

## The Epigenetic Replacement of Kaolinite by Lithiophorite in a Manganese–Lateritic Profile, Brazil

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### ABSTRACT

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The petrographical and mineralogical changes accompanying the accumulation of Mn oxides in the kaolinite matrix of a laterite from Azul (Brazil) are described. In this formation, the precipitation of lithiophorite (an Al-bearing Mn oxide) promotes the corrosion of the kaolinite matrix to such an extent that an in-situ replacement (i.e. an epigeny) of the silicates by the oxides can be identified. At the sites where the epigenetic replacement of kaolinite takes place, the original book-shaped structure of this mineral is preserved. The volumes formerly occupied by kaolinite are, however, filled with large and well developed lithiophorite crystallites. These observations indicate that the precipitation of lithiophorite in Mn-rich laterites can induce the same type of transformations as the precipitation of hematite in ferricretes. This similarity is due to the parallelism between the behaviour of Mn and Fe during the processes leading to the accumulation of their oxides. The protons released by the hydrolysis of both  $Mn^{4+}$  and  $Fe^{3+}$  produced in the oxidizing zone of water tables are the likely corroding agents responsible for the observed transformations.

### INTRODUCTION

Laterites are pedogenetic in origin and result from the chemical weathering of a variety of sedimentary, metamorphic and igneous rocks under humid tropical conditions (Lacroix, 1914). When the parent rock contains  $Mn^{2+}$  bearing minerals, the lateritic weathering mantle which is developed at its expense is enriched into manganese oxyhydroxides and oxides (Roy, 1968). As with iron, manganese accumulates in laterites both in a relative (i.e. as a result of the

losses of soluble elements) and in an absolute manner (i.e. by the addition of manganese coming from another part of the weathering mantle).

This applies to the description of the weathering profiles located in the Azul minefield area of Brazil (Valarelli et al., 1978; Beauvais et al., 1987).

This contribution focuses on a lateritic weathering profile of Azul and more precisely on samples collected in a profile at 20 m depth displaying well the relationships between kaolinite and manganese oxyhydroxides when absolute accumulation of Mn takes place within a kaolinite matrix.

The purpose of the present paper is to show that the behaviour of Mn during lateritic weathering is very similar to that of iron. The accumulation of Mn promotes the corrosion of the kaolinite matrix and in its latest stages leads similarly to the epigenetic replacement of this silicate by an oxide. In its essence, therefore, this article is an extension to the lithiophorite-kaolinite couple of an approach that was previously applied to the hematite-kaolinite couple (Ambrosi et al., 1986). This paper presents first the morphological evidences of epigeny and discusses later the chemical mechanisms responsible for the destabilisation of kaolinite in Mn-bearing laterites.

## MATERIALS AND METHODS

### *The area under study*

The sedimentary Precambrian rocks of Azul area have been weathered under lateritic conditions with development of very thick regoliths (~100 m). In the vicinity of the front where parent rock is still unweathered, the Mn oxides form pseudomorphs of the Mn-bearing primary minerals in the same manner as kaolinite forms pseudomorphs of the other primary silicates. As a consequence at these levels white to reddish kaolinitic zones alternating with black Mn-rich zones are common (Beauvais et al., 1987). Higher in the weathering profile, however, the volume occupied by the black-Mn-rich material gets more important: interbedded clayey zones are progressively invaded by finger-like nodules of manganese oxyhydroxides ("nodule" is here employed in the sense of Brewer, 1976). In the uppermost part of the profile, kaolinitic zones no longer exist but the thinly bedded original sedimentary structure may still be recognized in the hard manganiferous crust (Beauvais, 1984). The development of the manganese finger-like nodules within the clay matrix was especially studied in three pits identified as A1P-162, A1P-163 and A1P-170 (see Beauvais 1984, p. 60. for the precise location in the Azul area near Carajas, 6°15'S 50°30'W, Brazil). The results presented here were obtained on samples collected in pit A1P-162 at 20 m depth.

## Methods

Samples of the reddish kaolinitic matrix and of the indurated black manganese finger-like nodules (Fig. 1) were studied in great detail from a petrographical and mineralogical point of view by standard methods using the petrographic microscope, scanning electron microscope (S.E.M.) and electron microprobe. All these analyses were performed on undisturbed and oriented samples. Besides, microsampling allowed us to collect 7 kaolinite specimens from the reddish clay matrix, 7 manganese oxyhydroxide specimens from the cores of manganese finger-like nodules and 5 samples from the external limits of these nodules.

Microsamples were extracted by microsampling technique (Meunier and Velde, 1982) under binocular microscope from polished sections where main mineral phases (specimens) were previously recognized under reflected light. Each microsampling covered a surface of about 200 to 500  $\mu\text{m}^2$ . Sampling of a mineral zone was repeated as necessary to obtain enough material for XRD analyses. Before destroying a polished section by microsampling, however, the zones to be sampled were microphotographed and analyzed by means of an electron microprobe.

All these samples were then examined by X-ray diffraction ( $\text{CuK}\alpha$  radiation was used for Mn-oxyhydroxides;  $\text{CoK}\alpha$  radiation was used for kaolinite crystals, and either quartz or  $\text{Pb}(\text{NO}_3)_2$  was added as an internal standard), infrared spectrometry and electron spin resonance (E.S.R.). From the X-ray diffraction patterns, the mean crystallographic parameters of lithiophorite were computed, with use of the unit-cell program proposed by Tournarie (1969).

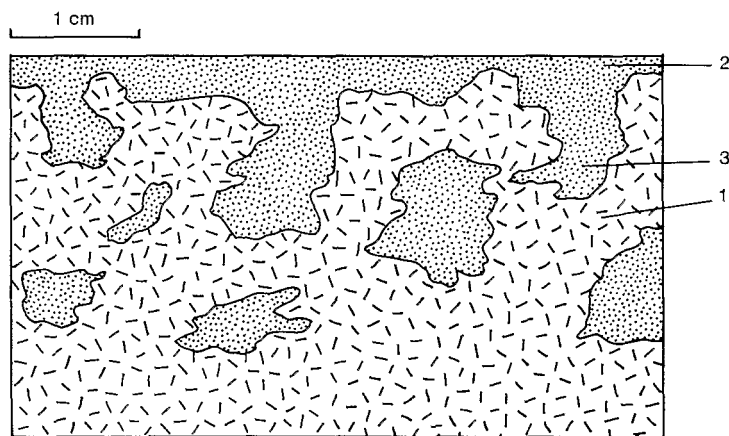
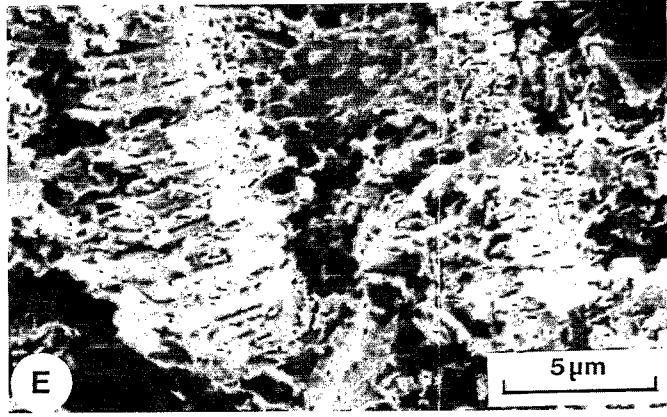
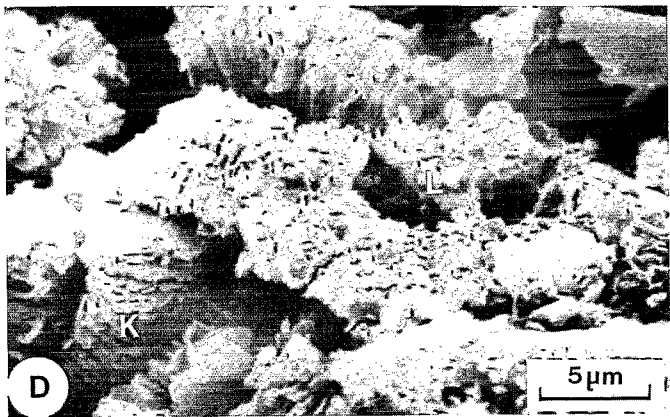
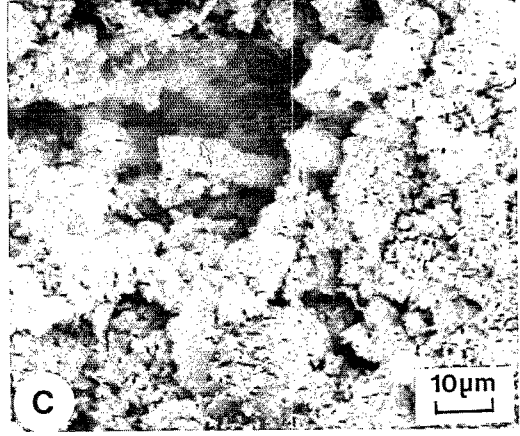
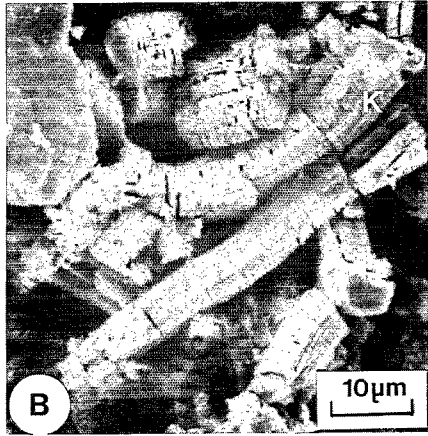
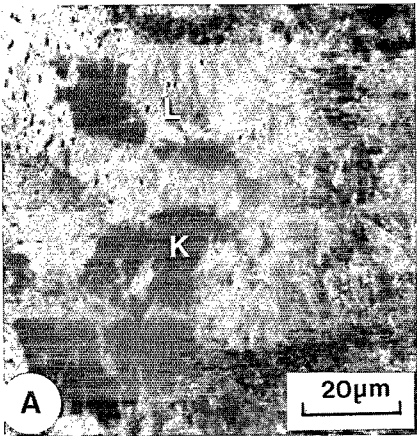


Fig. 1. Sketch of the transition between the reddish kaolinitic matrix and the manganese finger-like nodules observed in an undisturbed sample. 1 = reddish kaolinitic matrix; 2 = black manganese layer; 3 = black manganese finger-like nodules penetrating the clay matrix.



## POLARIZING OPTICAL MICROSCOPE OBSERVATIONS

The development of the finger-like nodules of manganese within the clay matrix can be characterized macroscopically as follows. Near contacts with finger-like manganiferous nodules, minute black manganiferous spots are randomly distributed within the clay matrix. These spots become more numerous, increase in size and merge into millimetric to centimetric nodules (Fig. 1).

Such a transition between the clay matrix and the manganiferous nodules can be observed under both polarizing transmitted light and polarizing reflected light. Thin sections observed under transmitted light (petrographic microscope) permit us to describe the reddish kaolinitic matrix (or plasma) which consists of tightly joined booklets of crystallites, the sizes of which range from a few microns to 200  $\mu\text{m}$  along with scattered quartz grains of silt size. The reddish colour is due to the presence of iron oxides as minute spots associated with clay and essentially consisting of goethite. The manganese zone is opaque under transmitted light, however, and observations were made on polished sections under reflected light. In the case, kaolinite booklets do not reflect the light well and appear almost black (Fig. 2A). Kaolinite booklets are marked by corrosion embayments and cracks which are filled with a manganiferous matrix (in grey in Fig. 2A). That is better expressed in a sketch (Fig. 3) which represents the same zone as does Fig. 2A. This sketch depicts the transition between the kaolinitic matrix and the lithiophorite matrix as observed by means of a polarizing optical microscope (reflected light). Along the transition (from the left to the right of Fig. 3) etching patterns become more numerous: the manganiferous matrix penetrates deeply into kaolinite booklets to such an extent as to cut them into several pieces. Near the cores of manganiferous nodules, small kaolinite relicts occur, then disappear in favor of the manganiferous matrix. Further ghosts of entire kaolinite booklets can be recognized within the manganiferous matrix. These ghosts are continuous in their shapes with relicts of unweathered kaolinite. This indicates in-situ weathering

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- Fig. 2. A. Transition between the kaolinitic matrix and the lithiophorite matrix observed with a polarizing optical microscope (under reflected light): *K*=relict booklets of kaolinite; *L*=lithiophorite matrix in which ghosts of pre-existing booklets of kaolinite can still be observed. B. Kaolinitic matrix observed by means of S.E.M.: booklets of kaolinite tending to curl and intertwine. C. Contact between the kaolinitic matrix and the lithiophorite matrix observed by means of S.E.M. The appearance of booklets of kaolinite is preserved by coatings of crystallites of lithiophorite (*L*). D. Contact between the kaolinitic matrix and the lithiophorite nodule observed by means of S.E.M.: some booklets of kaolinite are unaffected (*K*), some are coated or partially replaced by honeycomb like crystallites of lithiophorite (*L*). E. Cores of lithiophorite nodules observed by means of S.E.M. Ghosts of pre-existing booklets of kaolinite can be recognized.

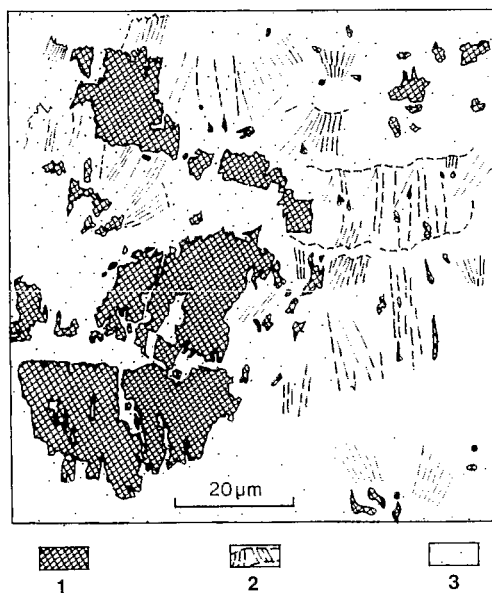


Fig. 3. Sketch of the transition between the kaolinitic matrix and the lithiophorite matrix observed in Fig. 2A: 1 = relict booklets of kaolinite affected by cracks and etching patterns; 2 = ghosts of original kaolinite booklets preserved in lithiophorite matrix; 3 = lithiophorite matrix penetrating booklets of kaolinite.

of the kaolinite crystals and their simultaneous replacement by the manganese matrix.

#### S.E.M. OBSERVATIONS

Each main stage of the replacement of the kaolinite crystals by the manganese oxides can also be observed by means of S.E.M. The unweathered kaolinite forms booklets which are tightly interwoven, leaving between them an important microporosity (Fig. 2B). At the contacts with a manganese nodule occasional kaolinite booklets are coated by minute crystals of Mn-oxyhydroxides (Fig. 2C) and the original clay matrix texture is largely preserved. Along the transition, these crystallites of oxyhydroxides, which form a honey-comb texture, invade the space made available by the dissolution of former kaolinite particles even though at this stage, other kaolinite booklets remain unaffected by manganese and still show packing of automorphic platelets (Fig. 2D). The mineralogical determination of the crystallites of Mn-oxyhydroxides with a honey-comb texture was checked by XRD on microdrilled samples and found to be lithiophorite. In the cores of Mn-nodules, lithiophorite crystallites are well developed and the kaolinite is no longer present, but the original struc-

ture of the booklets is preserved in the lithiophorite (Fig. 2E). Moreover, the microporosity which existed between booklets of kaolinite is, by and large, also preserved. These observations demonstrate dissolution of the kaolinite crystals and their in-situ (i.e. epigenetic) replacement by Mn-oxhydroxides.

#### GENERALIZATION TO OTHER Mn-RICH LATERITE OCCURRENCES

The example of epigenetic replacement of kaolinite by Mn oxides described above is far from being either unique or restricted to the Azul area. For instance, in the upper part of Mn lateritic profiles of both the Moanda area (Gabon) and Ziemougala area (Ivory Coast), kaolinite platelets were observed to be similarly dissolved and replaced by lithiophorite (Nziengui-Mapangou, 1981; Nahon et al., 1985). This shows that the phenomenon is quite common in Mn-bearing laterites and therefore warrants a general explanation.

#### MINERALOGICAL AND CRYSTALLOCHEMICAL DATA

In the samples collected for the present study, microdrilling permitted us to isolate three main stages of kaolinite replacement by Mn oxides: (1) the reddish kaolinite matrix (7 samples); (2) the diffuse limit between the kaolinite matrix and the Mn nodules (5 samples); and (3) the cores of the Mn nodules (7 samples). From stage (1) to stage (3), X-ray diffraction patterns (Fig. 4) illustrate the disappearance of kaolinite and its progressive replacement by lithiophorite.

The crystallographic parameters calculated from the X-ray diffraction patterns of lithiophorites (Table I) show that the crystal structure of these minerals differ slightly but nonetheless significantly from that of a synthetic reference Li-bearing lithiophorite (ASTM card No. 16.334; Giovanolli et al., 1973).

Chemical data were obtained on lithiophorite from in-situ microprobe analyses. A discrepancy occurs between the chemical analyses and the X-ray patterns of Fig. 4C in which kaolinite and goethite are present. This is due to differences in scales of analyses. The microprobe beam for the chemical determination is focused on lithiophorite ( $1 \mu\text{m}^2$  is the approximate surface area analyzed on thin sections). For XRD, microsamples were collected by microdrilling on bigger surfaces of about 200 to 500  $\mu\text{m}^2$ , including relicts of kaolinite crystals along with goethite particles. In contrast, lithium content (50 to 400 ppm) was not determined by microprobe analyses but by atomic absorption on the microsamples collected by microdrilling. These data demonstrate that these lithiophorites are virtually free of lithium and show that the chemical composition of natural lithiophorites departs systematically from the ideal composition in having very low Li/Al atomic ratios (Taylor et al., 1964).

The systematic departure is likely to be related to the oxidation stage of Mn cations in the natural lithiophorites. Pauling and Kamb (1982) showed that

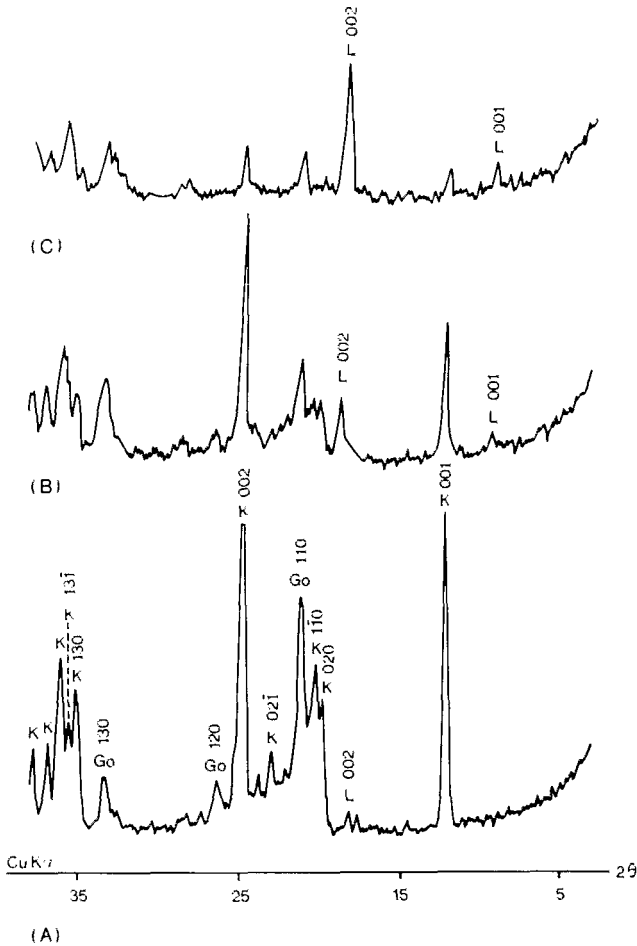


Fig. 4. X-ray diffraction patterns of the reddish kaolinitic matrix (A); of the transition zone between the clay matrix and the manganese nodule (B); of the core of the manganese nodule (C).

in the ideal lithiophorite (whose extended crystal formula is  $\text{Al}_4\text{Li}_6(\text{OH})_{42} \cdot \text{Mn}_3^{2+}\text{Mn}_{18}^{4+}\text{O}_{42}$ ), the  $\text{Mn}^{2+}/\text{Mn}^{4+}$  atomic ratio (3/18) in the Mn octahedral sheet is directly related to the Li/Al ratio (6/14) of the gibbsitic sheet. Therefore, in the absence of Li in the latter sheet, Mn in lithiophorite is likely to be essentially tetravalent. If this assumption is correct, the simplified crystal formula of natural lithium-free lithiophorite can thus be written as  $\text{Al}_2\text{Mn}_3\text{O}_9 \cdot 3\text{H}_2\text{O}$  and this simplified writing, which is close to that already proposed by De Villiers and Van der Walt (1945), will be used in the subsequent discussion.

#### DISCUSSION

A large variety of Mn oxides may form in soils and saprolites (see MacKenzie, 1977 for a review). Amongst them, however, only manganite, lithio-



TABLE I

Crystallographic data for lithioporite from the cores of manganese nodules (Azul, Brazil) (the data are mean values obtained from 7 different microsamples)

h k l	<i>d</i> observed (Å)	<i>d</i> calculated (Å)	<i>d</i> ASTM 16.364
001	9.32	9.410	9.45
002	4.68	4.70	4.71
003	3.13	3.13	3.11
111	2.36	2.35	2.37
112	2.29	2.29	2.28
112	2.10	2.11	2.13
005	1.88	1.88	1.88
115	1.59	1.58	1.57
020	1.45	1.45	1.45

Parameters calculated:	Parameters ASTM:
$a = 4.94 \pm 0.07 \text{ \AA}$	$a_0 = 5.06 \text{ \AA}$
$b = 2.90 \pm 0.01 \text{ \AA}$	$b_0 = 2.91 \text{ \AA}$
$c = 9.59 \pm 0.02 \text{ \AA}$	$c_0 = 9.55 \text{ \AA}$
$\beta = 101.18 \pm 0.06^\circ$	$\beta = 100.50^\circ$
$V = 134.76 \pm 1.65 \text{ \AA}^3$	

TABLE II

Chemical composition of lithiophorite from the cores of manganese nodules \*<sup>1</sup>

	1	2	3	4	5	6	7
SiO <sub>2</sub>	0.23	0.27	0.03	1.38	1.22	0.25	0.28
Al <sub>2</sub> O <sub>3</sub>	22.49	24.15	23.48	21.02	23.19	20.21	20.87
Fe <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	-
MnO <sub>2</sub>	63.47	59.13	60.13	59.81	61.01	66.05	62.75
MgO	-	0.02	0.03	0.04	-	0.05	-
CaO	-	0.05	0.01	0.01	0.03	-	-
BaO	0.22	0.10	0.12	0.21	0.23	0.79	0.56
CoO	0.12	0.16	0.07	0.46	0.33	0.15	0.38
CuO	0.31	0.47	0.53	0.72	0.65	0.52	0.91
NiO	-	0.03	-	-	-	0.06	-
Na <sub>2</sub> O	0.07	0.10	0.11	0.09	-	0.20	0.24
K <sub>2</sub> O	0.28	0.14	0.30	0.10	0.13	0.56	0.37
TiO <sub>2</sub>	-	-	0.01	-	0.02	0.01	-
H <sub>2</sub> O	12.81	15.38	15.18	16.10	16.19	11.11	13.63
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00

\*<sup>1</sup>Each column represents the average composition obtained on one site from 5 microprobe analyses; H<sub>2</sub>O is obtained by difference; - = below detection limit.

phorite and pyrolusite exhibit sizes large enough to allow their easy identification with either a petrographic microscope or a microprobe. Manganite, which is a  $\text{Mn}^{3+}$  oxyhydroxide, is a mineral characteristic of transition zones located in the vicinities of weathering fronts of  $\text{Mn}^{2+}$ -bearing primary minerals. On the other hand, both lithiophorite and pyrolusite are Mn oxides characteristic for more oxidizing environments (Bricker, 1965; Melfi and Pedro, 1974; Nahon et al., 1984).

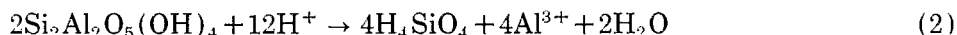
If we consider with Hem (1963) that  $\text{Mn}^{2+}$  is the major soluble Mn species present in the water tables in transit in laterites, the precipitation of either pyrolusite or lithiophorite in oxidizing conditions can be described by the following schematic equation:



where  $\text{MnO}_2$  stands for either pyrolusite or for the Mn octahedral sheet of lithiophorite.

Eq. 1 shows that the precipitation of any  $\text{Mn}^{4+}$  oxide at the expense of  $\text{Mn}^{2+}$  solutions is a process releasing two protons for each  $\text{Mn}^{4+}$  cation incorporated in the precipitate.

If we now take into account the petrographical observations already reported (i.e. the progressive replacement of kaolinite by lithiophorite in weathering zones invaded by  $\text{Mn}^{2+}$  solutions), the major question to be answered seems to be the following. Can the protons released by the precipitation of lithiophorite play a leading role in the dissolution of kaolinite? In other words, can the two following processes, i.e. the kaolinite dissolution:



and the lithiophorite precipitation:



be two coupled reactions?

Thermodynamic diagrams depicting the stability of kaolinite, gibbsite, lithiophorite and pyrolusite at 1 atmosphere and 25°C have been recently constructed by Parc et al. (1989). Fig. 5 is a cross-section in one of the tridimensional diagrams presented by those authors. It shows that, for an oxygen fugacity characteristic for oxidizing environments ( $\log f_{\text{O}_2} = -0.68$ ) and for activities of  $\text{Al}^{3+}$  and  $\text{H}^+$  controlled by gibbsite ( $\log [\text{Al}^{3+}]/[\text{H}^+]^3 = 8.205$ , Fritz and Tardy, 1974), solution conditions do exist in which the stability fields of both gibbsite and kaolinite are restricted by that of lithiophorite. This occurs where the concentration of  $\text{Mn}^{2+}$  ions is high, i.e. where the flux in soluble  $\text{Mn}^{2+}$

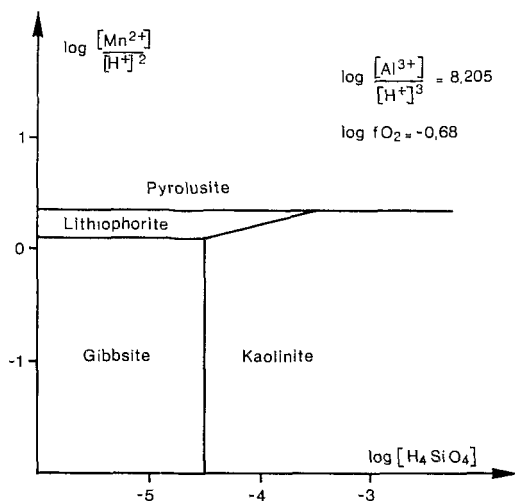


Fig. 5. Stability-field diagram of pyrolusite, lithiophorite, gibbsite and kaolinite at 25°C, 1 atmosphere for  $\log f\text{O}_2 = -0.68$  and  $\log [\text{Al}^{3+}]/[\text{H}^+]^3 = 8.205$ .

originating from water tables is important and can lead to the absolute accumulation of Mn oxides in the oxidizing zones of profiles.

The balance between eqs. 2 and 3 shows also that the replacement of kaolinite by lithiophorite is a process that makes more  $\text{Al}^{3+}$  cations soluble ( $4\text{Al}^{3+}$  in eq. 2) than necessary to precipitate lithiophorite ( $2\text{Al}^{3+}$  in eq. 2). This observation as well as Fig. 5 suggest that, in laterites where the epigenetic replacement of kaolinite by lithiophorite takes place, the formation of gibbsite and lithiophorite should be two closely related processes. Actually, it has been observed that at the top of the Mn-rich laterites (i.e. at locations where the flux in  $\text{Mn}^{2+}$  is likely to be less important than at the places where lithiophorite forms) of both the Azul area (Beauvais et al., 1987) and the Ziemougoula area (Ivory Coast) (Nahon et al., 1985), gibbsite seems to form at the expense of both lithiophorite and kaolinite.

## CONCLUSION

The morphological features reported in this paper as well as the chemical mechanism outlined in the discussion both indicate that the accumulation of Mn-oxides in lateritic profiles promotes mineralogical and geochemical changes comparable to these induced by the accumulation of iron oxides. Actually, this similarity is due to the similar behaviour of Mn and Fe cations. As with iron, manganese is translocated in solution in a reduced form. Again with iron, Mn is immobilized as oxides by reactions which imply both oxidation and hydrolysis. Finally this hydrolysis step also produces protons.

Hence, the precipitation of  $\text{Mn}^{4+}$  oxide can have a corrosive effect on alu-

mino-silicates to such an extent that, in Mn-rich laterites, an epigenetic replacement of kaolinite by lithiophorite, similar to the epigenetic replacement of kaolinite by hematite observed in Fe-rich laterites (Ambrosi et al., 1986), can occur. Because of lithiophorite is one of the major Mn compounds of soil nodules (Taylor et al., 1964), the observations reported here in a lateritic profile suggest that the epigenetic replacement of kaolinite by lithiophorite might well be a common weathering process.

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