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CHEMICAL WEATHERING OF ORTHOPYROXENES UNDER LATERITIC CONDITIONS

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ABSTRACT. The chemical weathering of orthopyroxenes under lateritic conditions in the Western Ivory Coast shows three main stages. The first stage is facultative and consists of the appearance of amorphous products, the chemical composition of which is very near that of the parent mineral. The second stage is marked by the occurrence of smectites + ferruginous talc-like minerals. The smectites range between di- and trioctahedral series, and their chemical compositions tend either toward the beidellite–nontrolite series or saponite. The third stage appears in the upper part of the soil profiles. It is an iron oxi-hydroxide stage in which well-crystallized goethite is found.

INTRODUCTION

Ultramafic rocks have been discovered in the Western Ivory Coast by the Société de Développement minier de la Côte d'Ivoire: S.o.d.e.m.i. (Sipilou and Moyango areas). Studies in pits have permitted the description of a thick weathering mantle (Mathez, 1976; Kadio, 1976; Nahon, 1977, 1978; Nahon, Paquet, and Delvigne, 1982) developed at the expense of a parent rock, which consists of serpentinized dunite with some local facies of harzburgite, peridotites, and pyroxenites. Here we present preliminary results obtained from studying the chemical weathering of orthopyroxenes. Studies have been conducted in areas with tropical climate with a long wet season and an annual rainfall rate of 1600 mm.

METHODS

Samples were studied by standard petrographic, mineralogical, and geochemical methods: polarizing microscope, X-ray diffraction, scanning electron microscope (SEM), microprobe, and Mössbauer spectrometry. All techniques were employed on undisturbed samples. In addition, pyroxenes were hand picked under the binocular microscope. In this case, the weathering products were extracted from these pyroxenes by ultrasonic cleaning, then dried, and prepared for X-ray analyses. Pyroxene isolates were also crushed, separated into several fractions, and analyzed by X-ray diffraction, chemical methods, and Mössbauer spectrometry.

RESULTS OF OBSERVATIONS

The parent minerals.—The parent rock is a finely granular pyroxenite (websterite variety) which consists essentially of orthopyroxenes (enstatite and sometimes bronzite) as identified by microprobe analyses. The average formulae obtained are the following:

enstatite: $[(Al_{0.029}\ Fe_{0.174}\ Cr_{0.028}\ Mg_{1.714}\ Ni_{0.003}\ Ca_{0.038})(Si_{1.949}\ Al_{0.051})\ O_6]$;

bronzite: $[(Al_{0.018}\ Ti_{0.03}\ Fe_{0.297}\ Cr_{0.018}\ Mg_{1.657}\ Ni_{0.003})(Si_{1.921}\ Al_{0.079})\ O_6]$.

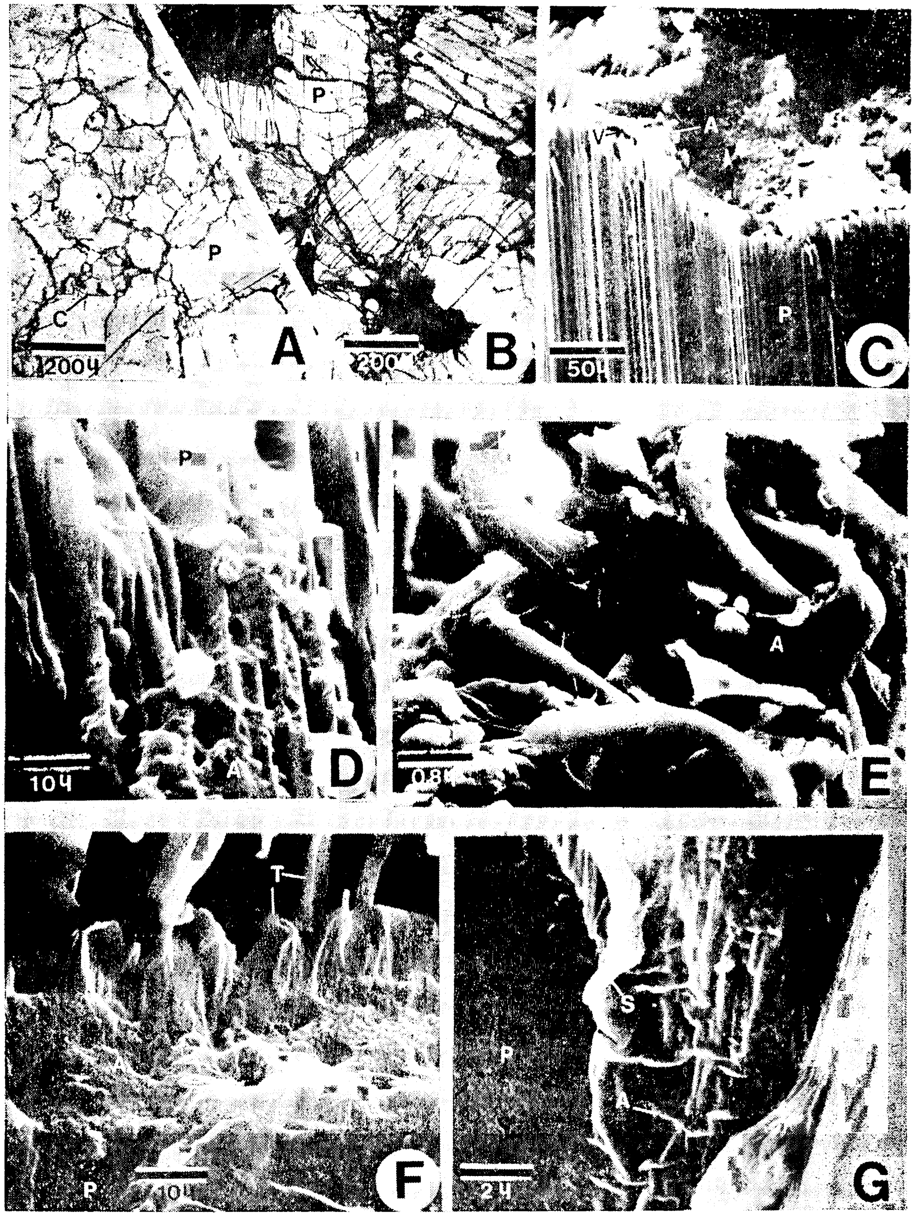
Under the optical microscope, in plane light, the pyroxenes are translucent and appear as subhedral and for the smallest grains anhedral crystals. Longitudinal sections (010 and 100) show unique and thin traces of different cleavages. Transverse or subtransverse sections present approximately two gross orthogonal cleavages (110) and thinner and more regular cleavage (010). These crystals are colorless or straw-colored to brown yellow with slight pleochroism. The dark colors usually underlie cleavages and cracks but sometimes are randomly distributed in diffuse stains. Cracks and fissures run across the crystals and are either confined to one crystal (intramineral cracks) or cut the rock (transmineral fissures) (see pl. 1-A). Minute and discontinuous inclusions occur widely in cracks and fissures, as well as in grain-boundary fractures, where they are sometimes associated with lizardite. These inclusions are opaque, gray, brown, or black and consist of iron oxide (magnetite) and chromite crystals as determined by microprobe results. Many cracks and fissures, however, remain clean.

First stage of pyroxene weathering.—The weathering of pyroxene originates from the voids where solutions penetrate but varies in intensity according to the kinds of voids. The first stages of pyroxene weathering appear along the boundaries of transmineral fissures, which are the most open fissures. Afterward, the weathering affects pyroxenes at the walls of grain-boundary fractures, then from intramineral sites (cleavage planes, cracks, et cetera). In any case, a thin weathered "amorphous zone" gray to colorless in plane light, isotropic under crossed polarizers, and X-ray amorphous appears at the pyroxene margin (see pl. 1-B). This zone consists, under optical microscope, of minute worm-shaped products or most often of agglomerates, less than 1μ in diameter. S.E.M. observations show that these amorphous products are either fibers of irregular thickness or, most often, shapeless aggregates (see pl. 1-C, -D, -E, -F, -G). The fibers tend to curl and can intertwine. Within them a fine porosity is developed. The fiber and aggregate surfaces are usually smooth, sometimes finely striated or rough.

Morphologically these noncrystalline constituents look like fibers and aggregates defined in the weathering products of volcanic rocks as imogolite and allophane by Yoshinaga and Aomine (1962), Wada (1966, 1977), Yoshinaga, Yotsamoto, and Ibe (1968), Grim (1968), Russell, MacHardy, and Fraser (1969), Eswaran (1972), Henmi and Wada (1976). However, these non-crystalline products show large differences with respect to imogolites and allophanes. Microprobe analyses show that the chemical composition is very similar to enstatite, although there are small differences: MgO decreases ($\sim$ 6 percent), and there is a relative increase of the other elements: SiO_2 ($\sim$ 2 percent), CaO ($\sim$ 2 percent), Al_2O_3 ($\sim$ 1 percent) and FeO ($\sim$ 2 percent).

Here these products are "amorphous" and have to be considered as a *facultative* transition product between unweathered pyroxenes and a secondary clayey phase that we describe below. Indeed, facultative means that these amorphous products appear only at the bottom of the weather-

PLATE 1



(A) Unweathered parent orthopyroxenes (P). C are cracks and fissures. Thin section in plane light.

(B) Orthopyroxenes (P) weathered to amorphous products along cracks and fissures. Thin section under crossed polarizers.

(C) Thin weathered amorphous skin (A) on orthopyroxenes (P). Note development of porosity (V) between P and A. Scanning electron photomicrograph.

(D) Weathering of orthopyroxene (P) to amorphous product (A). The bare surface of P is affected by dissolution etch pitting (see Berner and Schott, 1982). Scanning electron photomicrograph.

(E) Worm-shaped amorphous products (A) from weathering of orthopyroxenes. Scanning electron photomicrograph.

(F) Weathering of orthopyroxene (P) to agglomerates of amorphous product (A), then to talc (T). Scanning electron photomicrograph.

(G) Weathering of orthopyroxene (P) to amorphous product (A) then to smectites (S). Note minute worm-shaped amorphous product developed at the expense of the bare surface of P. Scanning electron photomicrograph.

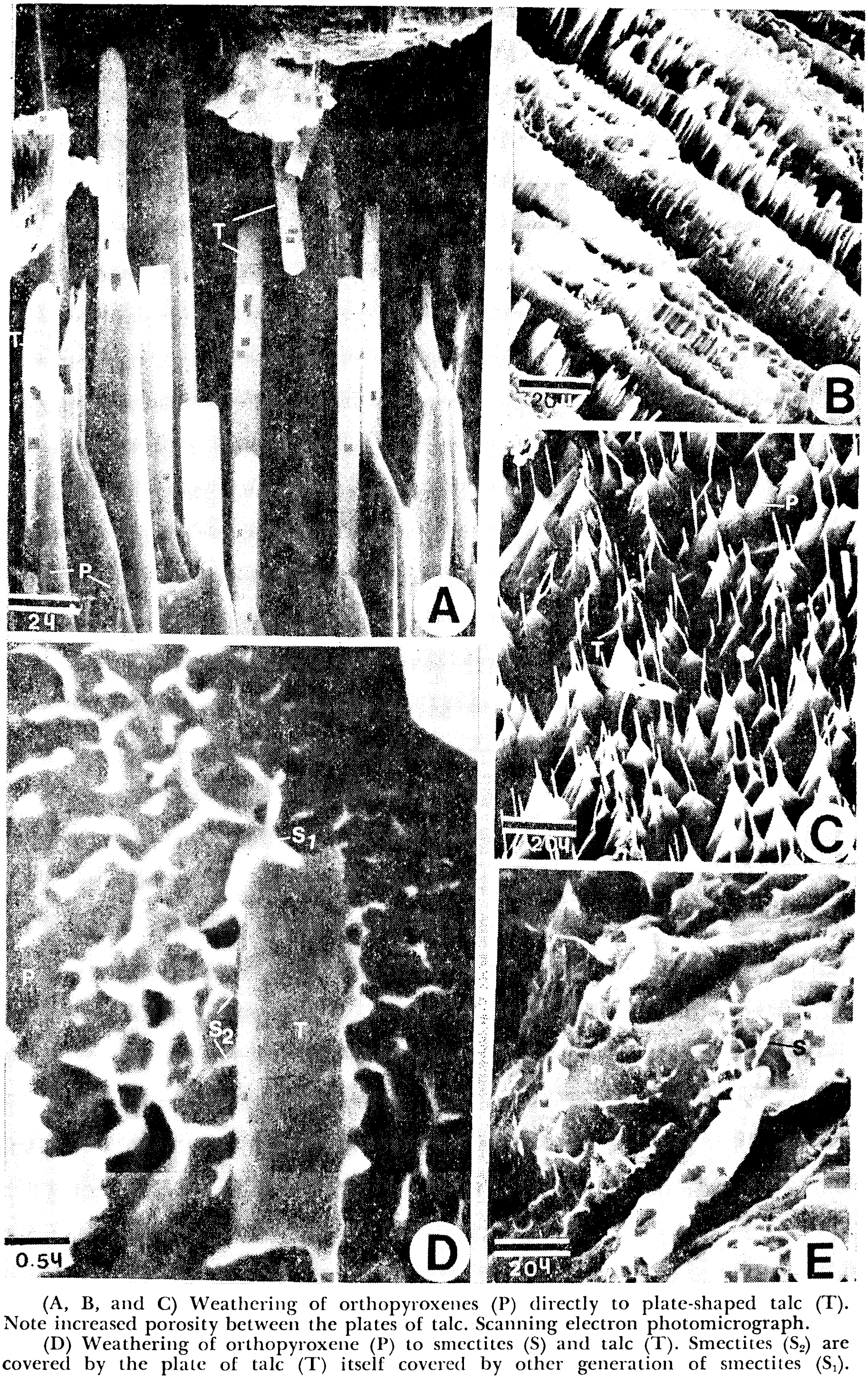
PLATE 2

(A) Weathering of orthopyroxenes (P) to phyllosilicates (wp). Weathered products are developed from cracks and fissures at the expense of orthopyroxenes. Thin section in plane light.

(B) Weathering of orthopyroxene (P) to phyllosilicates (wp), then to iron oxi-hydroxides (ox). Note that orthopyroxene is cut into several pieces which keep the same crystallographic orientation as the original grain. Thin section under crossed polarizers.

(C) Weathering of orthopyroxene to agglomerates of amorphous product (A), then to smectites (S) and talc (T). Note arrangement of smectites in honey-comb structure and talc in small plates. Scanning electron photomicrograph.

PLATE 3



(A, B, and C) Weathering of orthopyroxenes (P) directly to plate-shaped talc (T). Note increased porosity between the plates of talc. Scanning electron photomicrograph.

(D) Weathering of orthopyroxene (P) to smectites (S) and talc (T). Smectites (S_2) are covered by the plate of talc (T) itself covered by other generation of smectites (S_1). Scanning electron photomicrograph.

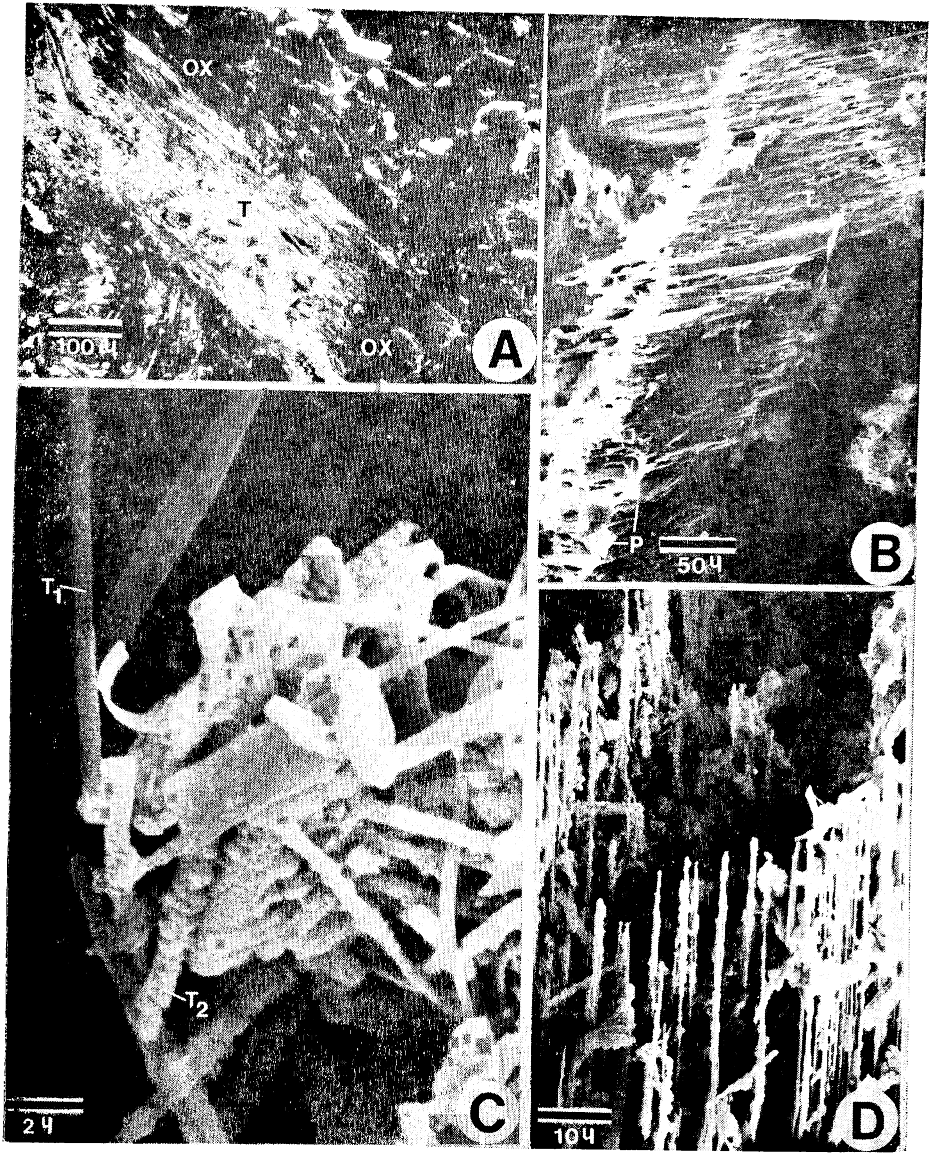
(E) Weathering of orthopyroxene (P) directly to smectites (S). Scanning electron photomicrograph.

ing profiles and particularly consist of a well-developed phase at the bottom of weathering profiles situated downslope of the sequence studied. But we will see that in the upper horizon, the clayey phase develops directly from orthopyroxene without intermediary amorphous phase. It is clear that these amorphous products are linked directly to the first stage of pyroxene weathering and correspond to residual products resulting from dissolution.

Phyllosilicate stage.—As we proceed up the soil profile (that is, with increased weathering), the transition zone becomes thicker and phyllosilicates appear as weathering products distinct from amorphous material (see pl. 2-C). However, more often, phyllosilicates appear to form directly from orthopyroxenes without an intermediate stage of amorphous products (see pl. 3) at this stage of weathering. These secondary products cut pyroxenes into several pieces. Under crossed nicols all the pieces originating from one original pyroxene exhibit simultaneous extinction. This indicates *in situ* weathering of the pyroxenes (see pl. 2-A, -B). Under the polarizing microscope, the phyllosilicates consist of tightly cemented gray vermicular aggregates and fibrous-shaped minerals with high interference colors. Analysis of optical behavior combined with X-ray diffraction of the clay fraction, obtained by ultrasonic cleaning from handpicked pyroxenes, shows that the fibrous-shaped minerals are talc-like minerals and that the vermicular aggregates consist of smectites. S.E.M. observations show that talc occurs as elongated laminae as well as small plates or laths (see pl. 3); smectites appear as short, mixed, and interlocked laminae, progressively organized into honeycomb structures (see pl. 2-C). The S.E.M. observations suggest that these minerals are authigenic overgrowths on amorphous products or on the bare surface of pyroxene. Optical microscopic observations demonstrate that phyllosilicates are developed inside the original pyroxene (pl. 2-A, -B). This transformation into phyllosilicates is an "isovolumetric transformation" in the sense of Millot and Bonifas (1955), which is characterized by a conservation of the parent mineral texture (for example, talc-like minerals and smectites are pseudomorphous after enstatite).

Both the talc-like minerals and smectites appear in paragenesis. It is common to observe laminae of smectite covered with a lath of "talc," itself covered with another laminae of smectite (see pl. 3-D). For each zone studied, the talc-like mineral appears either as a mainly non-swelling mineral with a normal basal spacing close to 9.35 Å or as a mineral with small proportions of swelling layers. Details of these analyses are given by Duplay, Paquet, and Nahon (1981). When swelling layers are clearly present, the talc-like mineral must be regarded as an interstratification in which the predominent constituent has a talc structure. The talc end-member appears to be a slightly nickel bearing mineral, and it is irregularly intergrown with swelling layers. These latter could be regarded as saponite, as suggested by both X-ray diffraction analyses and chemical analyses (Allieti, 1956; Veniale and Van Der Marel, 1968; Guenot, 1970; Weaver and Pollard, 1973; Trescases, 1975).

PLATE 4



(A) Talc (T) pseudomorph after orthopyroxene, weathering to iron oxi-hydroxides (ox). Note preservation of original textures. Thin section under crossed polarizers.

(B) Talc (T) pseudomorph after orthopyroxene. Observe relicts of unweathered orthopyroxene (P). Scanning electron photomicrograph.

(C) Weathering of talc (T_1) to talc-shaped iron oxi-hydroxides (T_2). Note the progressive transformation from smooth and flexible plate of talc to puffed, and rigid plate of iron oxi-hydroxides. Scanning electron photomicrograph.

(D) Iron oxi-hydroxides pseudomorphous after plates of talc. Note increased porosity. Scanning electron photomicrograph.

Microprobe analyses of the talc-like minerals demonstrate the mixed-layer character of these minerals as shown by the average formula: $[Ca_{0.139} (Mg_{5.419}\ Ni_{0.04}\ Ti_{0.02}\ Cr_{0.129}\ Fe^{3+}{}_{0.380}) (Fe^{3+}{}_{0.401}\ Al_{0.327}\ Si_{7.272})\ O_{20}\ (OH)_4]$. Furthermore, one notes that "talc" shows a deficiency of Si^{4+} in the tetrahedral sites because of substitution by Al^{3+} and Fe^{3+}. This resembles, with some differences, the chemical analysis given by Veniale and Van Der Marel (1968) for the mixed layer talc–saponite of Ferriere in Italy.

Smectites range in composition between di- and trioctahedral series. Compositions obtained tend toward the beidellite–nontronite series (smectite 1) or in the direction of saponite (smectite 2) and that even when a single minute aggregate is analyzed. The average formulae obtained are the following:

Smectite 1: $[Ca_{0.038}\ K_{0.008}\ (Mg_{1.030}\ Ni_{0.360}\ Cr^{3+}{}_{0.450}\ Ti_{0.010}\ Fe^{3+}{}_{2.62}\ Al_{0.221})\ (Al_{0.775}\ Si_{7.225})\ O_{20}\ (OH)_4]$

Smectite 2: $[Ca_{0.809}\ K_{0.017}\ (Mg_{3.650}\ Ni_{0.095}\ Cr^{3+}{}_{0.419}\ Ti_{0.070}\ Fe^{3+}{}_{0.432}\ Al_{0.507})\ (Al_{1.423}\ Si_{6.577})\ O_{20}\ (OH)_4]$

Hence, from enstatite, the weathering process yields a "talc" + smectite paragenesis in which smectites appear as a [real] solid solution series. Under the optical microscope these smectites will display a higher relief than normal smectites, due to the presence of iron in the lattice which is in agreement with Winchell's (1945) observations. Chromium and nickel contents increase in phyllosilicates relative to enstatite with this concentration being more important in smectites than in talc. Furthermore, if we consider that in the parent mineral the chromium to nickel ratio is about 9 whereas it is 1 to 4 in the smectites, we can point to a notable increase of the nickel content with regard to chromium. Overall in smectites the nickel concentration is about thirty times higher than in enstatite while chromium concentration has only doubled.

Iron oxi-hydroxide stage.—A third stage can be reached during the continued progress of weathering. This stage appears in the upper part of the profile where horizons become browner and more ferruginous. Smectites and talc are transformed into iron oxi-hydroxides. On plate 4, we can observe the progressive transition between talc, as pseudomorphs after enstatite, and iron oxi-hydroxides which are pseudomorphous after talc. These iron oxi-hydroxides generally occur in the form of well crystallized brown goethite, but an intermediary stage can exist which consists of opaque and brown amorphous iron oxi-hydroxides which contain significant amounts of magnesium and silica. The chemical analyses of these amorphous products are variable (table 1).

Thus, we have to consider the first part of the iron oxi-hydroxide as being X-ray amorphous or very poorly crystallized but the richest in foreign elements. This stage probably corresponds to the "ferrihydrite" described by Chukhrov and others (1973) and Schwertmann and Fischer (1973) and considered by Kuhnel, Roorda, and Steensma (1978) as a very poorly crystalline ferruginous phase, able to collect foreign elements by chemisorption or substitution.

The end product of weathering is goethite which is often well-crystallized. Chemical analyses of goethite show appreciable amounts of Si, Al, Cr, and Ni. Mössbauer spectrometry analyses, performed at the Laboratory of "Physique du Solide" at Nancy (France), indicate the presence of the elements that substitute for iron, although it was not possible to separate the goethite resulting from pyroxene weathering from that generated by olivine. Although Al substitutions mask others, chemical analyses require that Ni and Cr are the elements necessary to complete the 13 mole percent deficiency in iron (Nahon, Paquet, and Delvigne, 1982). This is in agreement with Schellmann (1978) who considers that soil goethite contains substituted Ni, Al, and even Cr in its lattice. The possibility of such substitutions was demonstrated by Forestier and Chaudron (1925) for chromium and by Correns and Engelhardt (1941), Norrish and Taylor (1961), Janot and Gibert (1970) for aluminum. If so, the pattern of silicon distribution shows that this element is probably found only as minute irregular silica-rich inclusions. The substituted goethite would have been generated by the dissolution of ferrihydrite and recrystallization *in situ.* Finally, some well-crystallized goethites are almost pure, without substituted Al, but with a low Cr and Ni content. These goethites are two times more chromiferous than nickeliferous (Cr ~ 0.1 percent; Ni ~ 0.05 percent) as we can see on the chemical analysis:

SiO_2	Al_2O_3	Cr_2O_3	NiO	Fe_2O_3	TiO_2	H_2O	Total
1.15	—	0.11	0.045	87.74	0.06	10.01	99.11

Part of the nickel is probably released near the bottom of the profile at the same time as a great part of the silica.

CONCLUDING REMARKS

Berner and others (1980) have demonstrated dissolution etch pits which occur on the bare surface of weathered pyroxenes and are developed on dislocation outcrops at the grain surfaces. In addition, studies of the surface composition of ultrasonically cleaned soil grains (Berner and Schott, 1982) and of partly dissolved minerals in the laboratory (Schott, Berner, and Sjöberg, 1981) indicate that initially a very thin (~ 10 Å) cation-depleted layer forms on the surfaces of pyroxenes, but subsequently

TABLE 1

Chemical analyses of amorphous iron oxi-hydroxides

SiO_2	13.71	20.00	17.34	26.63	10.20	18.57
Al_2O_3	4.57	3.98	5.22	4.50	4.56	5.36
Cr_2O_3	2.09	1.44	1.83	0.81	1.35	1.07
NiO	1.44	1.29	1.45	1.56	1.23	1.14
Fe_2O_3	60.65	47.57	54.28	40.66	58.09	48.66
MnO	—	—	—	—	—	—
MgO	2.14	7.07	2.97	3.95	1.07	2.14
CaO	0.09	0.23	0.11	—	—	0.21
K_2O	0.01	—	0.01	0.13	—	0.03
TiO_2	0.01	—	0.20	0.03	0.03	0.01
H_2O^+	15.25	18.40	16.72	21.68	23.45	22.98
Total	99.96	99.98	100.1	99.95	99.98	99.97

this layer maintains a constant thickness so that continued dissolution is congruent. This dissolution is a surface-reaction controlled process, and it constitutes the earliest stage of weathering.

Under lateritic conditions our results show that, upon continued dissolution, an amorphous product is formed first. This is a *facultative stage.* The chemical composition of the amorphous product is near that of fresh parent mineral: one notes mainly a slight Mg depletion and a disordered *in situ* reorganization of the remaining elements. This amorphous product can be separated from the bare surface of unweathered pyroxenes by ultrasonic cleaning and, therefore, constitutes a weathering skin from which secondary phyllosilicates can be generated.

Generally phyllosilicates as weathering products of ultramafic minerals, are most often designated by the useful term "garnierite" (Pecora, Hobbs, and Murata, 1949). In this study, they consist of talc and smectites associated in the same paragenesis. Talc identified by X-ray diffraction appears as a normal talc, interstratified with a small proportion of swelling mineral. We call it "talc-like mineral." This talc, which is found in pseudomorphs after pyroxene, may be different from the talc-like mineral described by Maksimovic (1966), Brindley and Pham Thi Hang (1973), Brindley and Maksimovic (1974), Brindley, Bish, and Wan (1977), Brindley (1978), Esson and Carlos (1978), Bailey (1980) and which is regarded as kerolite, that is, a partly disordered talc.

Smectites such as nontronites are known as products of ultrabasic weathering (Sherman and Uehara, 1956; Wilshire, 1958; Trescases, 1975; Bosio, Hurst, and Smith, 1975; Brindley and De Souza, 1975); saponites or saponite-like minerals are less common but also occur as weathering products of ultrabasic minerals (Craig and Loughnan, 1964; Wiewiora, 1978). In our study petrographic, mineralogical, and geochemical analyses show that it is very difficult to characterize these clay minerals, which seem to constitute a solid-solution between the nontronite–beidellite and saponite series.

The evolution of orthopyroxene weathering ends with iron oxi-hydroxides. Here we observe that a series exists between amorphous or poorly crystallized iron oxi-hydroxide, rich in foreign elements, and particularly in silicon, and well crystallized goethite in which Al, Ni, and Cr probably substitute for iron. Each successive stage of this iron oxi-hydroxide series develops from the one formed earlier by dissolution and recrystallization *in situ* with a release of a part of the foreign elements until an almost pure goethite is obtained. During this evolution from phyllosilicates to well-crystallized goethite, Ni and Cr are progressively released to solution.

Our results show that lateritic pyroxene weathering, including both dissolution and precipitation of new phases, is essentially congruent initially, but upon continued dissolution higher in the soil profile, magnesium and then silicon are lost preferentially to iron until ultimately a layer of almost pure goethite results. This suggests that the earliest stages of weathering take place under essentially closed system conditions with later weathering involving the flushing out of cations and silica, due either to slower dissolution rates or, more probably, to an increased rate of flushing of the soil by water (for example, Berner, 1978).

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REFERENCES

Alietti, A., 1956, Il mineral a strati misti saponite-talco di Monte Chiaro (val di Taro, Appenneno Emiliano): Atti della Accad. Nazionale dei Lincei. Rendiconti Classe di Sci. fisiche Math. Naturali., Roma, v. 8, p. 201-207.

Bayley, S. W., 1980, Summary of recommendations of AIPEA nomenclature committee: Clay Minerals, v. 15, p. 85-93.

Berner, R. A., 1978, Rate control of mineral dissolution under earth surface conditions: Am. Jour. Sci., v. 218, p. 1235-1252.

Berner, R. A., and Schott, J., 1982, Mechanism of Pyroxene and Amphibole Weathering. II. Observations of soil grains: Am. Jour. Sci., v. 282,

Berner, R. A., Sjöberg, E. L., Velbel, M. A., and Krom, M. D., 1980, Dissolution of pyroxenes and amphiboles during weathering: Science, v. 207, p. 1205-1206.

Bosio, N. J., Hurst, V. J., and Smith, R. L., 1975, Nickeliferous nontronite, a 15 Å garnierite, at Niquelandia, Goias, Brazil: Clay Minerals, v. 23, p. 400-403.

Brindley, G. W., 1978, The structure and chemistry of hydrous nickel-containing silicate and aluminate minerals: Bur. Recherches géol. minières (B.R.G.M.) Bull., v. 3, p. 233-245.

Brindley, G. W., Bish, D. L., and Wan, H. M., 1977, The nature of kerolite, its relation to talc and stevensite: Mineralog. Mag., v. 41, p. 443-452.

Brindley, G. M., and Pham Thi Hang, 1973, The nature of garnierite; I. Structures, chemical compositions and color characteristics: Clay Minerals, v. 21, p. 17-40.

Brindley, G. W., and Maksimovic, Z., 1974, The nature and nomenclature of hydrous nickel-containing silicates: Clay Minerals, v. 10, p. 271-277.

Brindley, G. W., and Souza, J. V., De, 1975, A golden-colored ferri-nickel chloritic mineral from Morro do Niquel, Minas Gerais, Brazil: Clay Minerals, v. 23, p. 11-15.

Chukhrov, F. V., Zvyagin, B. B., Ermilova, L. P., and Gorshkov, A. I., 1973, New data on iron oxides in the weathering zone: Internat. Clay Conf., Madrid, Proc., v. 1, p. 397-404.

Correns, C. W., and Engelhardt, W. V., 1941, Röntgenographische Untersuchungen über den mineralbestand sedimentärer Eisenerze: Nachrichten der Akad. Wiss. Göttingen, Math.-physik. Klasse, v. 2, p. 131-137.

Craig, D. C., and Loughnan, F. C., 1964, Chemical and mineralogical transformations accompanying the weathering of basic volcanic rocks from New South Wales: Australian Jour. Soil Research, v. 2, p. 218-234.

Duplay, J., Paquet, H., and Nahon, D., 1981, Variations in the composition of phyllosilicate monoparticles in a weathering profile developed on ultramafic rocks: Internat. Clay Conf., 7th, Bologna Italy, Proc., in press.

Esson, J., and Carlos, L., 1978, The occurrence, mineralogy and chemistry of some garnierites from Brazil: Bur. Recherches Géol. et Minières (B.R.G.M.) Bull., II, v. 3, p. 263-274.

Eswaran, H., 1972, Morphology of allophane, imogolite and halloysite: Clay Minerals, v. 9, p. 281.

Forestier, H., and Chaudron, G., 1925, Points de transformation des solutions solides d'alumine ou de sesquioxyde de chrome dans le sesquioxyde de fer: Acad. Sci. Paris, Comptes-Rendus, D, v. 180, p. 1264-1266.

Grim, R. E., 1968, Clay mineralogy: New York, McGraw-Hill Book Co., 384 p.

Guenot, B., 1970, Etude d'un minéral argileux du type interstratifié talc-saponite trouvé dans le Précambrien du Congo Kinshasa: Groupe Français des Argiles Bull., v. 22, p. 97-104.

Henmi, T., and Wada, K., 1976, Morphology and composition of allophane: Am. Mineralogist, v. 61, p. 379-390.

Janot, C., and Gibert, H., 1970, Les constituants du fer dans certaines bauxites naturelles étudiées par effet Mössbauer: Soc. Française Minéralogie Cristallographie Bull., v. 93, p. 213-223.

Kadio, E., 1976, Rapport de fin de mission; mission nickel Biankouma Est (Man): Rappt. Sodemi, v. 398.

Kuhnel, R. A., Roorda, H. J., and Steensma, J. J. S., 1978, Distribution and partitioning of elements in nickeliferous laterites: Bur. de Recherches Géol. et Minières (B.R.G.M.) Bull., II, v. 3, p. 191-206.

Maksimovic, Z., 1966, β-Kerolite-pimelite series from Goles Mountain, Yugoslavia: Internat. Clay Conf., Jerusalem, Proc., v. 1, p. 97-105.

Mathez, G., ms, 1976, Rapport de fin de mission; Prospection des indices de nickel de Foungouesso et de Sipilou: Rappt. Sodemi, v. 347, 87 p.

Millot, G., and Bonifas, M., 1955, Transformations isovolumétriques dans les phénomènes de latéritisation et de bauxitisation: Service de la Carte géol. d'Alsace-Lorraine Bull., v. 8, p. 3-20.

Nahon, D., ms, 1977, L'altération des roches ultrabasiques de la région de Biankouma, Côte d'Ivoire, I. Le massif de Sipilou Nord: Univ. d'Abidjan, Dépt. Sci. de la Terre, Rappt., v. 21, 22 p.

———— ms, 1978, L'altération des roches ultrabasiques de la région de Biankouma, Côte d'Ivoire, II. Le massif de Moyango: Univ. d'Abidjan, Dépt. Sci. de la Terre, Rappt., v. 22, 16 p.

Nahon, D., Paquet, H., and Delvigne, J., 1982, Ultramafic rocks weathering and nickel concentration in Western Ivory Coast: Econ. Geology, v. 77, n° 5.

Norrish, K., and Taylor, R. M., 1961, The isomorphous replacement of iron by aluminium in soil goethites: Jour. Soil Sci., v. 12, p. 294-306.

Pecora, W. T., Hobbs, S. W., and Murata, K. J., 1949, Variations in garnierite from the nickel deposit near Riddle, Oregon: Econ. Geology, v. 44, p. 12-23.

Russell, J. D., MacHardy, W. J., and Fraser, A. R., 1969, Imogolite, a unique aluminosilicate: Clay Minerals, v. 8, p. 87-99.

Schott, J., Berner, R. A., and Sjöberg, E. L., 1981, Mechanism of pyroxene and amphibole weathering. I. Experimental studies of iron-free minerals: Geochim. et Cosmochim. Acta, v. 45, p. 2123-2136.

Schellmann, W., 1978, Behaviour of nickel, cobalt and chromium in ferruginous lateritic nickel ores: Bur. Recherches Géol. en Minières (B.R.G.M.) Bull., II, v. 3, p. 275-282.

Schwertmann, U., and Fischer, W. R., 1973, Natural "amorphous" ferric hydroxide: Geoderma, v. 10, p. 237-247.

Sherman, G. D., and Uehara, G., 1956, The weathering of olivine basalt in Hawaii and its pedogenic significance: Soil Sci. Soc. America Proc., v. 20, p. 337-340.

Trescases, J. J., 1975, L'évolution géochimique supergène des roches ultrabasiques en zone tropicale; formation des gisements nickélifères de Nouvelle Calédonie: l'Office Recherche Sci. et Tech. Outre Mer (O.R.S.T.O.M.), Paris, Mém., v. 78, 259 p.

Veniale, F., and Van der Marel, H. W., 1968, A regular talc-saponite mixed-layer mineral from Ferriere, Nure Valley (Piacenza, Italy): Contr. Mineralogy Petrology, v. 17, p. 237-254.

Wada, K., 1966, Deuterium exchange of hydroxyl groups in allophane: Soil Sci. and Plant Nutrition, v. 12, p. 176-182.

Wada, K., 1977, Allophane and imogolite, *in* Dixon, J. B., and Weed, S. B., eds., Minerals in Soil Environments: Soil Sci. Soc. America Proc.,, p. 603-638.

Weaver, C. E., and Pollard, L. D., 1973, The chemistry of clays minerals: Amsterdam, Elsevier Sci. Pub., 213 p.

Wieviora, A., 1978, Ni-containing mixed-layer silicates from Szklary, Lower Silesia, Poland: Bur. Recherches Géol. et Minières (B.R.G.M.) Bull., II, v. 3, p. 247-261.

Wilshire, H. G., 1958, Alteration of olivine and orthopyroxene in basic lavas and shallow intrusions: Am. Mineralogist, v. 43, p. 120-147.

Winchell, A. N., 1945, Elements of optical mineralogy. II. Description of minerals: New York, John Wiley & Sons, Inc., 551 p.

Yoshinaga, N., and Aomine, S., 1962, Allophane in some Ando soils: Soil Sci. and Plant Nutrition, v. 8, p. 6-13.

Yoshinaga, N., Yotsumoto, H., and Ibe, K., 1968, An electron microscopic study of soil allophane with an ordered structure: Am. Mineralogist, v. 53, p. 319-323.