CHLORITES AND CHLORITIC MIXED-LAYER MINERALS IN PROFILES ON ULTRABASIC ROCKS FROM MOYANGO (IVORY COAST) AND ANGIQUINHO (BRAZIL)

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ABSTRACT: Different types of chlorite and related mixed-layer minerals have been found in profiles developed on ultrabasic rocks of Ivory Coast and Brazil. Normal chlorites, with low K and Ni contents, are of hydrothermal origin and are situated at the bottom of the alteration profile. At the top of the profile the mixed-layer minerals are Ni-chlorite/vermiculite, which formed under weathering conditions, or K-chlorite/vermiculite, resulting from the alteration of mica. The Ni-content of the chlorite/vermiculite can reach 10% NiO.

Clay minerals formed as alteration products of ultramafic rocks (by hydrothermal alteration or weathering) include several types of mixed-layer species: talc-saponite (Veniale & Van Der Marel, 1968), saponite-swelling chlorite (Veniale & Van Der Marel, 1963), chlorite-swelling chlorite (Mejsner, 1978; Casanova & Knopf, 1969), chlorite-saponite (Trescases, 1975; Wiewiora, 1978), chlorite-montmorillonite (Wackermann, 1975), chlorite-smectite (Wilshire, 1958; Pion, 1979); chlorite-vermiculite (Brindley & De Souza, 1975a,b; Trescases, 1975; Wackermann, 1975; Ducloux *et al.*, 1976; Wiewiora, 1978; Nakamuta, 1981; Dubinska, 1984). Some of these minerals have been found in ultramafic bodies in Moyango, Ivory Coast, and Angiquinho, Brazil, which have been studied for their Ni content. At Moyango, Ni occurs only in clay minerals and the grade is too low for exploitation. At Angiquinho, however, serpentines and clay minerals are nickeliferous and the deposit is being exploited. This paper describes chlorites and mixed-layer minerals containing a chlorite structure found in alteration profiles on the Moyango and Angiquinho ultramafic bodies.

THE MOYANGO PROFILE

The Moyango P2 profile was first described by Nahon (1978). It occurs at the top of a topographic slope in the Moyango ultramafic body (Nahon *et al.*, 1982). The parent rock at the bottom of the profile is composed mainly of olivine, which is almost completely serpentinized. In a transitional layer (A), relicts of fresh olivine crystals have been altered to smectites and iron oxyhydroxides. In an ochreous ferruginous layer (B), the serpentines are transformed into amorphous material and the centres of olivine crystals have been filled with quartz (Nahon *et al.*, 1982). A siliceous–ferruginous crust formed in this horizon

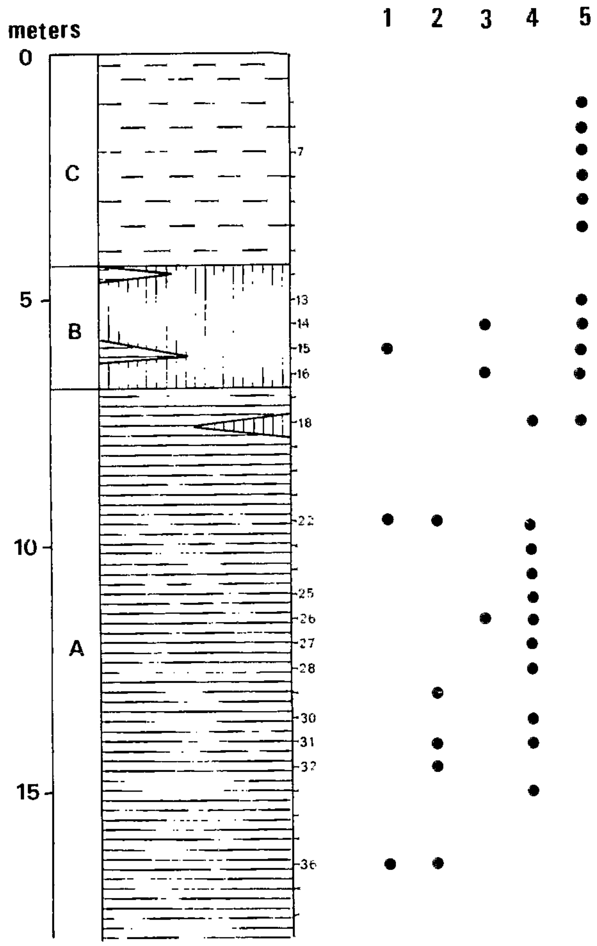
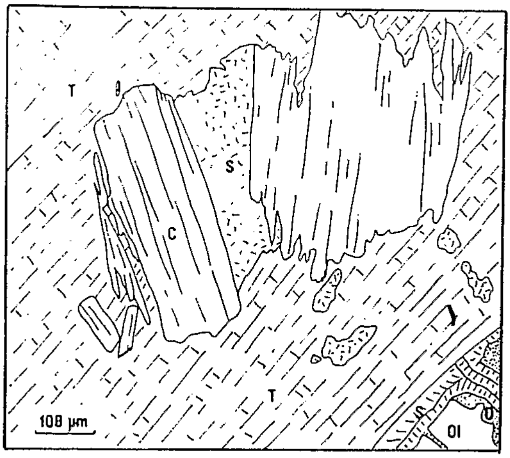


FIG. 1. Schematic diagram of the Moyango profile, Ivory Coast (after Nahon, 1978) and distribution of the different chlorites and chloritic mixed-layer minerals. A = transitional layer; B = ochreous ferruginous layer; C = reddish-purple ferruginous layer; 1, 2, ... = types of chlorites or chloritic minerals; 7, 13, ... = sample number.

(Nahon, 1979), and has high Ni content (up to 3·5%). At the top of the profile, a reddish-purple ferruginous layer (C) consists of a dark red to black matrix of talc, chlorite and quartz. In the whole profile, five types of chlorite or 'chloritic mixed-layer' minerals have been found (Figs 1 and 2).

Type 1. In several samples, 5-mm wide cracks cross the rock and are filled with talc and large massive chlorite crystals. This chlorite is colourless in plane-polarized light and dark grey under crossed polars.

FIG. 2. Different types of chlorites and mixed-layer minerals of the Moyango profile in thin section. A = amphibole; a = altered amphibole; C = chlorite; c = altered chlorite; cl = clay minerals; CV = chlorite-vermiculite; O = iron oxhydroxides; Ol = olivine; Q = quartz; S = serpentine; T = talc; V = void; Ve = vermiculite.



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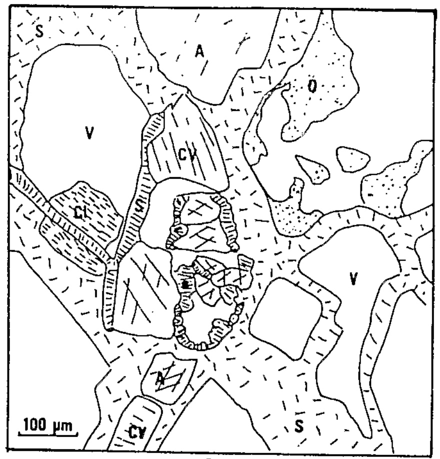

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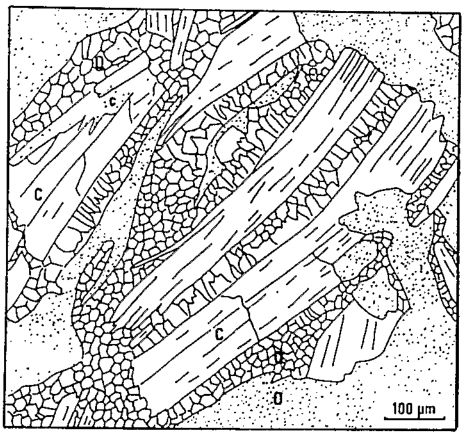

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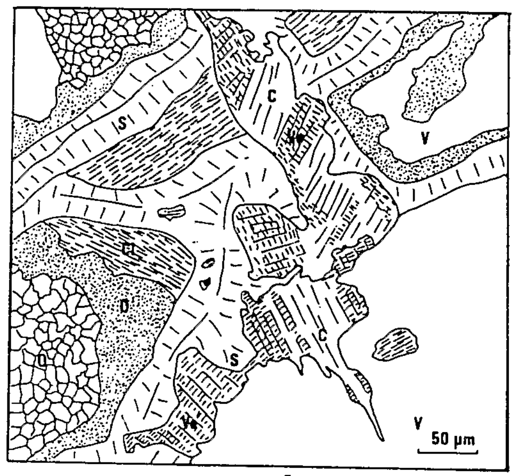

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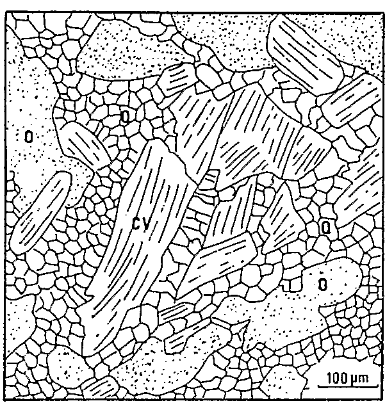

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Type 2. Chlorite of type 2 is colourless in plane-polarized light and light grey under crossed polars. However, some parts of the crystals show yellow-orange colours under crossed polars. This chlorite is developed, without defined forms, in the serpentine matrix only in layer A.

Type 3. This type is composed of large grey crystals, isolated within the serpentine or siliceous matrix. Opening up of lamellae is sometimes observed. In one sample, this type of chlorite has been altered to a microcrystalline product showing second-order interference colours.

Type 4 occurs as small (< 100 μm) grains, colourless in plane-polarized light and light grey or yellow under crossed polars. These grains are associated with slightly altered amphiboles (pargasitic hornblende or magnesio-hornblende). X-ray powder diffraction patterns showed peaks at 14·3, 9·4 and 7·3 Å which did not shift after ethylene glycol treatment. After K-saturation, the peaks were displaced to 12·2, 8·1 and 6·2 Å.

TABLE 1. Average microprobe analyses and structural formulae (based on 14 oxygens) of chlorites and mixed-layer chlorite-vermiculites from the Moyango profile, Ivory Coast.

Type	1	2	3	4	5
N	27	17	26	41	28
SiO_2	32·30	35·09	31·23	36·81	32·92
TiO_2	0·05	0·02	0·05	0·80	0·37
Al_2O_3	13·34	9·59	16·39	14·20	14·22
FeO	2·80	3·94	2·69	2·23	3·07
MnO	0·02	0·02	0·02	0·04	0·02
MgO	34·34	34·79	33·18	25·94	21·67
CaO	0·03	0·04	0·03	0·29	0·22
Na_2O	0·03	0·02	0·02	0·07	0·09
K_2O	0·01	0·03	0·01	1·05	0·37
NiO	0·16	0·28	0·28	2·83	9·00
Cr_2O_3	2·93	1·86	1·46	0·85	0·61
TOTAL	86·01	85·68	85·36	85·11	82·56
Si	3·108	3·391	3·010	3·558	3·415
Al_t	0·892	0·609	0·990	0·442	0·585
Al_o	0·621	0·483	0·872	1·176	1·154
Fe + Mn	0·227	0·320	0·219	0·183	0·266
Mg	4·927	5·013	4·768	3·738	3·352
Ca	0·003	0·004	0·003	0·030	0·024
Na	0·006	0·004	0·004	0·013	0·018
K	0·001	0·004	0·001	0·129	0·049
Ni	0·012	0·022	0·022	0·220	0·751
Cr	0·223	0·142	0·111	0·065	0·050
Ti	0·004	0·001	0·004	0·058	0·029
Σ	6·024	5·993	6·004	5·612	5·695

N number of analyses.
Total iron as FeO.
TOTAL Total of analysed oxides (H_2O not analysed).
Σ = number of octahedral cations.

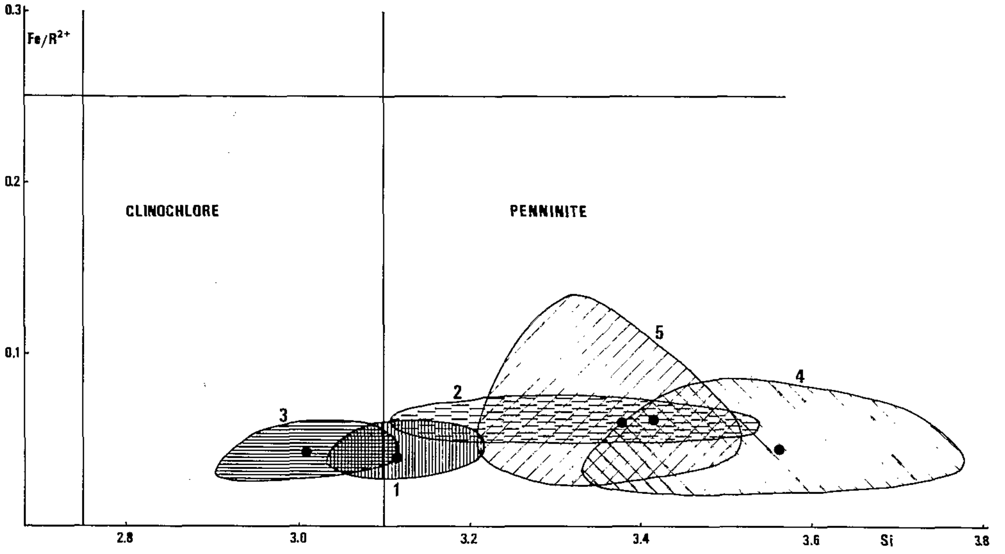

FIG. 3. Positions of the different types of chlorite and mixed-layer minerals from the Moyango profile in the Foster (1962) classification. Black dots = average values.

After heating the 14 Å peak shifted to 12·1 Å. This behaviour is characteristic of a chlorite-vermiculite mixed-layer mineral (Thorez, 1975; Nishyama *et al.*, 1978). The type 4 mineral is only found in the transitional layer.

Type 5. In the C layer, 'chlorite-like' minerals occur as lamellae showing second-order interference colours. Lamellae are opened up at their extremities. The X-ray diffraction pattern was similar to that of the type 4 chlorite.

The five types were analysed with an electronic microprobe. The structural formulae were calculated on the basis of 14 oxygens (Table 1). Using the AIPEA nomenclature, types 1 to 3 are clinochlore (Bailey, 1980). According to Foster's (1962) classification, types 1 and 3 are at the boundary between clinochlore and penninite (Fig. 3). Type 2 chlorites appears to be penninite with some high Si values corresponding to vermiculitized chlorites. A plot of Si vs. Ti, K and Ni indicates three groupings (Fig. 4):

Types 1, 2 and 3 with low Ti, K and Ni content;

Type 4 with high Ti and K content;

Type 5 with high Ni content.

THE ANGIQUINHO PROFILE

This profile in the Niquelandia ultrabasic area, studied by Colin (1984), is developed on dunite, peridotite and pyroxenite and capped by a silcrete (Fig. 5). The degree of serpentinization varies with the nature of the parent rock. In a coarse saprolite, pyroxenes have been altered to serpentines (bastite), along with sinuous minerals and amphibole crystals (Fig. 6). The sinuous minerals show second-order interference colours under crossed polars. The X-ray diffraction patterns and the chemical compositions are similar to those of the type 4 chlorite-vermiculite of Moyango. For these reasons, these minerals can be also considered as mixed-layer chlorite-vermiculites. At the top of the profile, in the

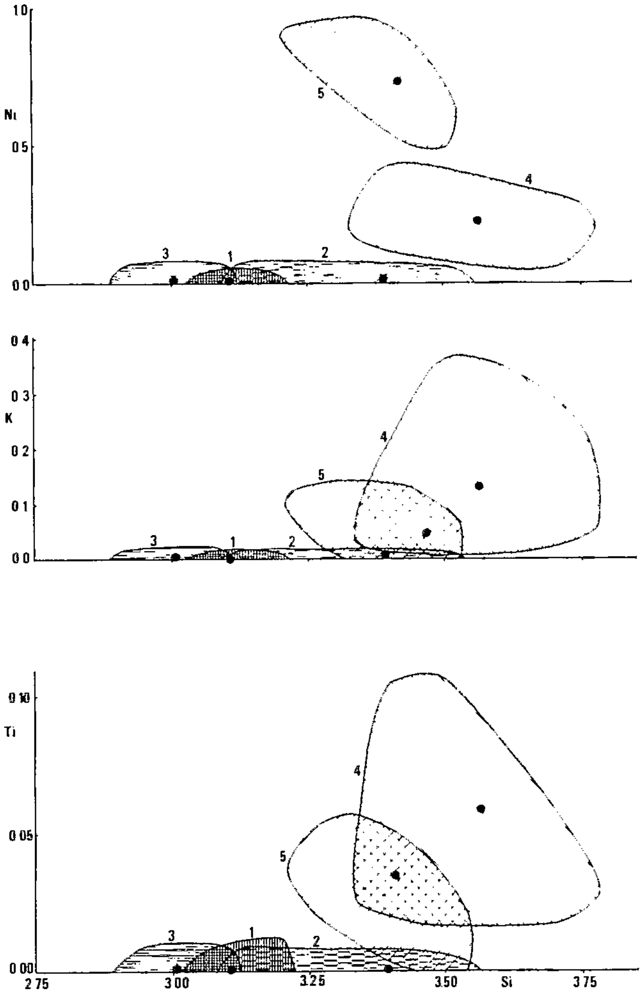

FIG. 4. Si *vs* Ni, K and Ti diagrams for the chlorites and mixed-layer minerals from the Moyango profile. Shaded areas = fields of composition of the different types. Black dots = average values.

ferruginous saprolite, Colin (1984) described white veinlets crossing the ferruginous kaolinitic plasma. He showed that these veinlets were composed of Ni-chlorite (polytype 1*a*) associated with asbolanes. However, based on their chemical compositions (Table 2 and Fig. 7), these minerals can also be considered as mixed-layer chlorite-vermiculites. The chemical analyses show high MnO contents (up to 10%) and CoO contents (up to 4%) corresponding to the asbolanes (Colin, 1984). This is the reason for the low totals of the analyses in Table 2. These Ni-chlorite-vermiculites are similar to type 5 of Moyango.

DISCUSSION

This study of two lateritic profiles developed on ultramafic rocks shows clearly the presence of five different types of chloritic minerals. Chlorites of type 1 either occur in veins

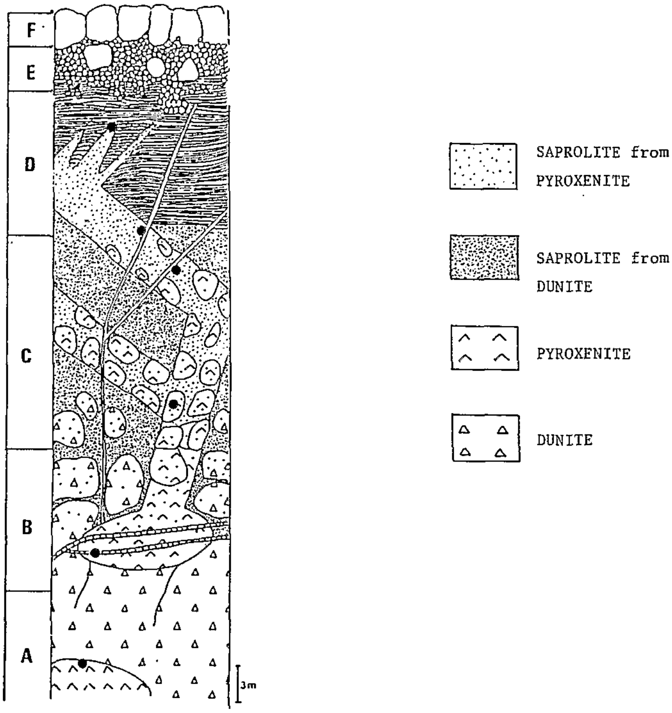

FIG. 5. Schematic diagram of the Angiquinho profile, Brazil (after Colin, 1984). A = parent rock; B = partially altered rock; C = coarse saprolite; D = ferruginous saprolite; E = dusty ferruginous saprolite; F = silcrete.

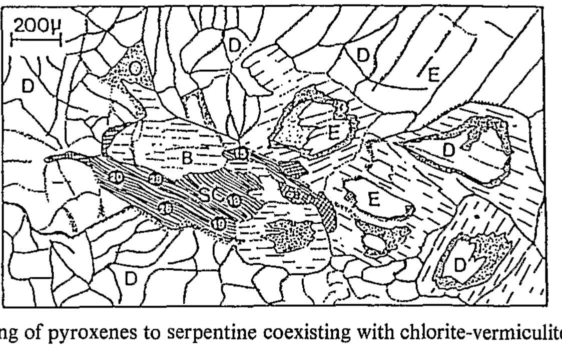

FIG. 6. Weathering of pyroxenes to serpentine coexisting with chlorite-vermiculite in the partially altered rock from the Angiquinho profile (after Colin, 1984). E = enstatite; D = diopside; O = iron oxhydroxide; B = bastite; SC = chlorite-vermiculite; number = analysis point.

with talc or in the serpentine matrix. The chemical composition is that of typical chlorites in serpentinized rocks. These data suggests an hypogene origin for such chlorites.

Type 2, within the serpentine matrix, has been locally transformed into vermiculite. The average chemical composition shows a high silica content but, when the structural formula is calculated on the basis of 22 oxygens, the alumina content is too low and the Mg content too high for a vermiculite. In the MR^3–$2R^3$–$3R^2$ diagram of Velde (1977), the type 2

TABLE 2. Microprobe analyses and structural formulae (based on 14 oxygens) of chlorite-vermiculites from Angiquinho (Brazil) (Colin, 1984). A = chlorite-vermiculite type 4. B = chlorite-vermiculite type 5.

	A				B					
SiO_2	31·77	34·65	33·15	32·85	21·28	25·08	25·08	26·17	29·46	29·10
TiO_2	1·69	1·80	1·58	1·51	2·56	1·51	2·59	1·63	2·03	1·55
Al_2O_3	14·93	15·63	14·86	14·11	12·01	13·16	13·69	16·04	17·97	17·43
FeO	3·56	3·22	3·22	2·89	3·28	4·08	3·76	3·00	3·00	2·40
MnO	0·06	0·14	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
MgO	27·03	21·43	22·35	20·64	16·59	16·80	16·74	16·05	15·23	13·96
CaO	0·52	0·23	0·37	0·13	0·29	0·43	0·35	0·54	0·41	0·48
K_2O	3·15	6·52	4·23	4·89	0·00	0·00	0·00	0·00	0·00	0·00
NiO	0·67	2·76	3·67	2·85	8·81	9·53	10·44	10·42	11·48	10·29
Cr_2O_3	0·70	0·89	0·91	0·74	0·89	1·34	0·78	0·73	0·79	0·69
TOTAL	84·41	87·27	84·34	80·61	65·71	71·93	73·43	74·58	80·37	75·80
Si	3·185	3·415	3·362	3·471	2·877	3·084	3·026	3·068	3·183	2·821
Al	0·815	0·585	0·638	0·529	1·123	0·916	0·974	0·932	0·817	1·179
Al	0·948	1·230	1·138	1·250	0·790	0·991	0·972	1·284	1·471	1·443
Fe + Mn	0·304	0·278	0·272	0·255	0·371	0·419	0·379	0·294	0·271	0·256
Mg	4·036	3·147	3·377	3·249	3·343	3·079	3·011	2·805	2·453	2·657
Ca	0·056	0·025	0·041	0·014	0·042	0·057	0·045	0·068	0·047	0·052
K	0·403	0·818	0·547	0·547	0·000	0·000	0·000	0·000	0·000	0·000
Ni	0·050	0·219	0·299	0·242	0·958	0·942	1·013	0·982	0·998	1·056
Cr	0·056	0·069	0·073	0·062	0·095	0·130	0·074	0·068	0·067	0·070
Ti	0·127	0·133	0·120	0·120	0·260	0·140	0·235	0·144	0·165	0·149
Σ	5·980	5·919	5·867	5·739	5·859	5·758	5·729	5·645	5·472	5·683

Total iron as FeO.

TOTAL = Total of analysed oxides (Na_2O and H_2O not analysed; MnO and CoO are considered to be present in the asbolanes).

Σ = number of octahedral cations.

composition lies on the line $2R^3$–$3R^2$ in the chlorite field (Fig. 7). Thus the type 2 mineral can be considered as a chlorite, but partially vermiculitized; from its petrographic characteristics and its high Cr_2O_3 content it is probably of hypogene origin. A similar occurrence has been described by Wackermann (1975) in the basalts of Senegal.

Type 3 consists of large crystals of chlorite together with fine-grained quartz or serpentines. Chemical compositions are close to types 1 and 2. In the MR^3–$2R^3$–$3R^2$ diagram, type 3 is also on the line $2R^3$–$3R^2$. These similarities could indicate an origin for type 3 similar to that of types 1 and 2.

Type 4 has high titanium and potassium contents. A petrological study of fresh parent rock of Moyango (Nahon, 1978) revealed the presence of phlogopite crystals. In samples where such a Ti- and K-rich chlorite-vermiculite was analysed, phlogopite crystals no longer exist. This K- and Ti-rich chlorite-vermiculite is therefore likely to be an alteration product of the phlogopite. In the MR^3–$2R^3$–$3R^2$ diagram (Fig. 7), analyses of type 4 are on the join phlogopite–chlorite. This transformation can be compared with the transformation of biotite to corrensite and/or chlorite-vermiculite in the acidic rocks. The temperature of this transformation is probably high but the Ni content (average 2·8%, maximum 5%) suggests a second stage of alteration at lower temperature.

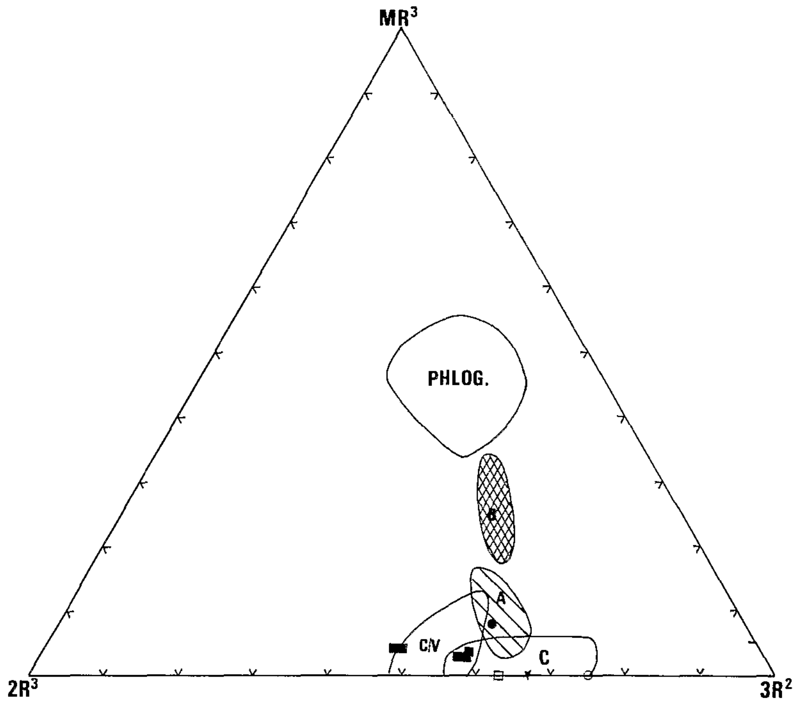

FIG. 7. Position of the different chlorites and mixed-layer minerals in the MR^3–$2R^3$–$3R^2$ diagram of Velde (1977). PHLOG = field of the phlogopite mica. C = field of Ni-chlorite in the literature. C–V = field of Ni-chlorite-vermiculite in the literature. ★ = chlorite type 1, Moyango. O = chlorite type 2, Moyango. □ = chlorite type 3, Moyango. A = field of the type 4 chlorite-vermiculite, Moyango. B = field of the type 4 chlorite-vermiculite, Angiquinho. ● = Ni-chlorite/vermiculite type 5, Moyango. ■ = Ni-chlorite-vermiculite, Angiquinho.

Type 5 corresponds to a Ni-bearing chlorite-vermiculite. Such mixed-layer minerals are common in lateritic profiles developed on ultrabasic rocks (Table 3). Three origins can be considered: (i) they formed hydrothermally during the serpentinization process, (ii) they were neoformed at low temperature from solutions, (iii) they were produced by degradation through weathering of parent minerals (Veniale & Van Der Marel, 1968). At Moyango and Angiquinho, a hydrothermal origin is at variance with field observations (Nahon *et al.*, 1982; Colin, 1984). All petrological and mineralogical analyses indicate that nickeliferous minerals only occur in weathering horizons at the top of the profiles. Such chlorite/vermiculites have not been observed in parent rock or at the bottom of the profiles.

In the literature, chlorite-vermiculite mixed-layer minerals are generally considered to be degradation products of chlorites, with a minimum of structural changes, and exchanges in some cases of Mg by Ni and Al by Si (Hayes, 1970; Herbillon & Makumbi, 1975; Wiewiora, 1978; Bailey & Riley, 1977; Nakamuta, 1981; Senkayi *et al.*, 1981). The data do not permit us to draw a similar conclusion for the Moyango and Angiquinho profiles. Furthermore, these Ni-bearing chlorites crystals are arranged as clusters within the weathering plasma which consists of silica and goethite. Enrichment of Al and Ni is a normal process at the top of lateritic profiles of Moyango and Angiquinho, i.e., layers

TABLE 3. Analyses of Ni-chlorites and Ni-chlorites-vermiculites from literature. C = chlorite; C/V = chlorite-vermiculite; V = vermiculite. *Ia*, *IIb* = polytypes.

References	Type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	NiO	Cr_2O_3	Total
Montoya & Baur (1963)	C *IIb*	32·70		14·50	3·50	2·50		29·60				3·20	0·30	86·60
Ostrowicki (1965)	C *IIb*	37·48		12·68	2·73	0·71		29·71	0·18	0·01	0·02	2·93		86·45
De Waal (1970)	C *IIb*	27·27		15·21	4·35	2·78	0·06	10·13	0·38			29·49		89·67
Edel'Shteyn & Zuzuk (1974)	C	33·32	0·37	13·95	4·89	0·51	0·11	27·56	0·28	0·35	0·06	6·84		88·12
Edel'Shteyn & Zuzuk (1974)	C	28·90	0·75	15·34		12·41		15·40	0·29	0·10	0·05	11·63		86·50
Wiewiora (1978)	C *IIb*	30·58	0·20	18·45	2·29	1·71	0·03	31·25		0·01		0·20		85·04
Wiewiora (1978)	C *IIb*	30·43	0·02	17·46	3·41	2·11	0·03	30·51		0·01		0·93		84·91
Esson & Carlos (1978)	C	33·74		9·01		3·21		20·41	0·55			18·95		86·09
Esson & Carlos (1978)	C	31·21		16·88		3·23		32·84				0·24	0·55	85·31
Schrauf (1882)	C/V *Ia*	33·79		15·47	4·01	3·26		25·87	1·38			5·16		88·94
Starkl (1883)	C/V *Ia*	33·89		14·88	3·90	3·62		24·15	1·50			5·78		87·72
Ostrowicki (1965)	C/V *Ia*	38·47		11·28	3·22	0·44		19·03	0·08	0·14	0·07	7·51		80·24
Ostrowicki (1965)	V *Ia*	35·20	0·08	13·90	3·98		0·01	25·25	0·04		0·01	2·31		80·60
Brindley & De Souza (1975a)	C/V *IIb*	34·50		15·05	12·05	3·07		18·12	0·09		0·02	6·01		88·91
Brindley & De Souza (1975a)	C/V *IIb*	33·60		14·35	14·40	2·17		17·75	0·10		0·07	5·75		88·19
Brindley & De Souza (1975b)	C/V *Ia*	35·00		14·55	6·22	0·25		24·40	0·16			5·50		86·08
Brindley & De Souza (1975b)	C/V *Ia*	34·58		17·01	4·22	0·35		23·30	0·11			7·50		87·07
Brindley & De Souza (1975b)	C/V *Ia*	36·00		12·40	8·53	0·29		22·00	0·25	0·04	0·02	7·00		86·53
Brindley & De Souza (1975b)	C/V *Ia*	36·00		13·60	4·55	0·58		22·50	0·40	0·12	0·06	8·00		85·91
Esson & Carlos (1978)	C/V	37·94		2·44		1·53		24·13				19·88		86·09
Esson & Carlos (1978)	C/V	34·04	0·48	17·22	4·67	0·43	0·21	22·15	0·69	0·05	0·17	6·02		86·13

TOTAL = Total of analysed oxides (H_2O not analysed).

where Ni-bearing chlorites occur. It is only in these horizons at the top of the profile that complete alteration of serpentines can be observed. Elements liberated from serpentines by dissolution may allow precipitation of nickeliferous chlorites. In this case, such minerals could appear as the result of a weathering process. At Moyango, the problem of the source of Al may be explained by the weathering of feldspathic rocks (probably gabbro) observed a few meters upslope, as shown by Mathez (1976). At Angiquinho, the clinopyroxenes of the pyroxenites coexisting with dunites are probably the source of Al. A supergene origin for the nickeliferous chlorite-vermiculite from the Moyango and Angiquinho profiles is the hypothesis best supported by field and microscopic observations.

CONCLUSIONS

Chlorites and mixed-layer chlorite-vermiculites have been found in two profiles in the Ivory Coast and Brazil. Three main origins can be considered for the five types identified: (i) an hypogene origin leading to an association with talc or serpentine (types 1 and 2), (ii) a transformation of phlogopite in K-bearing chlorite (type 4), (iii) a weathering origin as neoformed Ni-bearing chlorite (type 5). Types 4 and 5 have a chlorite-vermiculite structure which allows them to incorporate significant amounts of Ni into the structure. However, such chlorites are not abundant in the horizon as a whole. Moreover, the other minerals existing in this part of the profiles (quartz, goethite, kaolinite) are Ni-depleted minerals and the weathering horizons of the top of the Moyango and Angiquinho profiles cannot be regarded as nickeliferous ore.

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