Note the strong fissuration.

on the other (Fig. 9a). Thus, the micaceous structure is first preserved by Fe-kaolinite and then a structural transformation results in a new glomerular microstructure.

In the latter case, observation along the 001 planes indicates that laminae of the macrocrystals of Fe-kaolinite become fissured and cracked and that glomerules with dominant hematite develop and become predominant at the edges of macrocrystals (Fig. 9b).

Particular cases were analysed on a crystal scale.

(B) Transformations within macrokaolinites.

Fig. 10. Detail of Fig. 3 (SEM). Orderly relationship of four plasmic types within a macrokaolinite: *1* = laminae of macrokaolinite + helmatite; *2* = microkaolinite + hematite; *3* = plasma with glomerular microstructure; *4* = plasma with globular microstructure.

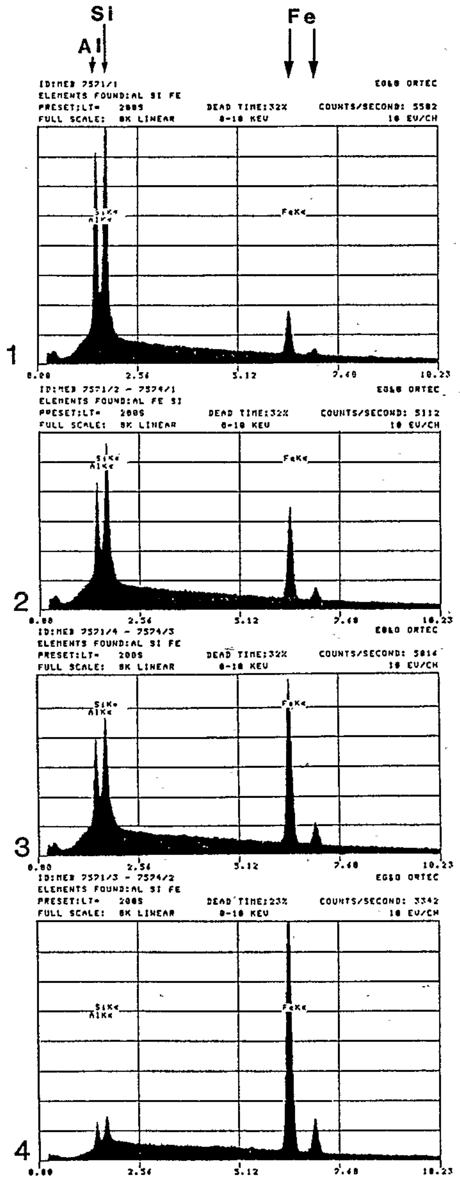


Fig. 11. In-situ quantitative analyses of phases 1, 2, 3, 4 (see Fig. 9).

(a) In the inner parts of some macrocrystals of Fe-kaolinite originating from mica weathering and whose interlamellar pores are partly filled by hematite, an orderly relationship of four plasmic phases can be observed as follows (Fig. 10): (1) laminae of macrocrystalline Fe-kaolinite on the faces of which hematite has crystallized; (2) arrangement of microcrystalline and more Fe-rich kaolinite in the alignment of the preceding laminae, accompanied by hematite; (3) plasma with glomerular microfabric and Al-hematite in which kaolinitic microcrystals are progressively less numerous and are randomly oriented; (4) plasma with globular microfabric and Al-hematite in which kaolinite is no longer discernible.

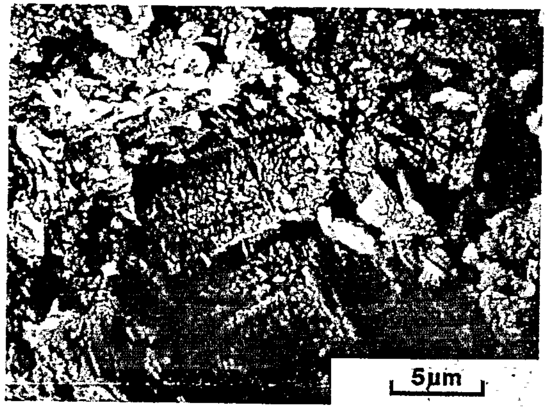
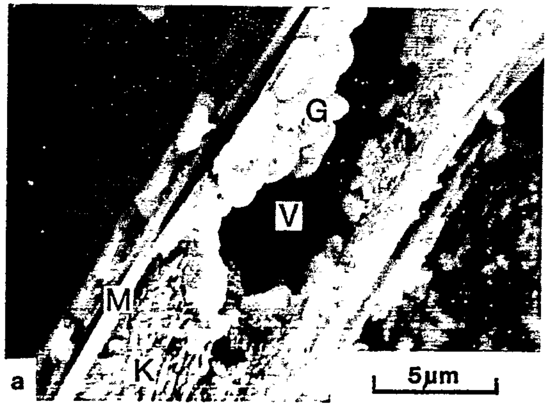


Fig. 12. Complete pseudomorphic replacement of a macrokaolinite by microkaolinite and hematite (SEM).



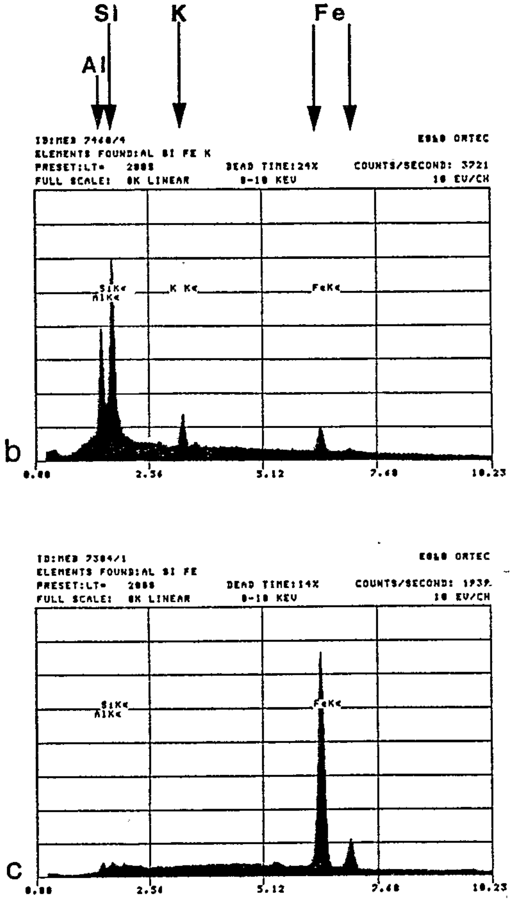


Fig. 13. Transformation within macrokaolinite. a. (SEM). Residual laminae of mica (*M*). Arrangement of Fe-microkaolinite and hematite (*K*). Plasma with globular microstructure (*G*). Intracrystalline vesicular porosity (*V*). b. In-situ semi-quantitative microanalysis of the residual laminae of mica. c. In-situ semi-quantitative microanalysis of plasma with globular microstructure.

Modifications in the nature and orientation of the voids are associated with this succession (Fig. 10). Mineralogical phases (1) and (2) show an interlamellar porosity oriented along the fabric of the original mica; in phase (3), microporosity is strongly reduced; in phase (4), a new porosity develops which consists of interglobular curved voids uncomformable to the interlamellar porosity.

Moreover, in-situ semi-quantitative analyses of these four phases by a microprobe show that a continuous and orderly geochemical progression corresponds to these structural changes (Fig. 11); iron contents increase while percentages of aluminium and silicon decrease from phase (1) to phase (4).

This orderly relationship of microfacies and geochemical stages from a macrokaolinite originating from mica weathering results thus from successive structural transformations together with mineral dissolutions and reprecipitations. These changes represent an evolutionary suite typical of an in-situ differentiation as follows.

(1) *Structural changes* leading from a crystalline to a plasmic organization. The crystalline organizations are characterized by the preservation of phyllitic textures. In fact, there is a successive pseudomorphic replacement of mica by Fe-macrokaolinites (phase 1) and by Fe-microkaolinites (phase 2), with structural continuity between these two phases. The plasmic organizations are characterized by disappearance of phyllitic textures (phase 3) and structural rearrangement (new textures resulting from association of kaolinite and hematite), giving way to a new system of pores (phase 4). Thus, there is a structural discontinuity between the last two and first two phases.

(2) *Mineralogical changes*, characterized by weathering of residual micas in the presence of hematite resulting in the formation of Fe-kaolinite and progressive but incomplete dissolution of the latter.

Thus, it appears that these structural and mineralogical evolutions are governed by the same geochemical mechanism, i.e. *absolute* accumulation of iron from an extraneous source as hematite in the intracrystalline pores of micas and of the kaolinites originating from the weathering of the latter. This accumulation is accompanied by loss of silica and alumina from Fe-kaolinites responsible in their turn for a residual iron accumulation (*relative* accumulation, D'Hoore, 1954). Thus, as progressive transformation of

kaolinites responsible in their turn for a residual iron accumulation relative-ital accumulation, D'Hoore, 1954). Thus, as progressive transformation of

The epigenetic replacement of kaolinite by iron oxide (Nahon, 1976) is only transitory and incomplete in the case studied here. It only takes place during phase (2), i.e. during the initial evolution from macro- to microcrystals of kaolinite, which preserves the crystalline textures, whereas more complete dissolution of kaolinite leads to a breakdown of these textures and to a reorganization of plasma.

(b) Numerous other observations show that this in-situ differentiation is more or less developed and can be limited to phase (2) corresponding to the transformations of macrocrystals to microcrystals (Fig. 12) or more advanced, generating a globular plasma almost entirely composed of iron oxide (Fig. 13, a and c). In the latter case, Fe-kaolinite is completely dissolved; moreover, this plasma which borders a mammillated void 5 to 10 μm in diameter, and which is clearly unconformable to the phyllitic texture,

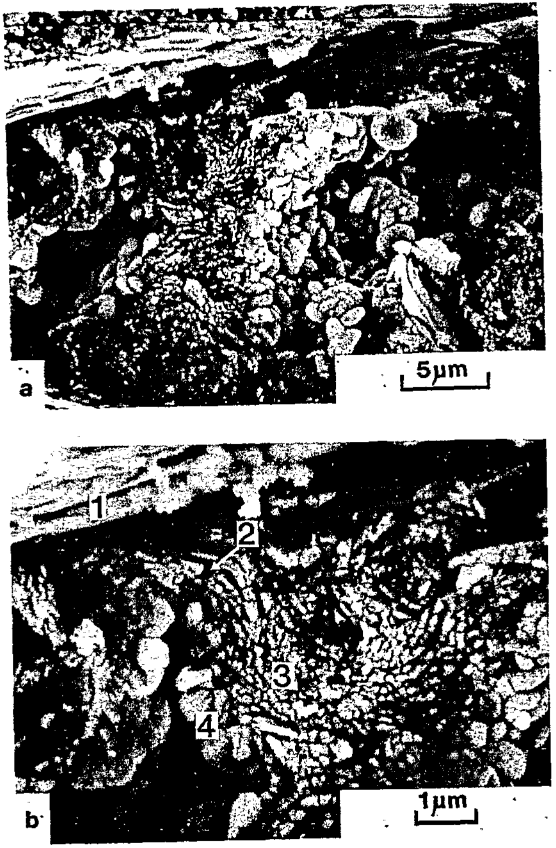


Fig. 14. Orderly affiliation of four phases within the nodular plasmic mass (SEM): *1* = macrokaolinite with residual laminae of mica + hematite; *2* = oriented plasma = arrangement of microkaolinite and of hematite; *3* = plasma with glomerular microstructure; *4* = plasma with globular microstructure. a. View of the ensemble. b. Detail.

argues for an evolution with loss of material resulting in intracrystalline vesicular porosity.

(C) Transformations within nodular plasmic mass.

By extension of these microanalytical data to the scale of the whole nodular plasmic mass, we conclude that this in-situ differentiation is a general phenomenon. Fig. 14 shows an example of orderly relationship between the four phases mentioned above: macrokaolinites + hematite → microkaolinites + hematite → plasma with glomerular microfabric → plasma with globular microfabric. But in this case, the plasma with glomerular microfabric is equivalent to the isotic plasma which comprises most of the nodular matrix and testifies to an incomplete dissolution of Fe-kaolinites. Moreover, the globular plasma here is more abundant than in the preceding examples and the vesicular pores are correspondingly larger in size (20—50 µm).

This in-situ differentiation of nodular plasmas can thus generate intranodular vesicular pores of more than tens of microns.

Mineralogical and microstructural relations at the edges of voids

Anisotropic plasmas develop at the edges of voids tens of microns in length. Such plasmas are composed of goethite, more or less Al substituted, in the form of zoned cutans. Observation by scanning electron microscopy shows a direct structural relationship between the plasma with glomerular microfabric and prevailing hematite and the different layers forming the goethitic cutans (Fig. 8).

Quantitative analyses made along a transverse section across one of these zoned cutans show a regular increase of aluminium from the nodular plasma to the void (Fig. 15). The calculated amounts of Al substitution are between 1 and 12% AlO(OH) moles.

In some nodules with more developed porosity, direct relationships (Fig. 16) are observed between the plasma with macrokaolinites whose intracrystalline micropores are more or less filled with hematite, the plasma with microkaolinites and hematite and an acicular crystalliplasma identified as goethitic (Van Oosterhout, 1960; Eswaran and Raghu Mohan, 1973; Schwertmann and Taylor, 1977).

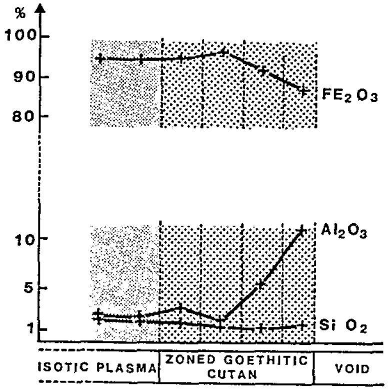


Fig. 15. Quantitative microanalyses along a traverse across a zoned cutan of Al-goethite.

Fig. 16. Direct affiliation between a plasma composed of macrokaolinite and absolute accumulation of hematite (*K*), a plasma made of microkaolinite and of hematite (*H*) and an acicular goethitic crystalliplasma (SEM). a. Global view. b. Detail.

The relative distribution of these goethitic plasmas and their direct relationship with the isotic plasma composed of Fe-kaolinite and Al-hematite show that the former originates from evolution of the latter. These plasmas, always related to voids, may thus be considered as final crystallizations of geodes.

DISCUSSION AND CONCLUSIONS

A general relation between iron accumulation and destruction of kaolinite has been documented (Lacroix, 1914; Frankel and Bayliss, 1966; Schmidt Lorenz, 1974). More recently, petrographic observations and mineralogical analyses of the different nodular fabrics observed from the bottom to the top of lateritic profiles suggest that glaebular evolution takes place in situ and principally in a vertical direction. On the basis of evidence of relationships and vertical successions obtained from structural as well as mineralogical and geochemical data, this evolution of glaebular fabrics have been shown to take place in situ as a result of successive transformations (Nahon, 1976; Leprun, 1979; Muller et al., 1981; Boulangé, 1984). These transformations are as follows.

(A) Macrostructural transformations: massive structures of iron crusts evolve into more and more fragmented structures (brecciated, nodular, pisolitic).

(B) Mineralogical transformations: these consist either of increasing iron concentrations by progressive replacement ("épigénie") of kaolinite by Al-hematite (Nahon et al., 1977), or of an evolution: Fe-kaolinite → Al-hematite → Al-goethite (Muller et al., 1981), or of a crystalline disorder accompanying increasing iron substitution in kaolinites and Al-substitution in iron oxi-hydroxides (Cantinolle et al., 1984; Didier et al., 1985).

The analysis presented here may help to better explain such differentiations studied on the scale of profiles and widely developed in lateritic zones. We have shown by microstructural, in-situ geochemical and mineralogical analyses of microsamples an orderly succession of transformations in the course of the formation of lateritic ferruginous nodules. Our study deals with an evolution beginning with a muscovite in order to show that this differentiation takes place in situ and to point out the pre-eminent role of absolute accumulation of iron from extraneous sources. At the same time, we think that the nature and the progression of these structural and mineralogical transformations are similar within authigenic kaolinitic phases in environments where iron is accumulated by different ways.

The in-situ differentiation has the following characteristics (Fig. 17).

(1) During ferruginous nodule formation, minerals resistant to weathering such as micas, whose intracrystalline pores are variously occupied by hematite, are pseudomorphically replaced by Fe-kaolinites.

(2) The Fe-kaolinites are themselves progressively destabilized in the presence of hematite. We propose that an increasing admission of iron in the kaolinitic lattices results in an increasing crystal disorder and in a progressive decrease of the crystal size (Cantinolle et al., 1984).

(3) During this initial transformation, essentially characterized by formation and then destabilization of Fe-kaolinites, the original crystalline organizations are preserved (phyllitic texture of mica), and the epigenetic replacement of kaolinite by hematite is only transitory and very incomplete.

(4) During a second stage of transformation, the crystal organizations of clay minerals are obliterated. New microstructures, typical of pedoplasmas, develop by association of Al-hematite and of more-and-more

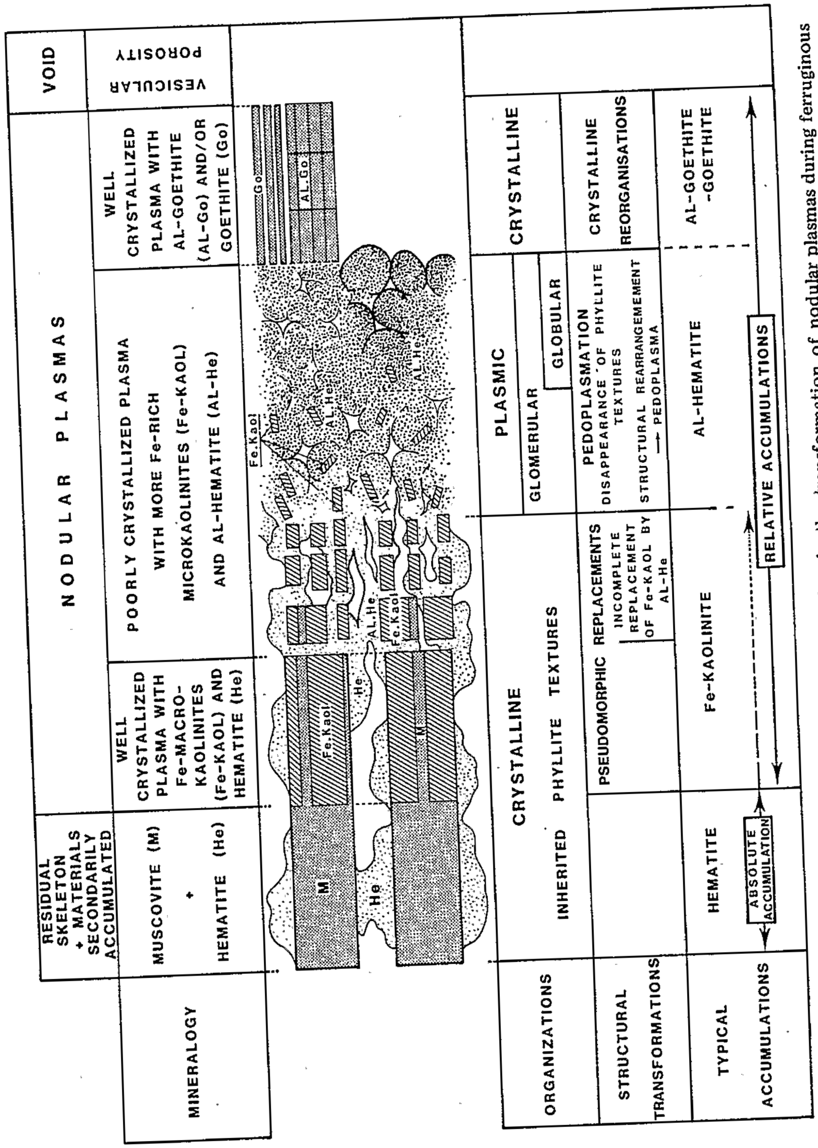


Fig. 17. Schematic representation of the orderly succession in the transformation of nodular plasmas during ferruginous nodule formation.

disordered kaolinite. The disappearance of the phyllitic textures is thus related to progressive dissolution of Fe-kaolinites, and a part of residual aluminium is then admitted into the hematite lattice.

(5) This subtractive geochemical evolution thus generates the accumulation of Al-hematite and vesicular transformation porosity due to formation of new glomerular and globular plasmic structures.

(6) Then, a third transformation takes place at the edges of voids created in this way and/or of voids resulting from quartz dissolution. During this stage the dissolution of Fe-kaolinite stops. The dissolution of Al-hematite begins and precedes the recrystallization of the total iron in the form of goethite. Goethite will be aluminous and/or non-Al-substituted, probably according to the type and development of intranodular microporosity — vesicular transformation porosity and residual porosity from weathering.

(7) During the first transformation, increased concentration of Fe induces destabilization of kaolinite by progressive Fe substitution in the lattice of the clay mineral. The question is then whether or not during the second transformation, residual aluminium could provoke destabilization of hematite by progressively entering the lattice of this iron oxide up to the formation of goethite.

Thus, the successive mineralogical transformations are characterized by (i) progressive substitutions (Fe, then Al) in the lattices, (ii) destabilization of clay minerals, and (iii) correlative increases of amounts of Fe and Al. In-situ microanalysis seems to be presently the best available method in order to identify these crystalchemical pathways.

(8) In nodules, all these transformations have three important consequences: densification related to ferruginous concentration, development of intranodular vesicular porosity and crystallization of goethitic geodes.

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PHOSPHORUS SORPTION BY ANDEPTS FROM THE SOUTHERN HIGHLANDS OF PAPUA NEW GUINEA

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ABSTRACT

Moody, P.W. and Radcliffe, D.J., 1986. Phosphorus sorption by Andepts from the Southern Highlands of Papua New Guinea. Geoderma, 37: 137—147.

P sorption curves (18 hours, 0.01 *M* $CaCl_2$) were determined for various A, AB, B and C horizons of six Andepts. Two of these soils were formed in alluvially sorted and redeposited volcanic ash. P buffer capacity (PBC) and equilibrium solution P concentration (EPC) were derived from the curves. PBC was high for all samples indicating large sorption capacities. Soils formed in alluvial ash had lower PBC than those developed in airfall ash. In the latter soils, PBC was affected by degree of weathering. Multiple regression indicated that most variation in PBC was accounted for by citrate-dithionite minus pyrophosphate extractable Al, oxalate minus pyrophosphate extractable Al, and pyrophosphate extractable Fe. This suggests that allophane, crystalline and non-crystalline aluminium hydrous oxides, and Fe associated with organic matter, account for the predominant P-sorbing sites. The low EPC figures, which were correlated with Olsen extractable P, indicate potential P deficiency as a limitation to crop production.

INTRODUCTION

Andepts formed in volcanic ash are the dominant cultivated soils in the central and western highland provinces of Papua New Guinea, where a semi-permanent agricultural system based on sweet potato (*Ipomoea batatas* L.) is commonly practised.

In spite of their extensive present use, highland Andepts have significant fertility problems, and P is frequently the most important single nutrient limiting crop production. Although total P in Andepts may be high (Fassbender, 1969), existing evidence (Parfitt and Mavo, 1975; Radcliffe, 1983) indicates that P deficiency is due to the high sorption capacities of these soils. The P status of such soils is therefore best described by parameters derived from P sorption curves.

P sorption curves describe the relationship between "adsorbed P" on

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