MANGANESE CONCENTRATION THROUGH CHEMICAL WEATHERING OF METAMORPHIC ROCKS UNDER LATERITIC CONDITIONS

Daniel NAHON, Anicet BEAUVAIS and Jean-Jacques TRESCASES

Laboratoire de Pétrologie de la Surface, E.R.A. 070.220
Université de Poitiers, 86022 POITIERS CEDEX (France).

Laterite profiles developed on manganiferous metamorphic rocks in the Ziemougoula area (North West Ivory Coast) permit the observation of chemical weathering of tephroites, manganocalcites, chlorites and spessartite garnets. Several stages are observed in the progress of weathering. In the lower part of profiles, tephroites and manganocalcites alter first into manganite, followed by chlorite into todorokite then by spessartites which weather into birnessite; the Al content of the parent garnet is leached out of the zone. Higher in the profile, garnets alter directly into lithiophorite; in this geochemical environment Al is no longer mobile. In such a layer, early-formed birnessite and manganite are transformed into nsutite along with minor cryptomelane. These later minerals can locally evolve into ramsdellite or pyrolusite. The associated nsutite and lithiophorite are the principal phases of the hard manganese crust capping the hill-rocks of the lateritic landscape of the Ziemougoula area.

1. INTRODUCTION

The lateritic weathering of manganese-bearing rocks was recently studied in tropical West Africa (28). The Ziemougoula area, in the north west of the Ivory Coast was especially studied (25, 26, 1). A thick weathered cover, in which Mn oxides concentrate, develops at the expense of a Birrimian metamorphic parent rock made up of gondites and tephroitites. These formations were prospected by the Société pour le Développement Minier de la Côte d'Ivoire (SODEMI) by pits and by borings with core sampling.
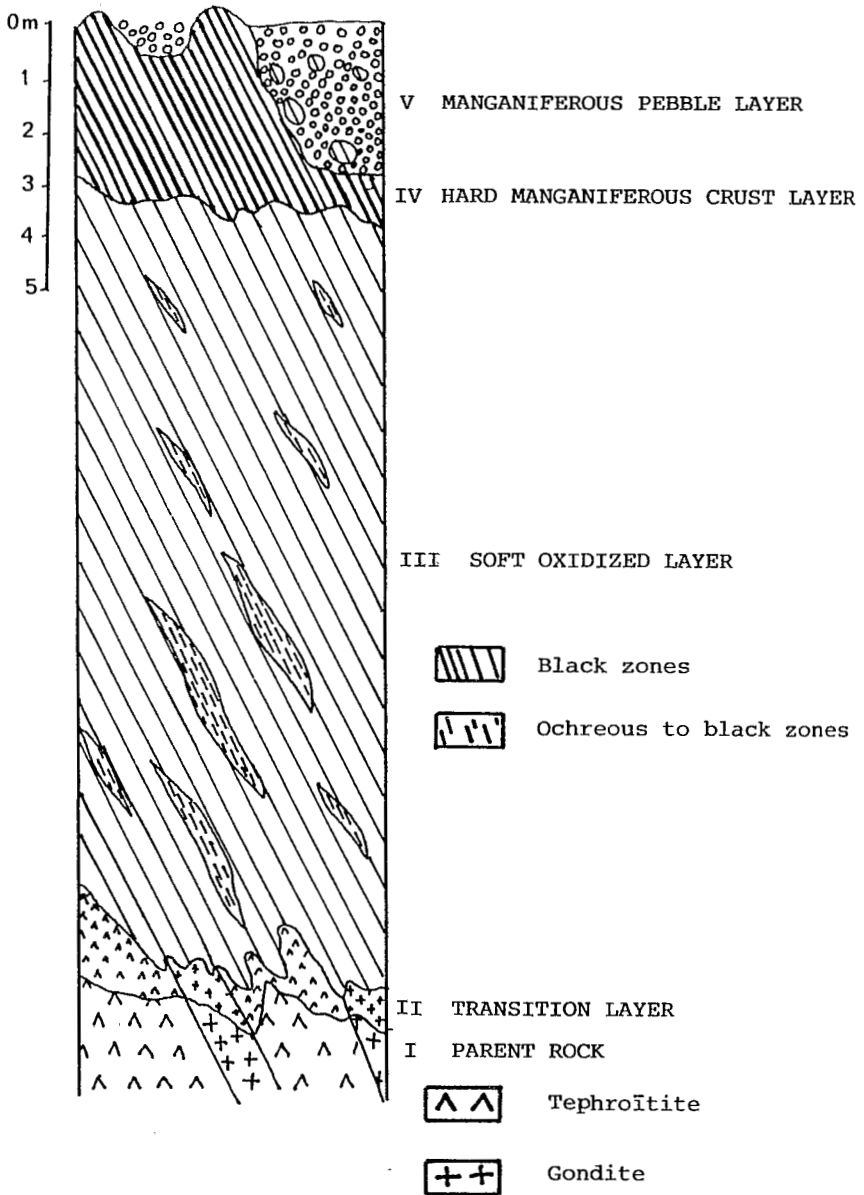
Figure 1. Sketch of weathering profile in the Ziemougoula area.

Oriented samples were collected after a detailed description of
the profiles was made in the field. These samples were studied
from a petrographic, mineralogical and chemical point of view by
standard methods using polarizing microscope, X-ray diffraction,
electron microprobe, infra-red spectrometry and scanning electron
microscopy. Through pits and borings conducted by the SODEMI, a
schematic profile can be drawn (Figure 1), showing main weathe-
ring layers developed along the profile. The study presented here
deals with the appearance and development of different weathering
stages of Mn-bearing parent minerals. The Birrimian metamorphic
rock is weathered first into soft oxidized mantle (layers II and
III, fig. 1) then in the higher part of advanced profiles into
hard manganese crust (layer IV) which is locally dismantled into
a pebble layer (layer V). The Birrimian metamorphic parent-rock
consists roughly of 50 % tephroite, 35 % spessartite garnet,
7.5 % quartz, 5 % manganocalcite, 2 % Mn-chlorite and 0.5 % sul-
fides. These minerals respond differently to weathering. Thus, at
the base of profiles, tephroite, then manganocalcite weather in
this chronologic order followed by chlorite. Mn garnets are
unweathered during these transformations and weather higher in
the profile. But the alteration of garnets differs depending on
their chemical composition; Ca-bearing garnet alters first.
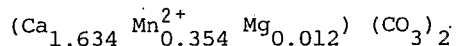
2. THE PARENT MINERALS (LAYER I)

Tephroite crystals are anhedral and tightly cemented into a
finegrained mosaic. The chemical compositions obtained by means
of microprobe yield the following average formula for the te-
phroite:

$$[(Si_{0.99}Al_{0.01})\ O_4]\ [Cr^{3+}_{0.001}\ Fe^{2+}_{0.010}\ Mn_{1.846}\ Mg_{0.136}Ca_{0.007}]$$
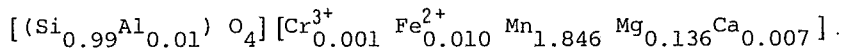
Nests of chlorite appear at the grain junctions of
tephroite crystals; from their compositions we can note the
following average formula for chlorite:

$$[(Si_{3.017}Al_{0.983})O_{10}]\ [Al_{1.068}Fe_{0.067}Mn_{0.680}Mg_{4.140}Ca_{0.002})(OH)_8]$$
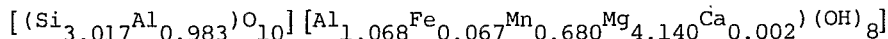
The manganocalcite evolves in patches which can locally
replace the border of other parent minerals. Thus, the mangano-
calcite appears as the last crystallized phase of the parent
rock. Here too, chemical compositions were obtained by means of
the electron microprobe. The average formula is :

$$(Ca_{1.634}\ Mn^{2+}_{0.354}\ Mg_{0.012})\ (CO_3)_2$$

Garnet crystals are euhedral and tightly cement each other
into a fine-grained mosaic arranged in thin layers or in islets
or nests included in tephroite or other parent minerals. The

	1	2	3	4	5	6	7
SiO_2	2.69	0.45	7.05	9.99	0.18	0.55	0.25
Al_2O_3	0.03	0.02	3.58	0.19	23.27	0.45	0.33
Fe_2O_3	0.10	0.08	0.13	2.07	0.18	0.40	0.02
Cr_2O_3	–	0.01	–	–	–	–	
Mn_2O_3	84.70	72.36	73.93	–	–	–	–
MnO_2	–	–	–	75.32	56.39	93.45	93.94
MgO	0.03	0.56	5.75	0.04	0.01	0.12	0.04
CaO	0.18	5.36	0.06	0.44	0.01	0.24	0.08
BaO	n.d.	n.d.	n.d.	n.d.	n.d.	–	–
CoO	0.06	0.15	0.07	0.11	0.15	0.07	0.39
CuO	n.d.	n.d.	n.d.	0.03	3.53	0.23	0.78
NiO	–	–	–	–	0.07	–	0.03
Na_2O	n.d.	0.03	n.d.	0,03	0.01	0.03	–
K_2O	–	0.03	0.01	0.06	0.01	–	–
TiO_2	–	–	–	n.d.	n.d.	n.d.	n.d.
H_2O*	12.22	20.95	9.42	11.72	16.20	4.46	4.14
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 1 – Average chemical compositions of manganiferous
oxihydroxides and oxides from weathering of parent minerals
in the manganese ore of Ziemougoula area.

1	=	Manganite from tephroite (7 analyses)
2	=	Manganite from manganocalcite (10 analyses
3	=	Oxihydroxide from chlorite (4 analyses)
4	=	Birnessite from garnet (5 analyses)
5	=	Lithiophorite from garnet (9 analyses)
6	=	Nsutite from birnessite (4 analyses)
7	=	Ramsdellite from nsutite (5 analyses)
–	=	Below detection limit
n.d.	=	Not determined
*	=	Obtained by difference

garnet phase was analysed by X-ray diffraction (main lines :
2.596 Å, 1.61 Å, 1.55 Å) and infra-red spectrometry (main lines :
937 cm^{-1}, 880 cm^{-1}, 645 cm^{-1}, 460 cm^{-1} and 370 cm^{-1}). Only spes-
sartite was identified. But the chemical compositions obtained by
means of the microprobe yield the following average formula :

$$[Si_3 O_{12}](Al_{1.998} Cr_{0.002}) (Mn_{2.657} Fe_{0.171} Ca_{0.092} Mg_{0.080})$$

These garnets of which the general formula is (Z) $R_2^{3+} R_3^{2+}$ are
actually intermediate between spessartite (88 %) and almandine-
pyrope-grossular (12 %).

3. EARLY STAGES OF MANGANESE OXIHYDROXIDE CONCENTRATION
   (LAYER II)

At the base of profile, tephroite, manganocalcite and chlo-
rite weather into either manganite or into a mixture of Mn oxi-
hydroxide + kaolinite. These transformations lead to a few-centi-
meters-thick weathering layer in which about half of the rock
remains unweathered.

3.1. The transformation of tephroite into manganite

In some pits we have noted an ephemeral weathering of
tephroite into Mn^{2+} smectites (24) which precedes the manganite
stage. But generally the manganite appears as the first product
of the replacement of tephroite. These modifications begin in
microfissures traversing tephroite crystals and develop as a
mosaic of euhedral manganite crystals easily recognized under
reflected light. Table 1 gives the average chemical compositions
obtained on such manganite with the electron microprobe (7 analy-
ses). One can note that silica is not entirely leached when
manganite appears. The irregular distribution of silica among
manganite crystals suggests a scattering of microconcretions of
SiO_2. In addition the pattern of distribution of Si shows that
silica is more abundant near the edges of unweathered tephroite.

3.2. The transformation of manganocalcite into manganite

A well crystallized manganite mosaic develops from cross-
cleavages and microfractures towards unweathered manganocalcite,
progressively isolating residual fragments of the parent carbona-
te. Each fragment retains the crystallographic orientation of the
origininal carbonate. This proves the in situ weathering of man-
ganocalcite. The compositions of these manganite crystals (Table
1) compared to that of manganocalcite enlightens us regarding the
source of the silica impurities. As the parent manganocalcite is
almost depleted in this element, we can consider a silica trans-
port from the surrounding tephroites which weather at the same
time as the manganocalcite.

3.3. The transformation of chlorite into Mn-oxihydroxides

The chlorite crystals show a progressive buckling and open-ing up of the lamellae as a Mn-oxihydroxide weathering plasma develops at the expense of the lamellae. Analyses of hand-picked weathered chlorites from crushed rocks, by X-ray diffraction and infra-red spectrometry, show that the weathering plasma consists of a mixture of Mn-oxihydroxides (todorokite) + minor kaolinite. Microprobe analyses confirm such a heterogeneity in which minute particles of residual chlorites were probably contained (Table 1).

4. DEVELOPMENT OF THE MANGANESE OXIDE LAYERS (LAYERS III and IV)

From the base to the top of profiles, all the parent mine-rals weather progressively into a Mn-oxide plasma, to such an extent that few parent relicts still occur near the surface. In fact, the intense concentration of Mn oxides in this part of pro-files is the result of (i) the progressive transformation of garnet crystals, (ii) the dissolution of quartz grains. Petrogra-phic analysis reveals that the early transformation begins at grain boundaries and in microfissures traversing garnet crystals, along which sulfides can occur. From boundaries of euhedral grains and fissures, a manganiferous matrix appears and spreads out at the expense of garnet. With the advance of weathering, etching patterns (corrosion pits, cracks...) get more numerous, filling with manganiferous matrix which reaches deeply into garnet grains and cuts them into several portions. In situ alte-ration of garnets leads progressively to a complete replacement of garnets by the manganiferous matrix through pseudomorphic relations. However, the products of the transformation of garnets are different depending on the degree of advancement of weathe-ring.

4.1. Transformation of garnets into birnessite

The first stage of garnet weathering consists of formation of a mixture of birnessite + amorphous silica. Birnessite is recognized under reflected light by intense pleochroism and strong anisotropy and by infra-red spectrometry (30) with adsorp-tion bands at 1100-1000 cm^{-1}. X-ray diffraction spectra seem to indicate a poorly-crystallized birnessite, probably mixed with todorokite or Z α-manganate phase. The main peaks on X-ray dia-grams are 9.567 Å (ASTM n° 18-1411, gives 9.65 Å for todorokite), 7.332 Å, 3.627 Å, 2.401 Å, with 2.401 Å best developed, and 7.332 Å, 3.627 Å, poorly developed. (5, 12, 6) show that the broadened 7-7.2 Å and 3.5-3.6 Å peaks correspond to poorly-crys-tallized birnessite, or to a mixture with other minerals. The

average chemical analysis of such birnessites (Table 1) permits us to note the following facts.

- One can note that silica is not entirely leached when birnessite appears. The irregular distribution of silica in the birnessite matrix suggests a scattering of amorphous silica intimately mixed with cryptocrystalline birnessite. The birnessite matrix alternates with dark zones, becoming isotropic when they are well segregated. Microprobe point analyses and patterns of Si distribution demonstrate clearly that the dark isotropic zones are strongly enriched in silica. Chemical analyses have been made with the microprobe, in a zone where garnets are the dominant parent mineral and where the birnessite matrix develops in corrosion embayments of garnets. This suggests that the retention of silica is related to areas of lower permeability.

- On the other hand, Al is strongly leached during the weathering of garnets, as one can observe in comparing the birnessite composition to that of the parent garnets (Table 1). It is clear that in this part of the weathering profile, geochemical microenvironments occur in which Al is mobile and birnessite evolves. This mobility of Al is probably linked to the weathering of sulphides occurring in fissures and grains boundaries and which alter at the begining of garnet weathering, resulting in a strong decrease in pH.

4.2. The transformation of garnets into lithiophorite

Higher in the profiles one observes a second stage in the weathering of garnets. Both relics of garnets, not entirely or still not altered into birnessite, weather into lithiophorite. In fact, lithiophorite appears as the main constituent, but always along with goethite. With the advance of weathering, one can observe every stage reached in the transformation of garnets : (i) unweathered garnets in the birnessite matrix; (ii) garnets partly altered at their peripheries or in their cores into lithiophorite; (iii) patches of lithiophorite occurring in the birnessite matrix. This indicates a change in the progressive alteration of a same garnet, i.e. weathering into birnessite during an earlier stage, and weathering into lithiophorite higher in the profile. There is pseudomorphic replacement of lithiophorite after garnets which follows the early pseudomorphic replacement of birnessite after garnets. The lithiophorite phase is well characterized by infra-red spectrometry (3510 cm^{-1}, 550 cm^{-1}) and X-ray diffraction (9.478 Å, 4.68 Å, 2.356 Å, 2.122 Å and 1.868 Å). Goethite appears either intimately mixed with cryptocrystalline lithiophorite, or is well differentiated into micronodules or into septa localized principally at the periphery of altered garnet. X-ray patterns show a slight displacement of the

main peaks, indicating Al substitution in the lattice. Fifteen goethites were studied. The degree of substitution is about 20 mole % of Al(OH)$_3$ in goethites. This is confirmed by microprobe analysis. The well crystallized mosaic of lithiophorite was analyzed by the electron microprobe. Average chemical composition is given in Table 1. One can note the high aluminum contents of such lithiophorite and the relative enrichment in copper. This Cu content of the lithiophorite of Ziemougoula is greater than those indicated by (9). Calcium, if present, and silica are strongly leached with respect to parent garnets; meanwhile Al and Mn keep an almost uniform distribution. The geochemical environment in which garnets weather is different from the underlying one where silica is not entirely leached and aluminum is mobile. In this latter environment a birnessite matrix develops.

4.3. Nsutite formation

As lithiophorite appears and develops at the expense of garnets one observes a destabilization of early-formed birnessite and manganite. Minute zones of nsutite + cryptomelane matrix begin to evolve in microfissures and cracks traversing the birnessite and manganite matrix. Nsutite + cryptomelane matrix rapidly develops at the expense of birnessite, progressively isolating irregular volumes of birnessite matrix and preserving zones of lithiophorite in the transforming mass. The nsutite + cryptomelane matrix consists of a cryptocrystalline phase in which the two minerals are tightly cemented, causing a strong induration on a field scale (manganese crust or "mangcrete"). Nsutite and cryptomelane have been characterized by X-ray diffraction and by observation under the reflecting microscope. The main X-ray peaks are for nsutite: 3.964 Å, 2.411 Å, 2.332 Å, 2.124 Å, 1.628 Å; and cryptomelane: 4.902 Å, 3.101 Å, 2.390 Å. Nsutite is the predominant phase and was analyzed (Table 1). The nsutite + cryptomelane matrix near fissures can be transformed into well-crystallized fan-shaped ramsdellite (Table 1). Locally, patches of pyrolusite may develop in the form of a well crystallized euhedral mosaic. Though scarce, this indicates a possible development of pyrolusite at the expense of nsutite + cryptomelane matrix.

Lithiophorite persists to the top of the profile as patches clearly separated from nsutite, or intimately mixed with it along sometimes with scarce relicts of garnets. Both oxides comprise the hard manganese crust which crops out in the Ziemougoula area. When this manganese crust breaks up to form a pebbly layer, one notes under the microscope many fissures crossing the indurated rock. Fissures are covered or filled with gibbsite crystals which are perpendicular to the walls. We chose clear crystals of gibbsite for microprobe analysis, nevertheless chemical analysis

show the presence of small quantities of iron and/or manganese
($Al_2O_3 \simeq 66$ %, $Fe_2O_3 \simeq 1$ %, $Mn_2O_3 \simeq 0.7$ %). This is probably Fe
and Mn substituted in gibbsite, as suggested by the slight shift
of main peaks on X-ray patterns (d_{002} : 4.81 to 4.83 Å).

5. DISCUSSION

5.1. Manganite formation in the weathering environments of Ziemougoula

Manganite could be hypogene, in veins or in diagenetic
stratified bodies, or supergene and generated by weathering of
such minerals as rhodochrosite $MnCO_3$ and rhodonite $MnSiO_3$ (18).
Through examples chosen in tropical and equatorial zones, one can
note that manganite is effectively generated from the weathering
of rhodochrosite as in Africa at Nsuta (28), at Moanda (27) or as
in Brazil at Conseilheiro Lafaiete (19, 2). Furthermore manganite
appears as the weathering product of Mn-pyroxenoids and Mn-
garnets (2).

In other cases, manganite has been noted in lateritic
profiles without references to the possible parent mineral (8;
31). Manganite is generally not found to be an abundant phase. In
the African examples which we have studied in minute detail,
manganite occurs as millimeter- or centimeter-thick layers at the
base of profiles twenty meters thick. In weathering environments
the geochemical conditions of manganite formation are limited. It
may be preceded by hausmannite (MnO, Mn_2O_3) formation at the
expense of the parent mineral, or the manganite may be followed
by the formation of birnessite, cryptomelane, nsutite and
pyrolusite (31). The limited stability field of manganite is
corroborated by the thermodynamic data. Some values of the free
energy of formation ΔF°_f were determined for manganite, γMnOOH,
by (35, 7, 21, 3). The results obtained by different methods are
all between -557.5 kj mole^{-1} and -571.5 kj mole^{-1}; (15, 16, 17,
11, 5) generally take ΔF°_f =-557.7 kj mole^{-1} for plotting sta-
bility fields of the different manganese oxi-hydroxides in pH-Eh
diagrams. Manganite appears as an intermediate mineral between
hausmannite and pyrolusite, β-MnO_2. In fact, the other "dioxi-
des", such as birnessite, cryptomelane or nsutite are rarely
considered in that type of diagram, because of their variable
thermodynamic values. Manganite may exist only in a pH region
higher than 7.5 (at 25°C and 1 atmosphere, for log $[Mn^{2+}]$ =
-6.00); its interval of stability, in Eh terms, is 0.15 V wide,
for Eh lower than 0.55 V.

When the fugacity of CO_2 is high (log f CO_2 = -2.5 versus
-3.5 in the "normal" atmosphere), the stability field of hausman-
nite is completly covered by that of rhodochrosite $MnCO_3$. In a

log f O_2 versus log $[Mn^{2+}]/[H^+]^2$ diagram, (4) shows that the field of manganite, between rhodochrosite and pyrolusite, is limited to between log f O_2 = -23 (for log $[Mn^{2+}]/[H^+]^2$ = 10.4) and log f O_2 = -18 (for log $[Mn^{2+}]/[H^+]^2$ = 9.3). Thus manganite appears as a transition phase between the carbonate of reducing environments and the dioxides of oxidizing environments. Chemical analyses show that: (i) the chemical composition of manganite is different for different parent materials; (ii) manganite crystallizes in microenvironments where foreign elements, such as Si, Ca, Mg, are present in weathering solutions; (iii) the purest manganite crystals are located in veins, cracks or fissures. Manganite crystals originating from manganocalcite are chemically different from those originating from tephroite. Each parent carbonate or silicate mineral is pseudomorphically replaced by manganite. This process of replacement includes both dissolution of the parent mineral and precipitation of the new Mn^{3+} phase. It is essentially congruent initially, and some of the Ca, Mg and Si (and other transition metals) are trapped and are either adsorbed to manganite crystals for Mg and Ca, or reconcentrated into microsilicifications (23, 25).

5.2. The chemical weathering of Mn-garnets

The garnets of the parent rocks in the Ziemougoula area consist essentially of spessartite (i.e. Al-Mn garnets). But some of them show an enrichment of Ca, particularly concentrated at their periphery. This slight chemical difference, probably due to compositional variations in the original sediment involved in Birrimian metamorphism, is sufficient to cause different reactivities of Ca-bearing and Ca-depleted garnets in lateritic weathering. The former begin to alter in the low part of the profile and continue to transform (if they are not entirely weathered) up the profile when spessartites, _sensu stricto_, commence to weather. It is clear that this behaviour of garnets plays a role in differentiating two stages in the lateritic transformation. However, the low content of Ca cannot entirely explain the evolution of the different manganese oxihydroxides that one observes. Even when garnets contain Ca they show significant Al contents ($\simeq$ 20 % Al_2O_3). It is likely that the geochemical environment changes as weathering proceeds. In this interpretation the behaviour of garnet during weathering differs in each zone and results in Al-depleted manganese oxihydroxides in one, and in Al-bearing oxihydroxides in the other. Thus garnets in a first stage alter into birnessite probably along with todorokite, and in a second stage into lithiophorite along with Al-goethite.

Birnessite is a naturally occurring poorly crystalline oxide (20), the common form of mineralized manganese in soils (33). In lateritic weathering profiles in Brazil, birnessite appears as a sparsely developed secondary product in the Conseil-
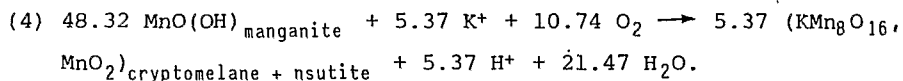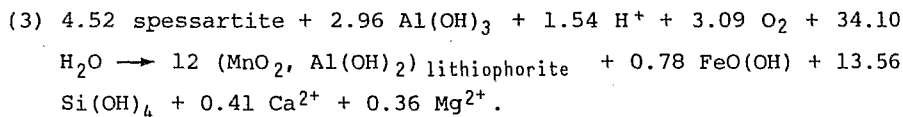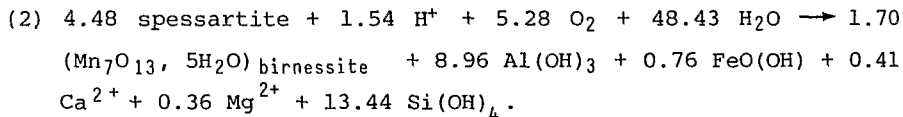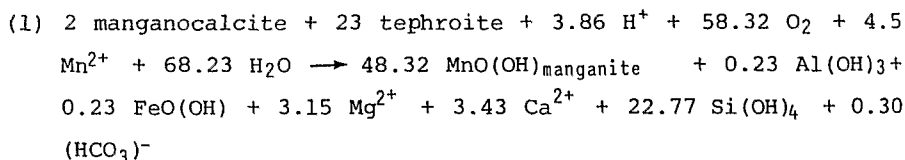
heiro Lafaiete area (19, 2, 22), where it originates from a pos-
sible transformation of manganite. Frondel et al. (10) have noted
the presence of mixtures of birnessite and γ type MnO_2 generated
from spessartite or rhodochrosite. In Tambao (Northern Upper
Volta), Perseil and Grandin (28) stress that the presence of bir-
nessite is generally linked to the first stage of rhodochrosite
weathering. In Ziemougoula, birnessite occurs in weathered zones
situated in the lower parts of profiles, and derives from garnets
of spessartite type by pseudomorphous replacement. Some of the
Ca, Mg and Si (and other transition metals) are trapped with the
birnessite. Microprobe data show clearly that SiO_2 is extra-
structural, and corresponds to amorphous microsilicification
showing that birnessite crystallizes in environments where silica
is not entirely leached, i.e., in a constricted microsystem.
Moreover, in view of the phyllomanganate structure of birnessite,
the incorporation of ions such Mg and Ca in the lattice is possi-
ble as attested by the regular distribution of these elements.
Considering the percentage of Al in the garnets, it is clear that
birnessite is formed in a geochemical environment in which alumi-
num is leached. This seems to characterize the lower part of
Ziemougoula profiles, where sulfides alter simultaneously, and is
the reason why lithiophorite appears higher in the profiles and
contains Cu. Todorokite is presumably present admixed with bir-
nessite. Todorokite is known as a supergene mineral in altered
metamorphic rocks containing spessartite in Bahia (Brazil) (10).
In the soil environment, however, todorokite appear to be unsta-
ble, and could be regarded as the hydrated precursor of birnessi-
te (13, 14).

The second stage reached in the progress of garnet weather-
ing consists of development of lithiophorite along with small
quantities of Al-goethite. Lithiophorite may incorporate foreign
ions and although Mn is predominantly tetravalent, the Mn^{4+}/Mn^{2+}
ratio can vary. Lithiophorite is essentially of supergene origin.
It is one of the major manganese compounds of soil nodules (33,
34, 36). In West Africa lithiophorite is present in lateritic
weathering profiles as a pseudomorphic replacement of spessartite
in the gondites of Mokta (Ivory Coast), Tambao (Upper Volta),
Nsuta (Ghana) (28). For these latter authors, the lithiophorite
would correspond to a transition with other Mn compounds stable
in the oxidation zone such as cryptomelane, nsutite and ramsdel-
lite. At Ziemougoula our observations are at variance with those
described in other West African manganese deposits. Here lithio-
phorite is formed in a geochemical environment where aluminum
released by weathering of garnets is abundant and not mobile.
Furthermore, lithiophorite does not appear as an evolution of the
early formed birnessite but appears at the second stage from the
direct transformation of garnets, in a single layer of the profi-
le, in which aluminum is not leached. Here, at Ziemougoula, nsu-
tite (along with cryptomelane) appears only as the alteration

product of early-formed birnessite or manganite, i.e. from a Mn-matrix depleted in alumina. Such an evolution can locally proceed to ramsdellite or pyrolusite, driving the oxidation process to completion (5). This transformation of birnessite and manganite into nsutite (γ MnO$_2$) was often noted in manganese deposits of West Africa, Brazil and France by Perseil and Giovanoli (29), and in Ghana by Sorem and Cameron (32).

At Ziemougoula, nsutite and lithiophorite formed in this way are associated making up the manganese crust which caps the hills of Ziemougoula landscape. At the top of profiles the manganese crust can be locally dissolved forming a discontinuous pebbly layer made up of relict pebbles of manganese crust in a red clay matrix consisting of gibbsite and Al-goethite (1). The manganese leached from the pebbly horizons can precipitates down-slope in the sequence, or lower in the profiles, and contribute to form crystallized oxides or oxihydroxides.

In conclusion, the different chemical transformations of Mn^{2+} bearing parent minerals and the secondary evolution of bir-nessite and manganite are isovolume transformations and could be indicated under the form of a sketch representing weathering of average parent rock (Figure 2) and through the following reactions :
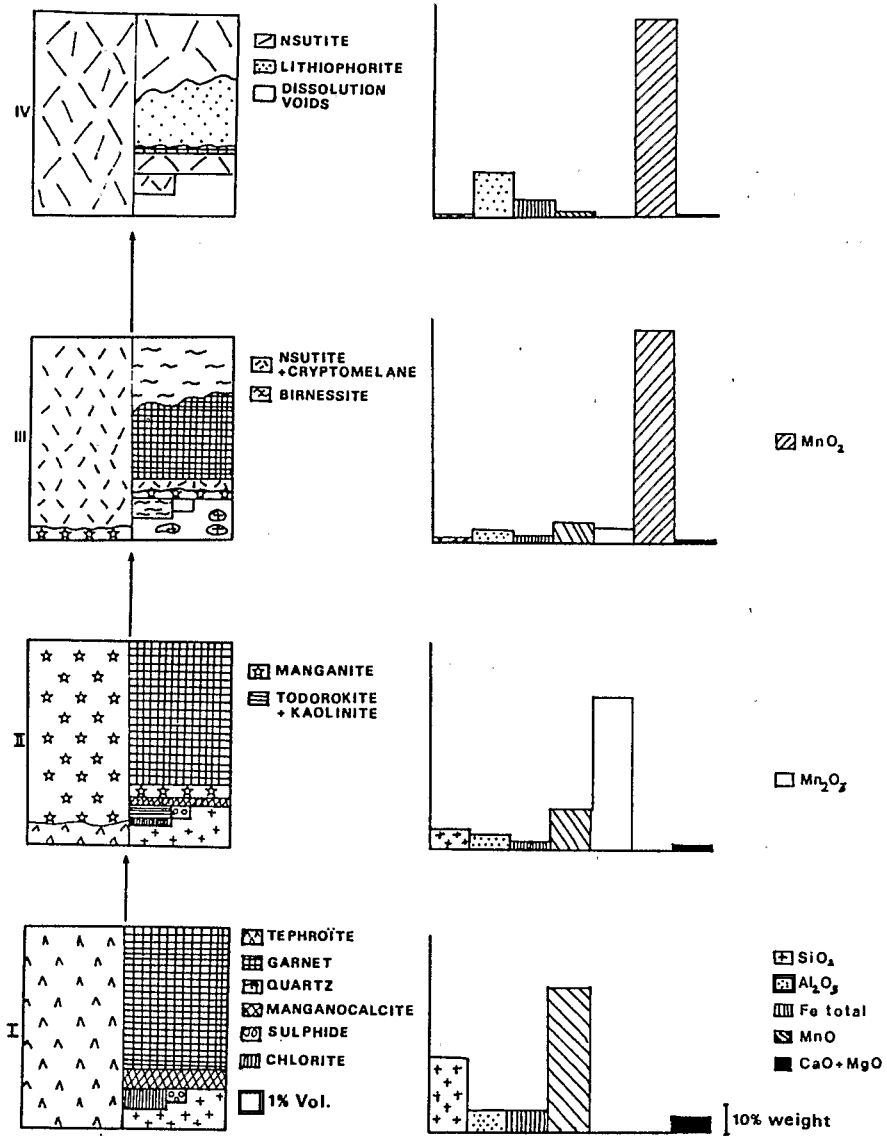
(1) 2 manganocalcite + 23 tephroite + 3.86 H$^+$ + 58.32 O$_2$ + 4.5 Mn^{2+} + 68.23 H$_2$O $\longrightarrow$ 48.32 MnO(OH)$_{manganite}$ + 0.23 Al(OH)$_3$+ 0.23 FeO(OH) + 3.15 Mg^{2+} + 3.43 Ca^{2+} + 22.77 Si(OH)$_4$ + 0.30 (HCO$_3$)$^-$

(2) 4.48 spessartite + 1.54 H$^+$ + 5.28 O$_2$ + 48.43 H$_2$O $\longrightarrow$ 1.70 (Mn$_7$O$_{13}$, 5H$_2$O)$_{birnessite}$ + 8.96 Al(OH)$_3$ + 0.76 FeO(OH) + 0.41 Ca^{2+} + 0.36 Mg^{2+} + 13.44 Si(OH)$_4$.

(3) 4.52 spessartite + 2.96 Al(OH)$_3$ + 1.54 H$^+$ + 3.09 O$_2$ + 34.10 H$_2$O $\longrightarrow$ 12 (MnO$_2$, Al(OH)$_2$)$_{lithiophorite}$ + 0.78 FeO(OH) + 13.56 Si(OH)$_4$ + 0.41 Ca^{2+} + 0.36 Mg^{2+}.

(4) 48.32 MnO(OH)$_{manganite}$ + 5.37 K$^+$ + 10.74 O$_2$ $\longrightarrow$ 5.37 (KMn$_8$O$_{16}$, MnO$_2$)$_{cryptomelane + nsutite}$ + 5.37 H$^+$ + 21.47 H$_2$O.

Figure 2. Sketch of mineralogical and chemical evolution of the weathering profile of the Ziemougoula area.

(5) $1.70 \ (Mn_7 \ O_{13}, \ 5 \ H_2O)_{birnessite} \ + 1.32 \ K^+ + 0.5 \ O_2 \longrightarrow 1.32$
   $(KMn_8O_{16})_{cryptomelane + nsutite} \ + 1.32 \ H^+ + 7.84 \ H_2O.$

(6) $6.69 \ (KMn_8O_{16}, \ MnO_2)_{cryptomelane + nsutite} \ + 6.69 \ H^+ + 1.67 \ O_2 \longrightarrow$
   $60.21 \ MnO_{2 \ nsutite} + 6.69 \ K^+ + 3.345 \ H_2O.$

(7) $12 \ (MnO_2, \ Al(OH)_2)_{lithiophorite} + 24 \ H^+ \longrightarrow 12 \ Al(OH)_{3 \ gibbsite} \ +$
   $12 \ Mn^{2+} + 3O_2 + 6 \ H_2O.$

This indicates that under lateritic conditions, alumina accumula-
tes in the upper part of weathering profile associating with Mn
or Fe to form oxides and oxihydroxides.

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(The) Chemistry of Weathering

edited by

James Irving Drever
The University of Wyoming,
Department of Geology and Geophysics,
Laramie, Wyoming, U.S.A.

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