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HYPOGENE AND SUPERGENE ALTERATIONS OF ORTHOPYROXENE IN THE KOUA BOCCA ULTRAMAFIC INTRUSION, IVORY COAST

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I - INTRODUCTION

The ultramafic intrusion of the Koua Bocca, located about 200 km NNW of Abidjan, dates from the Abronian period (2000 M.Y), an intra-Birrimian gap located between the "Supergroupe Volcano-Sédimentaire" and the later "Supergroupe de Comblement" (TAGINI, 1971). The intrusion is composed, in the lower levels, of clinopyroxenites containing olivine, orthopyroxene, clinopyroxene, opaque minerals and small quantities of hornblende and, after an intermediate level mainly composed of clinopyroxenites without olivine, in the upper levels, of melagabbronorites containing basic plagioclase, hornblende and clinopyroxene.

The Abronian ultrabasites are earlier than the orogenic period which emplaced the surrounding granites (1800 M.Y.) which are responsible for the progressive metamorphism observed in the ultramafic intrusion. In the inner part, the rocks are practically unmetamorphosed, but near the contact with the later granites, several concentric aureoles have developed, characterized by progressively more important metamorphism. In the sequence, olivines are the more unstable minerals, followed by orthopyroxene whereas clinopyroxene and plagioclase are more resistant minerals. Hornblendes are very stable minerals and are replaced only in the last aureole, directly in the contact with the surrounding granites.

The geomorphic history of the region began in the early Tertiary. The formation of several erosional surfaces is closely related to successive periods of weathering. The oldest surfaces are ferrallitic (kaolinite + gibbsite + ferruginous components) with some trace of bauxitic materials. The middle surfaces are fersiallitic (smectite + kaolinite) with ferruginous indurated crusts. The more recent lower level is vertic (smectite + vermiculite) with calcareous and manganesiferous concretions.

Only the alteration of orthopyroxenes is discussed here. Two different types of alteration occur : a deep alteration by late- or post-magmatic processes, and a shallow and superficial weathering.

II - PETROGRAPHIC STUDY

The orthopyroxene is much less abundant than the clinopyroxene and is generally associated with olivine. It occurs in several different forms :

- in the usual clinopyroxenic rocks, it is present as polygonal grains associated with the clinopyroxene in the granoblastic structure ;
- near or within the olivine-bearing levels we find orthopyroxene as porphyroblastic subhedral crystals, as large poikiloblastic crystals, or as irregular symplectic assemblages with magnetite (HAGGERTY and BAKER, 1967) around a central core of incompletely assimilated olivine grain ;
- in the middle metamorphic aureoles, it occurs as large porphyroblastic subhedral crystals, 3 to 5 mm long, surrounded by a poikiloblastic ring of green hornblende.

No matter what the crystal form, the orthopyroxene exhibits the constant chemical composition (Wo = 0.02 ; En = 0.72 ; Fs = 0.26) of a bronzite close to hypersthene.

III - HYPOGENE ALTERATION

Along the fractures formed by the post-magmatic processes as well as along the pegmatitic veins injected during the mobilization of the granites and within the metamorphosed rings, the pyroxenes suffered varied fates in accordance with the importance of and the proximity to these features. The orthopyroxene reacts much more rapidly and sooner than the clinopyroxene : near the contact with hydrothermal veins the orthopyroxene is completely transformed, whereas the clinopyroxene persists intact.

Near the thinnest hydrothermal veins, the transformation of the orthopyroxene leads to more or less complete pseudomorph of talc with small opaque grains representing the iron originally contained in the pyroxene but excluded from the talc. Ferriferous talc, is sometimes observed within the inner part of the pseudomorph or between the pyroxene remnants and the colourless talc ; the microstructures are similar but the opaque inclusions are in much smaller abundance or even absent.

The alteration is peripheral and centripetal, or accompanies the transmineral hydrothermal veinlets. The OPx remnants are irregularly shaped with gently denticulated limits along the c-axis of the mineral. The neoformed talc is rarely oriented but rather occurs as aggregates of small particles randomly distributed. The magnetite is either disseminated within the talc or concentrated near the outer margin of the pseudomorph. The transformation is generally isovolumetric. The symplectic structures are always well preserved during the transformation into talc.

With increased influence of the metamorphic and hydrothermal processes, the talc which was formerly the only mineral replacing the OPx is now associated with colourless amphiboles ; these can dominate or even be the sole mineral in the pseudomorph. When pseudomorphs are mainly composed of amphiboles with only small quantities of talc, Opx remnants have generally disappeared.

Normally the neoformed amphibole would belong to the cummingtonite - grunerite series ; however since natural cummingtonite, with composition similar to the magnesian orthopyroxenes of the Koua Bocca, do not exist (DEER, HOWIE and ZUSSMANN, 1972, v. 2, p. 235), the neoformed amphibole belongs to the tremolite - actinolite series, the necessary calcium coming from the concomitant CPx transformation. The excess iron crystallizes into magnetite with, eventually, a small quantity of cummingtonite associated with tremolite. If the three silicates are present together, the talc always appears between the pyroxene remnant and the neoformed amphibole.

These colourless amphiboles are often arranged in bundles of fibrous or acicular prisms parallel to the c-axis of the original pyroxene. The transformation seems to be isovolumetric. The symplectites are also transformed into tremolite, but the fine structures of magnetite lamellae are partly destroyed during amphibole crystallization : opaque lamellae become rounded and form inclusions or fill interstices between prisms or they recrystallize into small automorphic opaque grains.

In the outer aureole, near the contact with the surrounding granites, orthopyroxenes experiences no further transformation whereas, under these conditions, clinopyroxene is replaced by hornblende and actinolite, ilmenite by titanite and plagiocase by zoisite.

IV - SUPERGENE WEATHERING

The profiles associated with the oldest geomorphological surfaces gave rise to ferrallitic, occasionally bauxitic, profiles. In the old uneroded fersiallitic profiles, smectites are formed in the lower levels (below 12m depth) and kaolinite + iron compounds are formed in the upper autochtonous horizons by progressive degradation of the early formed smectite. In the most recent surfaces, the vertic weathered profiles are, from base to top, more or less similar to the deep smectitic horizons of the fersiallitic profiles.

Orthopyroxene is an accessory mineral in the majority fo the Koua Bocca rocks. Very susceptible to hydrothermal processes, it is often transformed, even at the base of the weathered profiles, into talc or amphiboles much more resistant to weathering than the original OPx.

The weathering generally begins along the transmineral fractures, more or less transverse to the c-axis of the prism or along the intermineral planes ; weathering then progresses peripherically. If fractures are open, the weathering progresses rapidly, but very often, thin cutans of nontronite form within these fractures. The cutans show varied colours and orientations and are easily distinguished from the neoformed smectites developed between these cutans and the pyroxene cores.

The smectites are slightly pleochroic (yellowish green to yellowish brown) and arranged parallel to the c-axis of the pyroxene. The fringe of the smectite bands is thinly denticulated and penetrates like sawteeths along the pyroxene cleavage planes. The central core has rectilinear limits where it parallels the c-axis and denticulated limits in other directions. All the residual cores within a single original crystal are tightly encased within the smectite and preserve their original straight extinction parallel to the extinction direction of the smectite. As the weathering progresses, the residual cores disappear and the pseudomorph will become well oriented and regular on the whole. The transformation is isovolumetric. In the event of the weathering of a symplectic mixture of OPx + Mgt, the delicate structures of the magnetite lamellae are not perturbed within the smectitic pseudomorphs.

The largest and/or the least fractured OPx crystals may be only partially weathered in the deep horizons. Residual cores may persist as high as the upper levels. Weathering processes, until now favourable for smectite formation, become, in the upper levels, favourable for the formation of iron hydroxide through more complete solubilization of the mineral. The result is a lace-like network consisting of a framework of smectite formed in the lower horizons, and empty pores corresponding to the later-weathered residual cores. These pores are coated with more recently formed iron hydroxides which impregnate the inner margins of the smectite.

The above described sequence is often also observed in the case of incomplete talc pseudomorph : pyroxenic residues are dissolved and the talc is partly degraded, becoming porous and fringed by brown hydroxide deposits. In the case of the degradation of a symplectic pseudomorph, the smectite is transformed into a lace-like network of residual iron hydroxide whereas the inner delicate structure of original magnetite lamellae is perfectly preserved.

In the oldest weathered levels and in the cortex which surround boulders on rock outcrops, orthopyroxenes are directly weathered into iron hydroxide without going through a prior smectite phase. Weathering penetrates the crystal along cracks, or from the mineral margins. The most open cracks are coated, on both sides, by an iron hydroxide deposit, the mid-plane of the fracture remaining empty. Later, hydroxides penetrate into the pyroxene along the cleavage planes, forming a denticulated pattern outward from the fracture. In the beginning, the hydroxides and the pyroxenic cores are joined. However, as denticulated residues decrease, an empty interplasmamineral pore appears : the residues become loose within the ferruginous cells so that they do not maintain a simultaneous extinction pattern. At the end, a porous pseudomorph is formed with a boxwork structure.

During the first steps of weathering, the iron hydroxide is very poorly crystallized, dark-brown-coloured and more or less isotropic. Aluminum never crystallizes into individual gibbsite crystals because the original Al-content of the orthopyroxene is always very low. Later, the early formed hydroxides recrystallize with a little loss of material, since a distinct reduction of wall thickness is always observed. But the most remarkable fact is the distinctive orientation of all the goethite particles throughout the whole pseudomorph. The extinction is simultaneous and parallel to the c-axis of the original pyroxene crystal. This conservation of the original orientation was masked during the first phase and only appears as poorly crystallized and amorphous material disappeared (DELVIGNE, 1965, 1970, 1977).

In the very old bauxitic crusts, the pseudomorphs after orthopyroxene, initially porous and only ferruginous are filled by late and allogenous secondary goethite and gibbsite. The allogenous origin of the secondary hydroxides is proved by the fact that the original orthopyroxene and the early formed pseudomorph do not contain aluminum. The largest crystals may fill the entire cavity of each cell without destroying the intercellular network of early formed hydroxydes.

V - GEOCHEMISTRY

More than fifty chemical compositions were obtained by electron microprobe analyses which were made on the primary orthopyroxene and on his secondary products. Structural formulae were calculated for each analysis and for the mean composition of each mineral species. These structural formulae (mean values) of the orthopyroxenes of the two studied weathering profiles KB3 and KD2 and these of both hypogene and supergene secondary products are given in the Table I. In the last column, structural formula of orthopyroxene calculated on the base of 24 oxygenes is also given in order to make easier the comparisons between the original pyroxene and his secondary products. By such a way of calculating, all minerals have a Z value of 8. The ferruginous end products of the weathering were not analyzed and do not appear in the next table.

These results allow clearly distinguishing the hypogene secondary products tremolite (Trm) and

TABLE I

	OPx	Tr m	T l c	Mns	Sm(OPx)	Sm(ill)	OPx(x4)
Si	1.958	7.983	7.975	7.944	7.535	7.320	7.832
Al	0.042	0.017	0.025	0.056	0.465	0.680	0.168
Al	0.024	0.003	0.007	0.041	0.313	0.172	0.096
Ti	0.003	0.000	0.000	0.000	0.039	0.019	0.012
Fc2	0.506	0.192	0.198	0.496	-	-	2.024
Fc3	-	-	-	-	3.113	3.444	-
Mn	0.009	0.016	0.000	0.000	0.011	0.007	0.036
Cr	0.001	0.000	0.003	0.032	0.009	0.001	0.004
Mg	1.416	4.789	5.783	5.377	0.514	0.357	5.664
Mg	-	0.060	-	-	0.117	0.172	-
Ca	0.041	1.937	0.009	0.040	0.324	0.322	0.164
Na	0.000	0.011	0.004	0.003	0.032	0.016	0.000
K	0.000	0.006	0.003	0.011	0.041	0.038	0.000
OH	-	2.000	4.000	4.000	4.000	4.000	-
Z	2.000	8.000	8.000	8.000	8.000	8.000	8.000
Y	2.000	5.000	5.991	5.946	3.999	4.000	8.000
X		2.014	0.016	0.054	0.514	0.548	

talc (Tlc) from the supergene smectitic (Sm) secondary products. The nontronitic smectite Sm (OPx) corresponds to the secondary products found within the pseudomorph after orthopyroxene whereas the smectite Sm(ill) which also have a nontronitic composition, belongs to an infilling of an open crack in the viccinity of the analysed pyroxene. Ferriferous talc minnesotaite (Mns) has a chemical composition intermediary between the chemical compositions of the two secondary products groups. In all the studied thin sections, the ferriferous talc was found in particular petrologic circumstances and its way of associating with pyroxene remnants, and/or with other secondary products, was always similar in all observed pseudomorphs :

- as within the smectitic pseudomorphs, the green ferriferous talc domains do not contain any secondary magnetite grains, an important part of the original iron being incorporated in the secondary talc ;
- the ferriferous talc was only observed in rocks in which the superficial weathering processes were as important as were the hypogene processes ;
- in the pseudomorphs yet containing orthopyroxene remnants, the ferriferous talc is always observed in the contact fringe between the OPx core and the external colourless talc. In the pseudomorphs without pyroxene remnants, the green talc is always located in the central part of the pseudomorphs as if it was corresponding to the supergene weathering of untransformed (by hypogene process) pyroxene remnants ;
- the ferriferous talc was never found associated with tremolite because, in the case of tremolitic pseudomorphs, the eventual residual OPx is always transformed into colourless talc ;
- the ferriferous talc was sometimes observed in secondary smectitic pseudomorphs but it does not appear as a necessary transitory stage between orthopyroxene and smectite.

All these observations show that the ferriferous talc is a product of hydrothermal process under relatively low temperature conditions and that it is not readily transformed during the early weathering phase.

The colourless magnesian talc and, mainly, tremolite are unquestionably formed under higher temperature hydrothermal conditions. These minerals show a little increase of Si-content and a little decrease of Al-content in comparison with the original orthopyroxene but these differences are very weak. The Fe-contents of the secondary products are very low because the mostly part of the original iron content was incorporated during the formation of distinct magnetite grains. The Mg-content of orthopyroxene and of talc are very similar whereas, in the tremolite, a significant Ca-content, coming from the partly transformed neighbouringclinopyroxenes, replaces a concommitant loss of Mg.

The balance formulae for both tremolite and talc formation are given below. The simplified formula (9 enstatite + 3 ferrosilite) corresponds quite well to the composition of the analysed orthopyroxene.

Serpentine or bastite formation was never observed in the Koua Bocca ultramafic intrusion.

$$\underset{\text{OPx}}{Mg_9Fe_3(SiO_3)_{12}} + 1/2O_2 + 3H_2O = \underset{\text{Tlc}}{3MgSi_4O_{10}(OH)_2} + \underset{\text{Mgt}}{Fe_3O_4}$$

$$\underset{\text{OPx}}{Mg_9Fe_3(SiO_3)_{12}} + 1/2O_2 + 3H_2O + 2CaO = \underset{\text{Trm}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{Mgt}}{Fe_3O_4} + 4MgO + 4SiO_2$$

The smectitic secondary clays Sm(OPx) have a chemical composition very similar to that of nontronite but with a lower Al-content and an higher Mg-content. These clays are probably composed of a mixture of nontronite and saponite. These differences with common nontronite compositions are due to the fact that these clays are formed by weathering of Al-poor magnesian orthopyroxenes. The illuviated smectite Sm(ill) has a chemical composition more closely related to the composition of a typical nontronite because an infilling clays material is much more influenced by the mean chemical composition of the environmental rock than are the pseudomorphs in which ion exchange are more restricted. In the upper parts of the weathered profiles, the lack of sufficient aluminum inhibits the kaolinite formation by degradation of the secondary smectitic clays and only iron oxyhydrates are formed at the expense of the early formed pseudomorphs. Compared with these smectites formed by weathering of orthopyroxenes, the smectitic clays formed by weathering of the clinopyroxenes, in the same Koua Bocca ultramafic intrusion (DELVIGNE, 1983) have an higher Al-content and lower Fe- and Mg-contents and have a mean chemical composition closely similar to that of a typical nontronite.

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