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# LATERITES OF THE SERRANIA DE LOS GUAICAS AREA (VENEZUELA) AND THEIR MOTHER ROCKS

*With 8 text-figures, 2 plates, 2 annexes and 1 geological map*


## ABSTRACT

In the Serrania de los Guaicas area, in Roraima sandstones, sills of diabase are located, from which laterite deposits have been formed by surface weathering. The results obtained by mineralogical and chemical analyses showed that the chemical composition of laterite depends on the mineral composition and structure of the mother rock. Genetic processes which lead to the forming of laterite have been described.

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# I INTRODUCTION

. The Serrania de los Guaicas area is located 230 km. south of Ciudad Bolivar and 12–17 km. west of the Canaima Falls. The central part of the explored area is located on the parallels 6° 11′ north latitude and 62° 55′ west longitude.
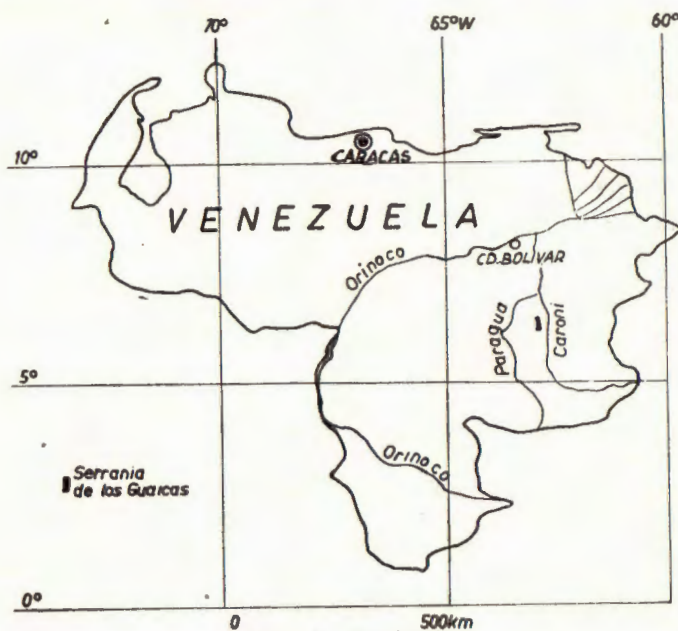


Fig. 1. Location map.
Sl. 1. Pregledna karta.

The country is of a mild topography. Above a relatively plane surface, which lies at an elevation of about 300 m., diabase ridges rise 50–200 m. high. The most prominent of them are Fila de los Guaicas, which is about 30 km. long, striking N 20° W, and the ridge west of Fila de los Guaicas, the length of which is 10 km., striking N 55° W.

The vegetation at the foot of the ridge in the adjacent lowlands is a thick jungle, while on the elevated parts of the ridge, where there is a laterite crust, the vegetation consists of low trees and thick bushes.

The climate is tropical, with two well-marked seasons: the dry season lasting from December to May, and the rainy one from May to December. The quantity of annual precipitations is about 2,000 mm. and the mean temperature is about 28° C.

The exploration of laterite was carried out in the southern part of the Los Guaicas ridge, in a stretch of 5 km. (zone A), and in the ridge which is located west of the Los Guaicas ridge, in a stretch of 6 km. (zone B). The exploration was carried out by test pits and test holes along profile lines set up perpendicularly to the strike of the ridge. The distance between profile lines was 1 km. Forty-four exploration works were performed, with the total depth of 362 m., out of which 356 samples were taken for chemical analysis.

## II GEOLOGY AND STRUCTURE

### 1. *Geological Description of the Area*

The sediments of the Roraima formation and magmatic rocks of the Roraima magmatic province are situated within the explored area.

The Roraima formation is placed discordantly on the Pastora series. The fundamental and essential characteristics of this formation is that it is composed of clastic sediments, prevailingly sandstones. As regards their properties, the sandstones are varying horizontally and vertically in their size and mineral composition, both in detrital particles and in the composition of the matrix. Sometimes they are almost pure quartz sandstones with quartz cement, showing transitional forms towards arkose and graywacke. Their colour ranges from white and red to dark grey. The grain size increases from base to top.

Conglomerate layers, 3–10 m. thick, sometimes containing porphyry fragments, were frequently encountered. The matrix is siliceous-hematite sandstone. The horizontal extension is up to 6 km.

Locally, there are some intercalations of red schists, 4–5 m. thick.

According to various authors, the thickness of the formations differs (650–2600 m.).

The age of the formations could not be exactly determined, because of the lack of palaeontological data. On the basis of a correlation to the other adjacent layers, it appears that, most probably, the Roraima formation belongs to the Cretaceous (C i v r i e u x, J. M. S., 1956, page 508).

The results obtained by analyses of sandstones from the exploration area showed that detrital grains are composed of quartz, plagioclase (0–15% *an*) orthoclase, microcline, muscovite, chert and rock fragments. The matrix is composed of microcrystalline quartz, chlorite, sericite, biotite, pyrite, zoisite, and epidote. Epidote is the predominant mineral of the matrix. Matrix minerals are comparatively coarse-grained.

The unusual mineral composition and texture of the matrix indicates that the sandstone underwent a change caused by the influence of the adjacent diabase sill, which caused the formation of new minerals from the primary sandstone matrix.

The Roraima Magmatic Province belongs to the Post-Roraima Cycle of magmatic activity, developed in the northern parts of the Brazil-Guayana shield, and forming intrusive rocks of the hypoabyssal type. The main types of rocks are: hypersthenic, olivinic and tholeiitic diabase, then myrmekite gabbro and quartz gabbro. »The Roraima formation was intruded by sills, dikes and laccoliths made-up of gabbroid rocks, the composition of which goes from quartziferous gabbros to oliviniferous diabases, going through intermediate types of magmatic differentiation.«

»The post-Roraima magmatic province, typically tholeiitic, is characterized by its low iron and alkali content and its absence of olivine. The magmatic differentiation process was mainly by fractional crystallization and gravitational separation. Such process was moderate, since the oli-

viniferous, granophyric and orthopyroxenic diabases are less frequent than the other types. The endomorphic and exomorphic processes (contact metamorphism) were slight. This shows the little mobility of the magma during the primary stage of the crystallization.« (B e l l i z z i a, A. G. 1956, p. 512–513).

There are two diabase sills in the explored area, forming two remarkable ridges: zone A (Fila de los Guaicas) and zone B. As no exposures were noticed there, it was not possible to carry out exact measurements of the thickness of the sills, but from the shape of the profiles of the ridges and the dip of the sills (20 degrees in the NW direction), it may be concluded that the thickness of the diabase sills amounts to 70—120 m.

## 2. *Tectonic Structure of the Area*

The explored region of Serrania de los Guaicas comprises a restricted surface too small for thorough explorations and examination which are necessary for more complete conclusions about the structure of the area.

On the geological sketch map it may be seen that the explored area represents a part of the anticline striking SE–NW, mildly pitching towards NW. This anticline is marked by diabase sills, concordantly pressed into Roraima sandstones. The general strike of the layers in the eastern part of the area is N–S, and in the western part NW–SE. The layers dip toward East, or NE by some 20⁰, resp., with the exception of the extreme western part of the area, where they dip to the West.

The area is cut by radial faults. The striking of faults N 25⁰ W and N 35⁰ E is especially prominent. These systems of faults have conditioned the directions of most of the water courses within the region.

It was not possible to determine the number of sills in the Roraima formation, but they are probably quite numerous. Due to the action of faulting, especially by the systems of faults striking N 25⁰ W, the number of exposures of diabase sills has been increased.

## 3. *Petrological Description of Diabase*

Detailed and thorough petrological examinations of zones A and B were carried out, as diabases of the two zones are somewhat different in texture and mineral composition, and so are laterites.

Zone A rock is of a dark colour with light columnar crystals and feldspar aggregations, clearly discernible, and with dark, nearly black, pyroxene aggregations. Zone B rock is of a dark green colour, microcrystalline, so that individual grains of feldspar and pyroxene cannot be distinguished. Sporadically, there are also very small pyrite nests.

Microscopically, quite a significant textural difference exists between rocks belonging to the two zones. Thus, rock from zone A is composed of comparatively more coarse-grained and generally idiomorphically developed prismatic crystals of plagioclase, forming about 60 volum. % of the rock. Within the plagioclase mass isolated aggregations of pyroxene prevail, but there are some individual xenomorphic grains of pyroxene. Plagioclase crystals surpass im size pyroxene grains, thus they are only partly enclosed by the latter. Hence, the texture of the rocks is subophitic.

Plagioclases of zone B rock form about 40 volum. % of the rock. They are also idiomorphic, but smaller in size, and generally enclosed by pyroxenes; hence, the texture is ophitic. (Plate I, Fig. 1, 2, 3).

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Beside plagioclase and pyroxene, the main mineral of the rock is amphibole. The accessory and secondary components are quartz, orthoclase, apatite, chlorite, sericite and leucoxene. In rocks from zone A there are also biotite and calcite while epidote was found in rocks from zone B.

The ore minerals are as follows: ilmenite, magnetite, pyrite, chalcopyrite, pyrrhotite, hematite and covellite.

## Microphysiography and Chemism of Diabase

*Plagioclases* occur as idiomorphically and hypidiomorphically developed columnar crystals. Normally, they are closely compacted, most frequently as polysynthetic twins and sometimes, but not so often, as twins. Zonar structure is rarely encountered. The most frequent among the twinning laws are the Karlsbad law, the Albite law, and sometimes other twinning laws.

The size of individual plagioclase crystals in rocks from zone A ranges from $0,2 \times 0,1$ to $2,0 \times 0,5$ mm., the average size being $0,6 \times 0,2$ mm., and in rocks from zone B, from $0,05 \times 0,02$ to $1,0 \times 0,2$ mm., the average size being $0,3 \times 0,1$ mm.

Plagioclases of zone A are nearly fresh, only in some places kaolinized and sericitized to a smaller degree. Plagioclase rocks of zone B are slightly more kaolinized and sericitized, with a remarkable epidotization.

By the measurement of plagioclases (Fedorov's method) it has been determined that the percentage of anorthite in rocks from zone A varies from $56^0/0$ to $62^1/2^0/0$ *an*. The mean value is $60^0/0$ *an*. The mean value of the optic axial angle is $2 V = +81^0$.

Plagioclase rocks of zone B contain $43^0/0$ to $57^0/0$ *an*, with the mean value of $52^0/0$ *an*. The mean value of the optic axial angle is $2 V = +78^0$.

From the above data we may conclude that plagioclases belong to labradorite.

*Pyroxenes* occur as xenomorphic mineral grains. Their size is $0,2 \times 0,1$ to $1,5 \times 0,5$ mm., the average being $0,4 \times 0,2$ mm. In rock specimens from zone B pyroxenes are evenly distributed throughout the rock, forming a basis between the columnar crystals of plagioclase. In rocks of zone A pyroxenes are most frequently encountered in aggregations, their size amounting to 3 mm. Pyroxenes are of a light brown colour with a pinkish tint, probably due to the admicture of titanium. Pleochroism has not been noticed.

By the measurement of the extinction angle and the optic axial angle, it was established that pyroxenes can be classed into two groups, i. e.: group I with $c \wedge Z = 34-37^0$, and group II with $c \wedge Z = 42-45^0$. The angle $2 V$ is the same for both groups, i. e. $2 V = +38-40^0$. According to the optic data, group I belongs to the group of clinoenstatite-diopsides, having about $60^0/0$ of diopside molecules. Pyroxenes of group II contain a higher iron percentage, therefore their $c \wedge Z$ angle has been increased. According to A. & H. Winchell (Winchel, A. & H. 1951, p. 408, 410),

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this is a transitional type of pyroxenes between augite and ferro-augite. Both pyroxenes were found together in the same rock, but is has become evident that group I is more frequently encountered in rocks of zone B, and group II in rocks of zone A. According to H. W i l l i a m s (Williams G. et al. 1955, p. 47), pyroxenes of groups I and II – in general – were crystallized at the same time, but ferroaugite still crystallizes after pyroxenes of group I have been formed.

*Orthoclase* is a normal and regular component of rocks of both zones, but its amount is considerably smaller than the amount of plagioclase. Its grains are xenomorphic, their size amounting to 0,4 mm., filling the voids left after the majority of minerals have been crystallized. Usually this mineral comes together with quartz, and they are graphically intergrown. Orthoclase is more intensively subjected to the process of alteration than plagioclase ,so that, as a rule, it becomes turbid due to the admixture of kaolin substance. Crystals are never twinned. The index of refraction is considerably lower than that of quartz.

Due to the effects of weathering of the grains and on account of the absence of crystallographic elements, there was no possibility for exact optical measurement, but – by the index of refraction and also by the usual occuring of smaller amounts of orthoclase in diabase – it may be concluded that the mineral dealt with is orthoclase. Besides, the presence of $K_2O$ (1,14% in the rock of zone A and 0,83% in the rock of zone B) indicates that the mineral in question is orthoclase. Differences in the percentage of $K_2O$, proved by a comparison of the rocks, are in accordance with the results of optical observation, for there is more orthoclase in rocks of zone A than in those of zone B.

*Quartz* occurs in the shape of xenomorphic grains, their size amounting to 0,6 mm., usually together with orthoclase. It is more wide-spread in rocks of zone A.

*Amphibole* is the main mineral of the rock. Most frequently it forms a kind of coating around pyroxene, and sometimes, but not so often, it occurs in the shape of independent xenomorphic grains. Generally, it has been developed by the uralitization proces (uralite). The process of uralitization is much more intense in rocks of zone B, where uralite is fibrous, while in rocks of zone A it is mostly lamellar with some bigger grains (their size amounting to 0,5 mm.). Pleochroism // X is light gren, // Y dark green and // Z dark green. The extinction angle is $c \wedge Z = 12–16^0$. From the results of chemical analyses it is obvious that the content of aluminium has been increased, especially in rocks of zone B, where there is more amphibole. Hence, it may be concluded that a part of alumina is bound to amphibole, which, accordingly, belongs to the group of hornblende.

*Apatite* occurs as columnar crystal in feldspar and quartz.

*Biotite* is usually irregularly shaped, its size amounting to 0,5 mm. Sections normal to (001) are showing intensive pleochroism: // Z

reddish–brown, // X light greenish–brown. According to pleochroism it may be concluded that the biotite contains titanium. It is of syngenetic origin with amphibole and sometimes they are parallel growth. Biotite has been noticed only in rocks of zone A.

*Epidote* occurs as individual crystal of a prismatic habitus, its size is about 0,1 mm. More frequently it is found in irregular small–grained aggregations within plagioclase. It shows a high refraction and birefrigence, its colour is yellow. It is encountered only in rocks of zone B.

*Chlorite* has been developed mostly from pyroxene and encountered together with uralite in the shape of irregular greenish lamellae. There are also individual xenomorphic chlorite grains of a larger size, in the voids left after the crystallization of the main minerals of the rock. Chloritization is much more expressed in the rock of zone B, where chlorite and fibrous amphibole are intimately intergrown. The above facts indicate that chlorite is not a product of superficial alteration of the ferromagnesian minerals, but it draws its origin from a later stage of the formation of the rock.

*Sericite* is encountered as very small lamellae within feldspar. It has a positive optic character of elongation.

*Calcite* is rarely encountered. Only a few grains were noticed in the rock of zone A.

For the determination of opaque minerals within these rocks optical examinations in reflected light were carried out. In this way the following minerals were determined: ilmenite, magnetite, pyrite, chalcopyrite, pyrrhotite, hematite and covellite.

*Ilmenite* is the most frequent opaque mineral of the rock. Usually it occurs in the shape of xenomorphic and skeleton grains, more seldom it is idiomorphic. Along the rims of grains there is sometimes a transition towards leucoxene. Ilmenite is often parallel growth with magnetite and there are oriented exsolutions of magnetite, as well as (less frequently) hematite.

*Magnetite* occurs as xenomorphic and idiomorphic grain, together with ilmenite and as exsolution lamellae in ilmenite.

*Pyrite* occurs either as individual grains or in small–grained bands.

*Chalcopyrite* is frequently encountered in the shape of very small grains. Rarely, at the margin, a transition towards *covellite* was noticed.

*Pyrrhotite* nearly always was encountered with chalcopyrite. It occurs in xenomorphic grains, their size amounting to 0,1 mm.

*Hematite* is a scarce mineral. It occurs in very small nests beside magnetite and as correctly aligned lamellae in ilmenite and magnetite.

Chalcopyrite and pyrrhotite were noticed more frequently in rocks of zone A, and pyrite and hematite in rocks of zone B.

To establish the quantitative mineral composition of rocks of both zones, an integration of thin sections of the rocks was carried out. Due to the fact that chlorite and hornblende are intimately intergrown, a discrimination of these two minerals was not possible (Table I).

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TABLE I

|  | A 12 %  | B 6 % |
|---|---|---|
| Feldspars | 59.1 | 38.2 |
| Pyroxenes | 20.2 | 11.4 |
| Hornblende and Chlorite | 9.1 | 42 8 |
| Quartz | 10.1 | 2.4 |
| Ore Minerals | 0.9 | 5.3 |
| Biotite | 0.6 | — |
|  | 100.0% | 100.0% |

Two chemical analyses were carried out, one of the rock from zone A and the other from zone B (Table II).

TABLE II

Analyst: D. Šiftar

|  | A 11 % | B 6 % | C % | D % |
|---|---|---|---|---|
| $SiO_2$ | 48.60 | 43.29 | 50.48 | 51.96 |
| $TiO_2$ | 1.48 | 2.60 | 1.45 | 0.78 |
| $Al_2O_3$ | 15.83 | 18.22 | 15.34 | 14.85 |
| $Fe_2O_3$ | 1.99 | 2.72 | 3.84 | 1.91 |
| FeO | 11.43 | 11.92 | 7.78 | 9.11 |
| MnO | 0.12 | 0.19 | 0.20 | 0.16 |
| MgO | 7.51 | 6.65 | 5.79 | 7.79 |
| CaO | 9.21 | 9.75 | 8.94 | 9.95 |
| $Na_2O$ | 2.45 | 2.33 | 3.07 | 1.99 |
| $K_2O$ | 1.14 | 0.83 | 0.97 | 0.66 |
| $P_2O_5$ | traces | 0.01 | 0.25 | 0.11 |
| $S_2$ | traces | 0.24 |  |  |
| $H_2O-$ | 0.10 | 0.16 |  | 0.12 |
| $H_2O+$ | 0.27 | 1.17 | 1.89 | 0 54 |
|  | 100.13 | 100.08 |  |  |
| $O = S_2$ |  | 0.06 |  |  |
|  |  | 100.02 |  |  |
| Sp. gr. | 2.92 | 2.94 |  |  |

A 11 = specimen from zone A
B 6 = specimen from zone B
C = average composition of diabase (D a l y, 1933)
D = average composition of Rorairna diabase (B e l l i z z i a, A. G., 1957)

## TABLE III

| CIPW Norm: | | | Niggli Values: | | |
|---|---|---|---|---|---|
| | A 11 | B 6 | | A 11 | B 6 |
| or | 7.24 | 5.00 | si | 110 | 94 |
| ab | 20.95 | 16.77 | al | 21 | 23 |
| an | 28.50 | 37.25 | fm | 50 | 48 |
| ne | — | 1.70 | c | 22 | 23 |
| di | 13.18 | 9.08 | alk | 7 | 6 |
| hy | 11.30 | — | k | 0.23 | 0.20 |
| ol | 10.09 | 16.90 | mg | 0.50 | 0.45 |
| mt | 2.78 | 3.95 | ti | 2.5 | 4.2 |
| il | 2.88 | 5.08 | $q_2$ | — 18 | —30 |
| pr | — | 0.84 | Magma type | normally gabbroid | normally gabbroid |

Magmatic parameters »III. 5.« 4. 4 II/III/. 5. 4. 4.

If the normative composition (CIPW) is compared with the modal mineral composition, it becomes obvious that they differ from each other in minerals as well as in quantities. These differences are especially obvious in specimen B 6. This is due to the fact that a considerable amount of minerals are not calculated in the normative composition. Thus, the ferromagnesian minerals are represented in the rocks by pyroxene (2 types), hornblende and cholorite, and in the normative composition there are diopside, hypersthene and olivine. The difference in the chemical composition of modal and normative ferromagnesian minerals becomes evident especially by the fact that with modal minerals a part of silica is replaced by aluminium, which does not happen with normative minerals. Therefore, olivine appears in the calculation, and the rock is unsaturated by $SiO_2$, while – in fact – it contains quartz. For the same reason the normative Sal : Fem ratio in specimen B 6 is greater than the modal Sal : Fem ratio.

If the percentage of anortite in plagioclase is calculated from the normative composition it amounts to 58% with rocks of zone A, which is in accordance with the results of the optic measurements. With rocks of zone B the calculation gives 69% an, while modal plagioclases are more acid. This is due to the fact that the part of calcium bound to anorthite in the calculation is actually bound to epidote and hornblende, and the $Al_2O_3$ to hornblende and chlorite.

The normative content of ilmenite is slightly greater than the actual content. This is quite possible as a part of titanium is bound to pyroxene, which is also indicated by the pinkish tint of this mineral.

As per Niggli values, both rocks belong to normal gabbroid magma, and the values of the A 11 rock are entirely in accordance with Niggli's standard values for the magmatic type (B u r r i, H. & N i g g l i, P., 1945), while the B 6 rock has a slightly lower si content. Accordingly, magmatic origin is the same for both sills, which appears quite a logical supposition if the geological conditions in the field are taken into consideration.

The ophitic (B 6) and the subophitic (A 11) textures show the vein type of the rocks, viz. the hypoabyssal level. According to these data and as regards the chemical and mineral composition of the rocks (labradorite, pyroxene, hornblende), and according to the geological con-

ditions, the explored rocks are to be classified as diabase, and the best suited name for them would be t h o l e i i t i c   d i a b a s e. Although these rocks contain quartz, especially in zone A, the rock has not been described as tholeiitic quartz diabase, as proved by our chemical analyses (unsaturated with $SiO_2$).

If the chemical composition of the explored rocks is compared with the average composition of diabase (Table II), one can notice that the explored diabases differ from the average composition of diabase by their lower percentage of $SiO_2$ and higher percentage of $Al_2O_3$, FeO, MgO and CaO. A specially characteristic feature is a more remarkable increase of the percentage of FeO, which certainly is one of the reasons for a high percentage of iron in the laterites originating from these diabases. An incerase of the FeO, MgO and CaO contents characterizes the entire Roraima magmatic province. (B e l l i z z i a, A. G., 1957). In addition to the increased amount of bases and the presence of quartz, the explored diabases are also characterized by quite a remarkable uralitization. In zona A the uralite »coating« around pyroxene grains frequently consists of coarse–grained hornblende, parallel growth with pyroxene. This hornblende draws its origin from the later part of the magmatic stage of the diabase development, when the remaining part of magma became enriched by volatiles. Simultaneously, hornblende became crystallized, partly directly, and partly by the process of uralitization of pyroxene. The theoretical explanation for such a development of uralite was given by M. T a j d e r (1942). There is another supposition that the ferro-magnesian mineral had started to be crystallized as pyroxene and afterwards – due to alterations in the composition of magma – its crystallization ended as amphibole. In the course of this process the crystals have become parallel growth. The structural and chemical similarity between pyroxene and amphibole substantiates this supposition.

Fibrous hornblende, which is particularly wide–spread in the diabase of zone B, was developed by the uralitization of pyroxene. The fact that it is intimately intergrown with chlorite proves the simultaneous origin of the two minerals and indicates that the fibrous hornblende had been developed in the final magmatic stage, or, more probably, in the epi-magmatic stage, which followed immediately after the magmatic stage. The mineral paragenesis of diabase and the intensive epidotization and silicification of the surrounding sandstones indicate that the epimagmatic stage had been rather strong. The epimagmatic stage was stronger at the diabase of zone B.

The sequence of the crystallization of diabase is as follows:

The magmatic stage: ilmenite, magnetite → labradorite → pyroxene → grainy hornblende, biotite → ortho-clase, quartz.

The epimagmatic stage: fibrous hornblende, chlorite, epidote, sericite, chalcopyrite, pyrrhotite.

In addition to a certain difference in the chemism of diabases of zones A and B (Tables II and III) there are also some mineralogical and tex-

tural differences. This is the reason for a certain textural and chemical difference between laterites of zones A and B. These differences between diabases of the two zones are due neither to the differently originated magma, nor to the different time of the diabase development, but they should be attributed exclusively to magmatic differentiation. It frequently happens that the mineralogical and chemical composition of diabase sills is different on different levels. (W i l l i a m s H. etc, 1955, p. 47; Z a v a r i c k i j, A. N., 1956, p. 181; B e l l i z z i a, A. G. 1957).

## III. LATERITE

### 1. *Form of Laterites*

Ferruginous bauxite deposits have been developed by the process of laterization of diabase sills, hence, they are connected with diabase exposures. Diabase sills compose clearly noticeable and prominent ridges, with laterites on their mildly rounded tops. Diabase sills are rather wide–spread in the area of Rio Caroni – Alto Chiguao and so are laterites. But, only a reduced portion of the deposits in this area were explored, which is enough to get an idea about the areal, mineralogical, and chemical properties of the deposits of this area.

The form of the deposit depends on the geological properties of the diabase sill (thickness, dip, faults). As diabase sills of zones A and B are characterized by similar geological properties, the morphological properties of the laterite of both zones will be similar too. Laterite blankets extend continually over diabase sills and their strike and length depend on the strike and length of each diabase sill exposure.

The width of the laterite cover is varying fro m200 to 500 m.; 400 m. on the average. The thickness of the upper part of laterite, of a ferruginous bauxite composition, varies from 2 to 14 m., the mean thickness being 7 m. The thickness of the argillaceous lower part of laterite varies from 3—9 m.

The greatest thickness of the ferruginous bauxite part of laterite was found out on the steep slope; it gradually diminishes towards the mildly dipping slope.
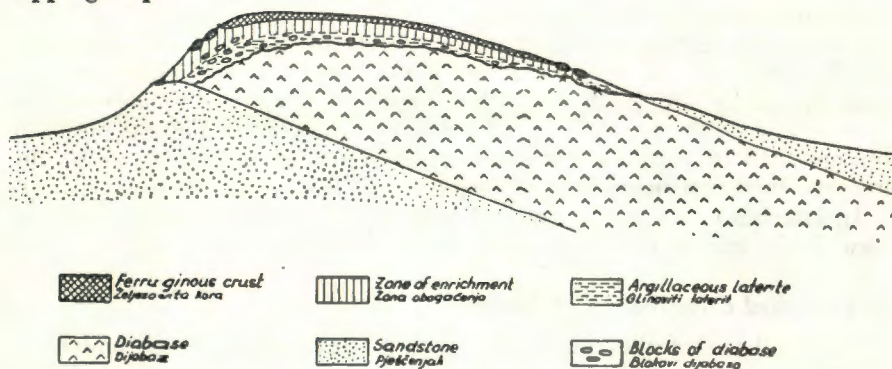


Ferruginous crust
Željezovita kora

Zone of enrichment
Zona obogaćenja

Argillaceous laterite
Glinoviti laterit

Diabase
Dijabaz

Sandstone
Pješčenjak

Blocks of diabase
Blokovi dijabaza

Fig. 2. *Shematic cross-section of the laterite deposit.*
Sl. 2. Shematski profil kroz lateritno ležište

## 2. *Physical Properties of Laterite*

The structure of ferruginous bauxites is not uniform, but it is varying with different parts of the deposit. The main structural varieties to be distinguished are the following:

1. Porous, comparatively hard ore, of a yellowish brown colour with bright spots (»roca celular«). The ore has a well-preserved diabase texture. The macrosopically visible bright spots represent the aggregations of gibbsite, developed from plagioclase, while the dark spots are a colloidal mixture of gibbsite and »limonite«, developed from ferromagnesium silicates (Plate, Fig. 4, 5, 6). The unit weight of this ore is 1, 6.

2. Hard, porous-granular ore of a brownish-red colour (»costra ferruginosa«).

3. Soft earthy ore of a colour ranging from reddish-brown to violet.

4. Soft earthy ore with hard nodules, their size varying from 0.5 to 10 cm. The nodules are mostly composed of a gibbsite and »limonite«« mixture, only occasionally of a nearly pure, white gibbsite.

5. Fanglomerate ore, composed either of cemented or of uncemented laterite fragments, noticed in the lower parts of the slope. It has been formed by mechanical disintegration and short transport of laterite fragments.

The lower, i. e. the clayey part of laterite is soft and earthy, its colour ranging from chocolate-brown to reddishbrown. Sometimes a well-preserved diabase texture is noticed. Sporadically, there are white lenses and clayey intercalations, the thickness of which amounts to 20 cm. Usually, the transition from clayey laterite to ferruginous bauxite is abrupt and clearly visible, except in the case when the structure of ferruginous bauxite is earthy.

In the lower parts of clayey laterite there are smaller blocks of unaltered diabase. Blocks of unaltered diabase, spherically shaped, 10–20 cm. in size, were sometimes encountered also in the lower parts of porous ore.

There are no great differences in the mineralogical and chemical composition of different structural varieties of this ore. Only the porous, comparatively hard ore contains a higher percentage of aluminium and lower percentage of iron, while the hard, porous-granular ore contains more iron and less aluminium.

Lateral alterations of structural varieties of the ore are generally small, while vertical alterations are considerably greater. Usually, porous or earthy ore (with or without nodules), lies above argillaceous laterite and on the top there is a hard crust composed of porous granular ore enriched by iron. The thickness of the crust varies from 1–5 m., the average thickness being 2 m.

In laterites of zone A the porous type of ore is predominant, while in zone B the earthy type with nodules is prevailing.

## 3. *Chemical Composition of Laterite*

On the basis of the results of chemical analyses, vertical and horizontal variations of the chemical composition were established. Particularly well expressed are vertical changes which permit the division of laterite into three zones:

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1. The upper zone, richer in iron, and low in alumina; the $Fe_2O_3$ content is often above 50%, and the $Al_2O_3$ is below 20%. As a rule, this is a hard, porous–granular ore.

2. The middle zone, enriched by aluminium; the $Al_2O_3$ content is 25–45%, and the $Fe_2O_3$ content is 30–45%; the $SiO_2$ content in both zones is 0,1–5%.

3. The lower zone, where the $SiO_2$ content suddenly gets increased above 5%; the $Al_2O_3$ content is 20–30%, and the $Fe_2O_3$ content is 20–40%.

Such a vertical cross–section is typical and it characterizes most of the laterites developed from basic rocks in humid tropical regions.

Horizontal changes in the chemical composition are less expresed; they can be noticed in the direction normal to the strike of the deposit (the ridge). The $Al_2O_3$ : $Fe_2O_3$ ratio is highest on the steep slope, while in the direction towards the mildly dipping slope it turns in favour of $Fe_2O_3$.

There is also a difference between the chemical composition of zone A and that of zone B. Thus, it was proved that the $Al_2O_3$ percentage in laterites of zone A is higher and the $Fe_2O_3$ percentage lower, than in laterites of zone B. The average chemical composition of ferruginous bauxite in zone A is $Al_2O_3 = 34.5\%$, $Fe_2O_3 = 37.0$, $SiO_2 = 1.73\%$, $TiO_2 = 3,7\%$ and in zone B, $Al_2O_3 = 31,0\%$, $Fe_2O_3 = 43,5\%$, $SiO_2 = 1,42\%$, $TiO_2 = 5.5\%$.

Table IV shows the chemical composition of laterite, noticed at exploration works $A_{13}$ bis and B 3 + 3. These data were used for the study of the genesis of laterite. The same samples served for the mineralogical examination of laterite.

## 4. Mineralogical Composition of Laterite

Examinations of the mineralogical composition of laterite were carried out in polarized and in reflected lights. But, on account of the partly cryptocrystalline and gel structure of laterite, differential–thermal investigations (DTA), thermogravimetric analyses (TGA), X–ray, analyses and infrared spectra were applied and the question of the mineral composition of laterite was definitely and completely resolved.

*Microtexture and Microstructure of Ore.* A typical feature of porous ore (»Roca celular«) is a well–preserved diabase texture (Plate I, Fig. 4). But the original minerals have been completely destroyed, with the exception of ilmenite and partly quartz. The plagioclase laths have been replaced by gibbsite, but the plagioclase shape and sometimes even its cleavages have been preserved. (Plate II, Fig. 5, 6). Pyroxenes, amphiboles and chlorites have been replaced by the undifferentiated cryptocrystalline and gel mass of gibbsite, goethite and of yellowishbrown »limonite«. Idiomorphic and xenomorphic grains of ore minerals were also noticed, as well as xenomorphic grains of quartz.

The hard porous–granular ore is composed of a cryptocrystalline gel mass of gibbsite and of reddish–brown »limonite«. Within this mass there are some individual coarse grains of gibbsite and quartz, some nests of gibbsite and ore minerals.

Due to the leaching of gypsite and migration of Fe hydroxide in the ferruginous crust, the structure of the hard porous–granular ore is cellular with voids whose size reaches several centimeters.

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# TABLE IV

## CHEMICAL ANALYSES OF LATERITE AND DIABASE

ZONE A – TEST HOLE A 12 bis

Analyst: *D. Šiftar*

| № = of samp. | DEPTH m | ROCK (ORE) | Chemical composition % | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $H_2O$ |
| A 1 | | Diabase | 48.60 | 1.48 | 15.83 | 1.99 | 11.43 | 0.12 | 7.51 | 9.21 | 2.45 | 1.14 | 0.27 |
| A 2 | 14.0–14.3 | Arg. laterite | 29.79 | 2.79 | 28.29 | 23.62 | | 0.05 | tr. | 0.10 | — | — | 11.55 |
| A 3 | 11–13 | Ferr. bauxite | 3.80 | 3.67 | 36.82 | 34.85 | | 0.06 | — | 0.06 | — | — | 18.55 |
| A 4 | 5–6 | " | 0.16 | 3.65 | 36.56 | 37.84 | | 0.07 | — | 0.04 | — | — | 20.81 |
| A 5 | 3–4 | " | 0.16 | 3.80 | 27.09 | 50.34 | | 0.07 | — | 0.05 | — | — | 17.20 |
| A 6 | 1–2 | " | 0.10 | 3.94 | 20.70 | 59.67 | | 0.07 | — | 0.05 | — | — | 13.53 |

ZONE B – TEST PIT B 3 + 3

| № = of samp. | DEPTH m | ROCK (ORE) | Chemical composition % | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $H_2O$ |
| B 1 | | Diabase | 43.29 | 2.60 | 18.22 | 2.72 | 11.92 | 0.19 | 6.65 | 9.75 | 2.33 | 0.83 | 1.17 |
| B 2 | 10 | Arg. laterite | 11.20 | 5.13 | 27.60 | 38.60 | | 0.15 | — | 0.05 | — | — | 15.18 |
| B 3 | 5.5 | Ferr. bauxite | 0.56 | 5.66 | 36.02 | 36.15 | | 0.15 | — | 0.05 | — | — | 20.12 |
| B 4 | 2.5 | " | 0.58 | 5.63 | 32.91 | 40.30 | | 0.15 | — | 0.05 | — | — | 18.27 |
| *B5–6 | 2–3 | " | 0.50 | 4.08 | 41.95 | 27.80 | | 0.08 | — | 0.05 | — | — | 24.64 |

* Test pit B 5 + 6

The colour of nodules changes from light to dark brown, depending on whether the nodule has been enriched by gibbsite or by goethite. The texture of diabase is not well–preserved. Gibbsite nodules consist chiefly of fine–grained gibbsite, sporadically with brown nests of the gel mass of gibbsite and goethile. Nodules enriched with iron correspond to the hard porous—granular ore by their structure and composition.

Paragenesis and Microphysiography of Laterite Minerals. The following mineral composition of laterite was determined: gibbsite, kaolinite, halloysite, quartz, »amorphous limonite«, goethite, hematite, ilmenite and leucoxene.

*Gibbsite* is represented by two forms: the cryptocrystalline and the crystalline ones.

Cryptocrystalline gibbsite occurs together with goethite and »amorphous limonite« in undifferentiated opaque masses, or is of colloform texture. Cryptocrystalline gibbsite was treated only by thermal and X–ray methods.

Crystalline gibbsite is colourless, replacing plagioclase by micro- and fine-grained aggregations. It occurs either in lamellar, tabular and square-shaped forms, or in radial-fibrous aggregations. Polysynthetic twins, parallel to (001), are frequent. Cleavage, parallel to (001), is clearly noticeable, and the extinction angle — according to the mentioned cleavage – is 23⁰. The refraction index is greater than that of Canada balsam.

The size of the gibbsite particles is varying from 10–150 $\mu$. A characteristic feature is that the size of gibbsite particles increases towards the surface of the ferruginous bauxite zone. So, at a depth of 6 m .(test pit A 10+6), the average size of gibbsite particles is 10 $\mu$, at a depth of 4.5 m. 30 $\mu$, at 3.5 m. 50 $\mu$, and near to the surface 100 $\mu$. This proves that all the time, along with the process of laterization, there is a recrystallization and gibbsite crystals are steadily growing.

An interesting fact is that some of the optic characteristics of gibbsite depend on the size of grains. Small crystalline gibbsite has a considerably smaller birefringence as compared to more coarse-crystallized gibbsite. Thus, with small-grained gibbsite the interference colours are white-grey (the first order), while with coarse-grained gibbsite (above 0.1 mm.), they are reddish -blue, i. e. transitional colours between the first and the second orders. To make possible the replacement of small-grained gibbsite with kaolinite, thermal and X-ray analyses of samples A 11 + 6, from 6 m., and 3.5 m. depths, were performed. It was ascertained that the mineral studied is gibbsite (Fig. 3). The same optic anomalies of gibbsite had been mentioned by S. I. Beneslavskij (1958, p. 14).

*Quartz* is frequently encountered, but in small amounts. It occurs in the form of xenomorphic grains, their size varying from 50 to 200 $\mu$. As quartz is more resistant than other silicates against laterization process, it can be supposed that this quartz draws its origin from diabase.

*Goethite and »Amorphous Limonite«* occur together with a larger or smaller amount of gibbsite, as an undifferentiated opaque mass, filling the interestices of microcrystalline gibbsite, that has been developed

from plagioclase. In the hart porous-granular ore goethite represents the largest part of rock, and in this »limonite« there are individual coarse grains of gibbsite and quartz, as well as gibbsite aggregations. The presence of goethite in irregular voids and its colloform texture indicate a local migration of iron hydroxides.

It is not possible to determine the degree of crystallinity of Fe hydroxide by optical methods, due to its criptocrystalline and gel structure. Well-marked lines of goethite were recognised by means of X-ray analysis. Accordingly, it can be concluded that the major part of Fe hydroxide is in the form of goethite.

The »limonite«-gibbsite mass has been developed from ferromagnesian minerals of diabase.

*Ilmenite* is a very resistant mineral, having sometimes preserved its idiomorphic form, or displaying a xenomorphic form, because on its margin it has been, to a smaller or greater extent, transformed into leucoxene. It is the most frequent ore mineral in laterite.

*Hematite* forms very small microcrystalline aggregations within »limonite«, or – more frequently – it is a product of the transformation of magnetite into hematite (martite). When ilmenite and magnetite are in parallel growth, magnetite is entirely martitized, while ilmenite has remained intact (Plate II, Fig. 7, 8).

## Thermogravimetric (TG) and Differential-thermal (DT) Analyses

Early and hard varieties of laterite were studied by thermal methods. In addition to the cited minerals, determined by optical method, the existence of kaolinite and halloysite was established by thermal methods.

Fig. 3 shows thermobalance and differential-thermal curves. A remarkable loss of weight is stated on dehydration curves, within the temperature range from 200° to 320° C, provoked by the dehydration of gibbsite. Goethite and »amorphous limonite« are indicated by a loss of water in the temperature range from 320° to 450° C, which is more clearly remarkable on samples $A_4$, $A_5$ and $A_6$. Boehmite is indicated by a step at temperature 450° to 500° C and kaolinite by a step at temperature 625° to 680° C (B 2). Halloysite is indicated by a loss of water at 40° and 500° C (A 2).

The most remarkably expressed endothermic effect, noticed on differential-thermal curves, is that of gibbsite within ° and 320° C, which can be seen in all curves. The endothermic effect of goethite and »amorphous limonite« is noticed from 365° to 380° C, and particularly expressed on samples A 5, A 6 and B 4, while – on the other samples – it is hidden by the effect of gibbsite. Boehmite is characterized by en endothermic effect. Kaolinite shows an endothermic effect at 500° and an exothermic effect at 900° (B 2). Halloysite has an endothermic effect at 90° and at 500° (A 2).

Some effects, which indicate the presence of boehmite are recognizable on thermal curves. However, since boehmite was not detected by X-ray or infrared analyses, it can be concluded that the mentioned effects originate from »secondary« boehmite developed from gibbsite during the heating of the sample.

TG and DT analyses of laterite were performed by Dr. Ing. O. Švarc-Lahodny, Institute of Physical Chemistry, University of Zagreb.

## X-ray Analysis of Laterite

The X-ray analysis of laterite has been performed by means of Philips automatic-stabilizer generator, copper-monochromatic radiation (Ni-filter), Geiger-Müller counter, and electronic recorder with chart. Paper running was 800 mm. per hour.

**TABLE V**

Sample A 12 bis, 0–1 m

| d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I |
|-------|-----|-------|------|-------|------|-------|--------|
| 7.31 | 3 | 4.33 | 2 G | 3.05 | 1 G | 2.69 | 3 Gt+H |
| 6.97 | 2 | 4.15 | 4 Gt | 3.01 | 2 | 2.509 | 2 H |
| 6.47 | 2 | 3.76 | 2 | 2.96 | 1 GT | 2.437 | 3 Gt |
| 6.33 | 2 | 3.63 | 2 H | 2.89 | 1 | 2.391 | 2 G |
| 4.85 | 10 G | 3.34 | 4 G+Q | 2.726 | 2 G | | |

Sample A 12 bis, 13–14 m

| d (Å) | I | d (Å) | I | d (Å) | I | d (Å) | I |
|-------|-----|-------|------|--------|--------|-------|-----|
| 7.30 | 2 | 3.68 | 2 H | 2.66 | 2 Gt+H | 2.157 | 2 G |
| 6.95 | 1 | 3.54 | 2 | 2.548 | 1 I | 2.04 | 1 G |
| 5.62 | 1 | 3.34 | 4 G+Q | 2.508 | 1 H+Gt | 1.99 | 2 G |
| 4.85 | 10 G | 3.26 | 1 | 2.45 | 2 G+Gt | 1.914 | 1 G |
| 4.37 | 3 G | 2.83 | 1 | 2.42 | 4 | 1.84 | 1 H |
| 4.14 | 4 Gt | 2.74 | 1 I | 2.386 | 2 G | | |
| 3.85 | 2 | 2.70 | 2 Gt+H | 2.212 | 2 Gt | | |

G = gibbsite; Gt = goethite; H = hematite; Q = quartz; I = Ilmenite.

Samples from test hole A 12 bis, taken from the depth of 0–1 m (ferruginous crust) and from the depth of 13–14 m (clayey laterite) were analysed. (Table V) The presence of gibbsite, goethite, hematite, quartz, and ilmenite was established by means of X-ray analyses. The X-ray analyses were performed by Dr. S. Ščavničar, Institute »Rudjer Bošković«.

## Infrared Absorption of Laterite

In order to establish definitely whether boehmite is contained in laterite, an infrared spectral analysis of laterite was performed. This method enables the determination of a very small quantity of boehmite. Samples taken from test hole A 12 bis, at the depth of 0–1 m and 13–14 m, were analysed.

The tests were carried out at the Institut »Rudjer Bošković« by means of infrared spectrometer, Type 221, Perkin-Elmer manufacutre. KBr-pellet technique was applied.*

The characteristic part of a spectrogram from the wave number 3700 to 3100 cm⁻¹ and from 1100 to 700 cm⁻¹ is shown on Fig. 4. Infrared absorptions of wave numbers 3450, 3515, 3610, 3685 cm⁻¹, which show their minimum size on the spectrogram, originate from gibbsite. Boehmite absorbs infrared rays of wave number 3100 and 3290 cm⁻¹. There is no absorption of the tested samples under the above mentioned wave numbers, which means that they do not contain boehmite. As one of the tested samples draws its origin from clayey laterite, i. e. from that part of laterite where the process of laterization begins, while the other from the ferruginous crust, i. e. from the place where this process terminates, it can be concluded that boehmite is not the product of the process of the laterization of diabase in the Serrania de los Guaicas area.

## IV. GENESIS OF LATERITE

Geological conditions of the area of Serrania de los Guaicas indicate undoubtedly that the laterites located within this area are of Quaternary and recent age and of an autochtonous origin and that they were formed by a surface alteration of diabase.

### 1. Mechanism of Laterization Process

One of the very important factors in the process of laterization is the regime of ground waters. Factors influencing the final forming of laterite depend upon the circulation of ground water and its quantity as well as upon the ground water level and its oscillation. In the first place, these are pH factor and its oscillation into vertical direction and the possibility of the migration of solution.

Ground water conditions depend on several factors, the most important being the climate, the configuration of the area, and the structure of rocks. The humid tropical climate, as the climate of the area of Serrania de los Guaicas, with great amounts of rainfall, and alternating rainy and dry periods, favour an increased and uneven percolation of ground water, as well as an oscillation of the ground water level.

The mildly dipping diabase sills, emplaced into Roraima sandstones have conditioned a specific configuration of the area. Parts of the sills, subjected to the process of laterization, are elevated above the surrounding ground level, which enables a more rapid ground water circulation, especially in the direction of the steep slope (Fig. 2). The ground water level in laterite is low and unstable. In that connection an especially important fact is, that the ground water level is below the ferruginous-bauxite zone of laterite. Namely, the process of the alteration of the

* The writer wishes to thank Dr. S. M a r i č i ć and Mr. Z. M e i ć of the Institute »Rudjer Bošković« for advice about the infrared spectrum methode.

mother rock, below the ground water level, ends with the development of hydrated aluminium silicates, while a complete desilicification takes place only above the ground water level.

The permeability of a rock depends on the texture and structure (jointing) of the mother rock. Diabases are insufficiently permeable for water solutions, and therefore, the laterization process is slow and the thickness of laterite comparatively small, 12 m. on the average (zone A), while the laterite originating from granitoid rocks is usually some 20–60 m. thick. But, different textural varieties of diabase might also have quite a considerable influence on the forming of baterite. Diabases of zone A are more coarse-grained, having a subophitic texture and a greater Sal : Fem ratio, and consequently, laterites of zone A are porous, giving the possibility for a good circulation of water solutions. Diabases of zone B are small-grained, having an ophitic texture and a smaller Sal : Fem ratio, and consequently, laterites of zone B are earthy and of an insufficient permeability.

In the course of the laterization process water solutions are penetrating more easily along certain surfaces, which have been developed by the jointing of the mother rock. Spheric jointing, noticed to a smaller degree in diabase, has conditioned an inhomogeneous downward progress of laterization, and consequently, individual round-shaped blocks of unaltered diabase have been formed in the ferruginous-bauxite zone. These blocks are characterized by a greater strength and a smaller permeability, and they are not so easily subjected to the laterization process. On account of this, individual diabase blocks of a larger size, not altered by laterization, were sometimes noticed on the surface.

Another important factor in the laterization process is the pH value on different levels. The data concerning the pH value are different for different deposits, but it can be guessed therefrom that the medium in laterite is slightly acid to neutral and that pH gets increased with the depth. I. I. Ginzberg (Ginzberg, I. I. et al., 1962), when exploring laterites in Brazil, established that at the dept of 30–40 cm. pH = 4.1, and at the depth of 200–210 cm. pH = 5.5. According to the data, given by G. I. Bušinskij (1958) for different deposits of laterite in tropic regions, the pH value is 4.3–6.9. But, in the lowest portion (decomposition horizon) pH = 7–9.

According to I. I. Ginzberg (1962), one of the essential processes for the decomposition of rocks is the replacement of the bases of silicates by hydrogen ions. The hydrogen ion ($H^+$), in fact represented by hydroxonium ($OH_3^+$) in a water solution, has a greater radius (1,27 A) and energy coefficient (ek) than most of the bases ($Mg_2^+$, $Fe_2^+$, $Ca_2^+$, $Na^+$), which provokes the replacement and decomposition of the primary silicates of the mother rock.

The solubility of different elements and compounds is of the first rate significance in the transformation of the mother rock into laterite. Most of the bases, which are released by a decomposition of silicates are giving easily soluble compounds carried away by the percolation of

ground water. But aluminium, iron and titanium behave differently, and consequently, they become concentrated in laterite.

According to the results of investigations, performed by M a g i-
s t a r d (quot. – G. I. B u š i n s k i j, 1958), the solubility of $Al_3O_3$ with pH 5.0–7.5 is not surpassing 1 mg./lit., and with pH below 4.5 and above 8.5 the solubility becomes suddenly increased and surpasses 10 mg./l. At pH below 4 and above 10, $Al_2O_3$ is easily soluble. But, in natural water, the solubility of $Al_2O_3$ is getting considerably lower under the influence of dissolved $SiO_2$, calcium oxide and magnesium oxide, as well as of sulphatic and phosphatic ions. Under acid conditions, with pH 4–5, $SiO_2$ precipitates $Al_2O_3$, whereby gel is produced, giving minerals from the kaolinite group.

Iron oxide ($Fe_2O_3$) is by pH $>$ 3 practically insoluble. The compounds of bivalent iron are more easily soluble and with greater pH values, but while the primary silicates are being decomposed, the bivalent iron is immediately getting oxidized due to the positive redox potential. Meanwhile, if $Fe_2O_3$ has been stabilized by humus acids or by $SiO_2$ sol, it may be transported as sol. But, at temperatures above $25^0$ C and full aeration, the humus acids cannot exist for a longer period, which is the case in the area of Serrania de los Guaicas. Local migration of iron is possible in the lower zones of laterite (argillaceous laterite), where the $SiO_2$ content is increased and the influence of the group water level is evident.

It was determined by the microscopic and chemical analyses of the laterite of Serrania de los Guaicas that there are local migrations of Fe hydroxide throughout the whole profile of laterite, and in the ferroginous crust particularly.

$TiO_2$ is soluble by pH $<$ 2 (B u š i n s k i j, G. I., 1958), and a concentration of titanium in laterites is due chiefly to the resistibility of the primary minerals of titanium.

According to C o r r e n s (quoted by M a s o n, B., 1958), the solubility of $SiO_2$ in an acid medium is low, but as pH increases, the solubility also increases. In a moderate climate, where humus is contained in the soil, pH is low, provoking an accumulation of highsiliceous colloidal fractions. In tropic regions, where small amounts of humus are contained in the soil and, accordingly, pH is higher, the silicates of aluminium are getting more intensely hydrolyzed, while silicon ions are replaced by OH, which results in releasing $SiO_2$ and entering into solution. But, the amounts of rainy water should be sufficient to yield an intensive percolation of ground water, so that strong bases are carried away, especially those which form heavy soluble Mg and Ca compounds with $SiO_2$ and which are strong coagulators of negative colloids (M a t t s o n, S., 1932).

The solubility of $SiO_2$ increases with the increase of temperature. O k a m a t o et al. (quoted by L i s i c i n a, N. A., 1962) discovered by experimental methods that the solubility of amorphous $SiO_2$ by pH 5–8 slightly changes; it depends much more on the temperature. Accordingly, at the temperature of $0^0$ C the solubility of amorphous $SiO_2$ in

this pH interval is 100 mg./lit., and at 22⁰ Cit increases up to 180–200 mg./lit.

Examinations of the chemical and mineralogical composition of laterite from Serrania de los Guaicas, and considering the physicochemical conditions, favourable to the development of laterite, have given the following picture, showing the processes of laterization from bottom to top:

1. In the lowest zone, at the very contact between the laterite cover and diabase, diabase minerals are affected by hydration processes, causing an increase of the volume and a disintegration of the rock. Silicate bases are replaced by hydroxonium $(OH_3^+)$. The leaching out of the bases of silicates gets accelerated as hydration processes progress. Na is replaced first and afterwards K, Ca and Mg. By the entering of bases into the solution the medium becomes alcalic. This medium enables the development of montmorillonite. As bases are carried away by ground water circulation, the medium becomes first neutral, then acid, which helps the transformation of montmorillonite into kaolinite and halloysite.

Due to the great amounts of rainfall and the elevated terrain, the ground water percolation is intensive, and consequently, the montmorillonite zone is thin. No montmorillonite was noticed in the laterites of Serrania de los Guaicas, but it may be assumed that a thin zone of montmorillonite exists in the lowest part of this area.

During the leaching process of bases, silicates are getting hydrolized, whereby a part of $SiO_2$ is carried away. Owing to a less intense ground water percolation in the lower portion of laterite, greater amounts of $SiO_2$ could not be carried away.

Silicates containing iron (pyroxenes, amphiboles, chlorites) undergo easily oxidation and hydrolysis. Simultaneously, free oxides of iron and hydrated aluminium silicates develop and intimately intermix.

In this way a zone of argillaceous laterite has been created, in which the main minerals are kaolinite, halloysite, and iron hydroxide. There is a considerable amount of gibbsite in the upper part of this zone.

2. On the higher laterite level hydrolysis is more intensive, due to a higher temperature and a stronger percolation of ground water, causing decomposition of hydrated aluminium silicates and forming free hydrated alumina and $SiO_2$. In this medium the pH value is around 5, and hence, the newly developed hydrated alumina, being insoluble, remains in its place, while the soluble $SiO_2$ is carried away by ground water percolation. In this way a desilicification occurs, and clayey minerals are transformed to gibbsite.

Although the largest part of gibbsite draws its origin from primary minerals by an intermediary way (through kaolinite and halloysite), one part of gibbsite nevertheless has been developed directly, from primary diabase minerals. Blocks of diabase, which remain in the ferrugionous-bauxite zone, due to their greater resistibility, are transformed directly to the final product of laterization at their margins without transitional products. This process is conditioned by the increased amount of oxigen, a higher temperature, and a more intensive percolation of ground water. For this reason the medium is not suitable for the development of kaolinite. According to C o r r e n s (quoted by M a s o n, B., 1958), the elements pass in a short time into the proper solution during the first stage of the decomposition of silicates. Accordingly, if at this moment corresponding conditions for the removal of strong bases and silicon exist, the remaining alumina crystallizes as gibbsite, not binding to $SiO_2$, as in the development of kaolinite. By the thermal and optical analyses of specimens taken from the marginal lateritized parts of blocks, immediately beside the fresh diabase, is was established that this laterite does not contain hydrated aluminosilicates, but gibbsite (Fig. 3, curves A I and A II). No univocal opinion has been found in literature about the possibilities of a direct transformation of aluminosilicate minerals into gibbsite. Some of the investigators (A l l e n, V. T., 1952; H a r d e r, E. C., 1952) are of the opinion that silicates of aluminium are first transformed to hydrated silicates of aluminium and later to gibbsite. Some other investigators (H a r r i s o n, J. B., 1933, G i n z b e r g, I. I., et al., 1962) are of the opinion that – under the adequate

physicochemical conditions – an immediate transformation of aluminosilicates into gibbsite is possible by alteration. Basic plagioclases are especially subjected to such alteration. The explorations in Serrania de los Guaicas proved the opinion that direct transformation of plagioclase into gibbsite is possible, and perhaps the transformation of other primary aluminosilicates into gibbsite as well.

In the second (middle) zone, which is situated above argillaceous laterite, laterite is enriched in aluminium, and the main minerals are gibbsite and iron hydroxides.

3. In the uppermost zone of laterite the pH value is the lowest, i. e. from 4.1 to 5, approx. Within this range of pH values $Al_2O_3$ is partly soluble, while $Fe_2O_3$ is entirely insoluble. This is the reason for the migration of one part of aluminium from the uppermost zone, due to which the iron content gradually increases and a crust of ferruginous laterite has developed. The main minerals of the zone are iron hydroxides and gibbsite.

Accordingly, the three basic zones may be distinguished in laterites (direction: from top to bottom):

1. *Ferruginous crust*
2. *Zone of enrichment*
3. *Zone of argillaceous laterite*

2. Migration of Elements in the Course of Laterization.

According to the behaviour during laterization, the oxides of elements may be divided into three groups:

I. Sol- $(CaO, MgO, K_2O, Na_2O)$,
II. Ins- $(Al_2O_3, Fe_2O_3, TiO_2)$,
III. Si – $(SiO_2)$.
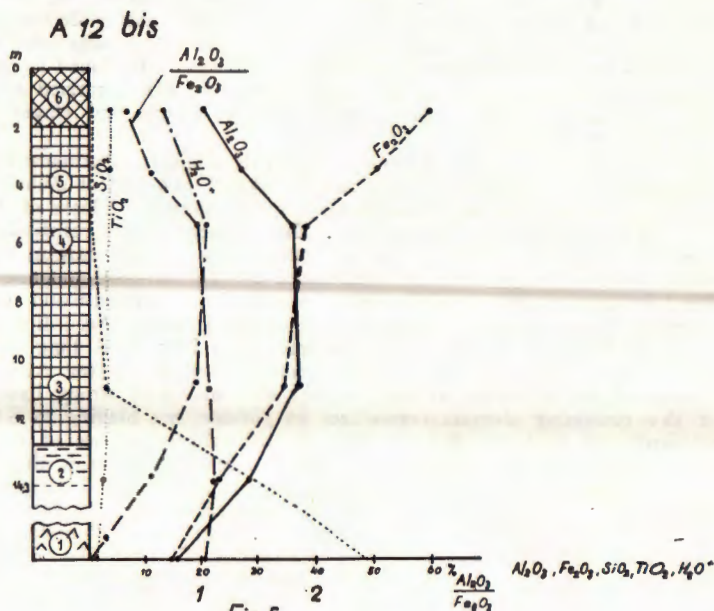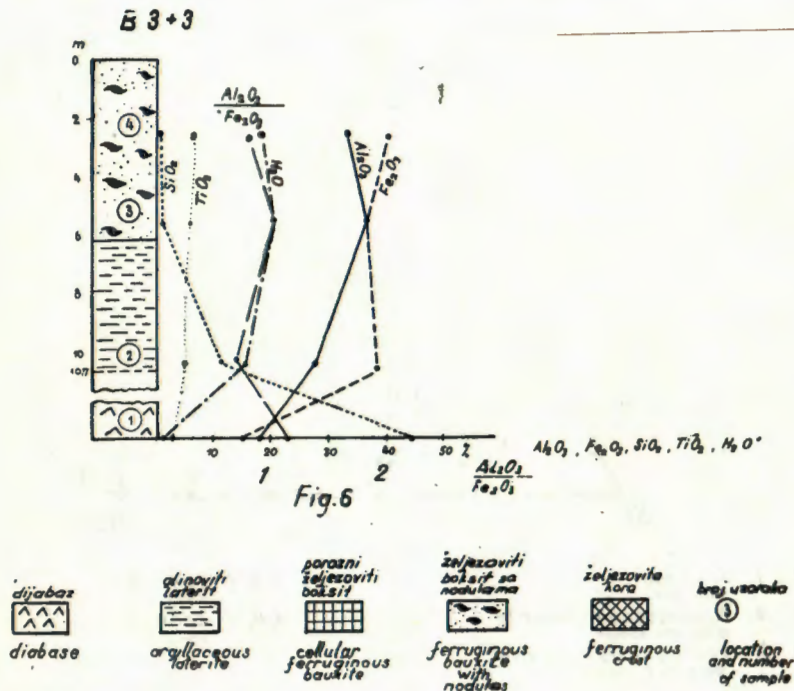


Fig 5

Figs. 5, 6. Diagrams of the chemical composition of laterite and diabase.
Sl. 5, 6. Dijagrami kemijskog sastava laterita i dijabaza.

In Fig. 5 and 6, where the variations of the chemical composition of different laterite zones in the test hole A 12 bis and the test pit B 3 + 3 are represented (See Tab. IV), as well as the ternary diagram of Si-Sol-Ins (Fig. 7), it may be seen that oxides of the Sol elements are disappearing rather quickly from laterite. Thus, they are not encountered in the lowest parts of laterite, or are encountered only in traces. The main reason for the quick loss of the cited oxides is the to neutral character of water solutions in the laterite (the conditions under which these elements are soluble) and relatively intense ground water percolation.

The loss of silica from laterite is somewhat slower. In the starting stage of laterization silica was partly bound to alumina, developing hydrated aluminosilicates (zones of argillaceous laterite), and the loss of silica is nearly complete only in the zone of ferruginous bauxite. The reason for such a behaviour of silica was described earlier.

The concentration of titanium is mainly due to the fact that ilmenite, being a resistant mineral, either remains in laterite, or gets partly altered to leucoxene.

It is evident from the gain and loss chart (Fig. 10) that there is not only a comparative, but a real, concentration of iron in laterites, espe-

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Fig. 7. SI–SOL–INS diagram of laterization.
Sl. SI–SOL–INS dijagram laterizacije.
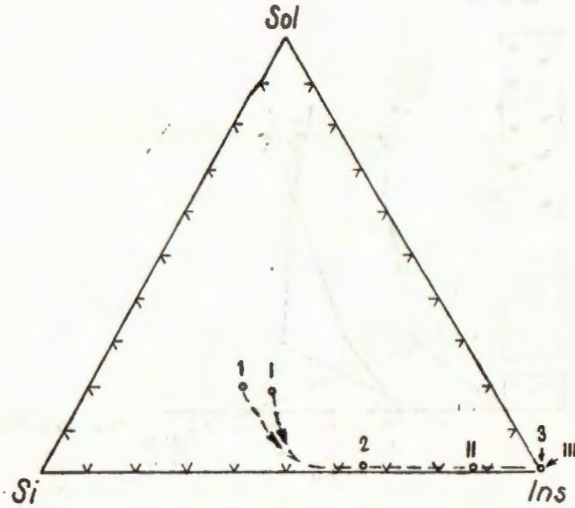
1. . I  Diabase
        dijabaz
2. II  Argillaceous laterite
        glinoviti laterit
3. . III Ferruginous bauxite
        željezoviti boksit

1,2,3  Zone A
        zona
I, II, III  Zone B
        zona



a) test hole  A 12 bis
   bušotina   A 12 bis

b) test pit  B 3÷3
   okno      B 3÷3
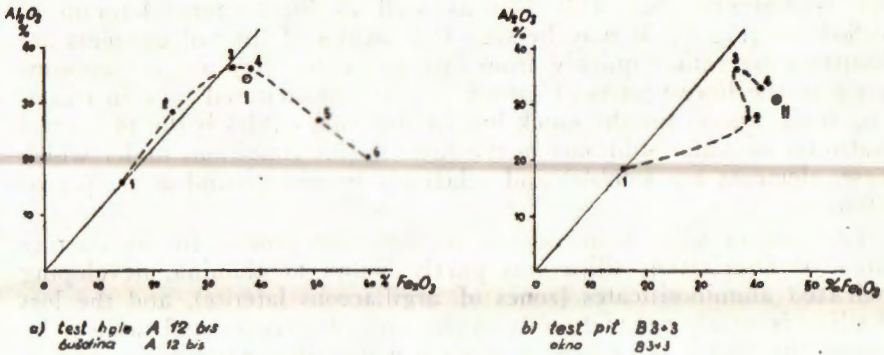
Fig. 8    DIAGRAMS OF THE $\frac{Al_2O_3}{Fe_2O_3}$ RATIO

DIJAGRAM ODNOSA $\frac{Al_2O_3}{Fe_2O_3}$

cially in zone B. So, the average gai nof iron is 113 mg./ccm. in the ferruginous-bauxite zone of the A area, while in the B area it amounts to 155 mg./cm. As in argillaceous laterite a real concentration of iron has been brought about, it may be assumed that the iron has been imported into laterite by a migration from the higher (the overlying) and now eroded parts of laterite. This migration of iron in downward direction is happening simultaneously with the progress of laterization (by the lowering of the laterite level) and with the erosion of the overlying (»older«) parts of laterite. Accordingly, it may be concluded that one of the factors of the concentration of iron in laterite is the duration of the subjection of a magmatic body to the process of laterization, viz. the amount of the eroded laterite. With the pH conditions proper for laterite, $Fe^{3+}$ cannot migrate like a true solution. Although humus acids are not stable in the tropics (under the conditions of high temperature and strong aeration), it may be assumed that $CO_2$ and certain organic compounds formed as products of the decay of tropical vegetation, are of a primary importance for the migration of iron. The stability of the $Fe_2O_3$, $Al_2O_3$ and $SiO_2$ colloids, which makes possible their migration, may be attributed to the protecting action of the mentioned compounds.

Due to the lower pH values in the superficial part of laterite aluminium is displaying a greater mobility, being capable to migrate as a true solution. This produces a loss of alumina from the uppermost parts of laterite. In case of a good porosity of laterite, water solutions with aluminium (and the colloid $Al_2O_3$) are migrating downwards, where in the deeper parts of laterite a precipitation and concentration of alumina occur. In this way a real concentration of alumina, amounting to 46 mg/ccm., has been brought about in the ferruginous bauxite of the A area (Fig. 10). The mobility of alumina is comparatively great, reaching even into argillaceous laterite, which may be seen in the diagram of the $Al_2O_3/Fe_2O_3$ ratio (Fig. 8a. – the numbers are corresponding to the analyses given in Table IV). If the $Al_2O_3/Fe_2O_3$ ratio were constant in the course of the laterization process, which would be in case there were no migration be situated along the line jointing the starting point of the system of co-ordinates with point 1 (diabase). It may be seen that there is a certain concentration of alumina in the argillaceous laterite compound to $Fe_2O_3$, and in the upper part of laterite there is a concentration of $Fe_2O_3$. Point I, representing the average value of the ferruginous-bauxite zone, is situated below the 0–1 line, indicating that, in this particular zone the concentration of $Fe_2O_3$ is greater than that of $Al_2O_3$, i. e. that a part of $Al_2O_3$ has been lost from laterite. In zone B the earthy type of laterite is predominant, while only the ferruginous upper part is more porous. Therefore, only a smaller part of solutions with aluminium – developed in the upper part of the laterite – is migrating in downward direction, to lower, deeper portions of laterite, while the larger quantity of aluminium percolates through the ferruginous crust, descending down the mountain slopes. Thus, one part of aluminium is lost (21 mg./ccm.). Iron (being less mobile) is subjected to such a kind of transport to a considerably smaller degree. Hence, the

$Al_2O_3/Fe_2O_3$ ratio is not so favourable in laterites of zone B. (Fig. 8b. Point II is the average value of ferruginous-bauxite in zone B).

From the above material it may be seen that the main reason for an increased concentration of iron and a reduced concentration of alumi-
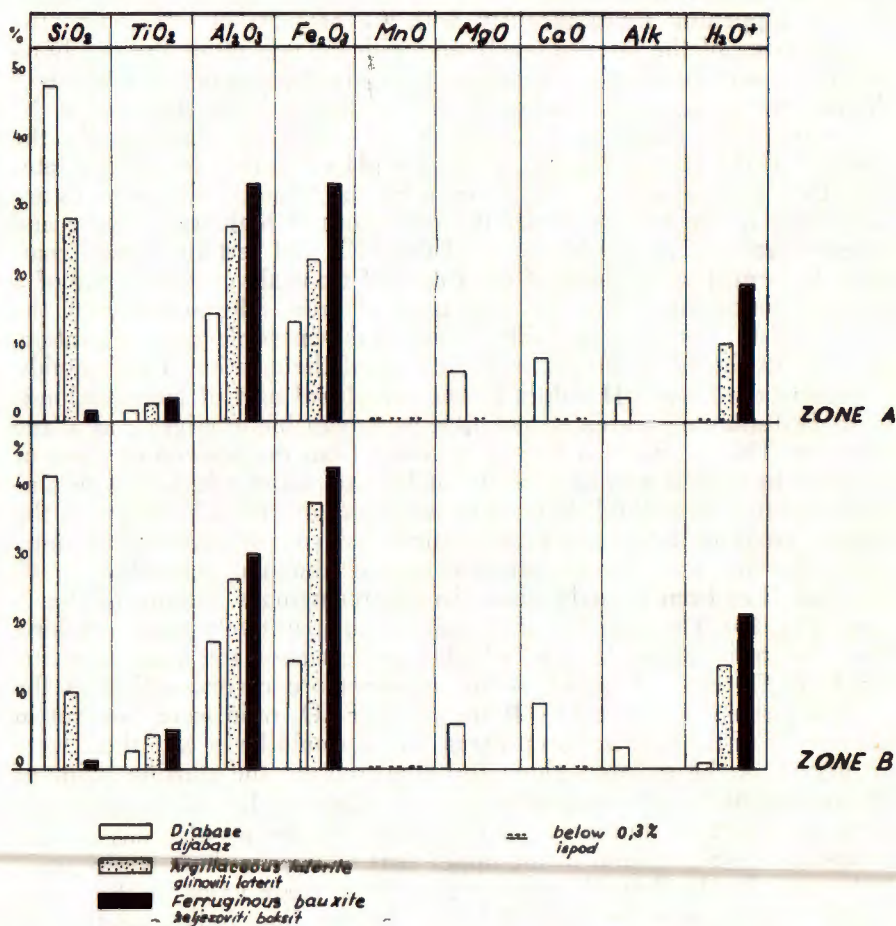


Fig. 9. *Chemical composition of diabase argillaceous laterite and ferruginous bauxite from the zone A and B.*
Sl. 9. Dijagram kemijskog sastava dijabaza i laterita zona A i B.

nium in zone B is the texture and the Sal : Fem ratio in the mother rock (diabase), causing the development of earthy, scarcely porous laterite. As the climatic morphological and geological conditions of zones A and B are exactly identical, the differences in laterite of the two zones could not be attributed to them.

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According to E. S. S i m p s o n (1912) the alternation of rainy and dry seasons is favourable for the development of laterite, because in the dry season a capillary ascension and migration of oxides of iron and aluminium occur and they precipitate while moisture is evaporating. C. F. M a r b u t (quoted by B u š i n s k i j, G. I., 1958) proved that the amount of water ascending capillarily during the dry season is very small, and the amount of iron and aluminium oxides in the water is
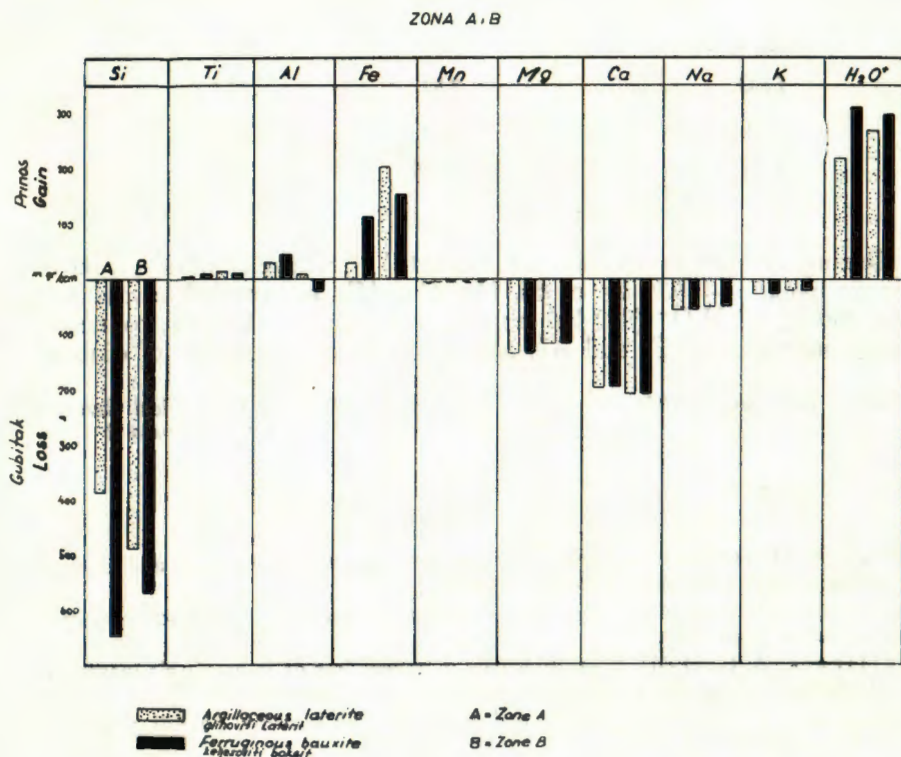
ZONA A·B



Fig. 10. Gain and loss chart for laterite deposits of the zones A and B.

Sl. 10. Dijagram migracije elemenata u lateritu.

negligibly small; consequently, this kind of transport of iron and aluminium oxides has no importance for their concentration. It was proved by our studies that there is a great probability that the concentration of iron and aluminium oxides depends on the downward percolation of water solutions. But the alternation of wetting and drying accelerates the decomposition of clayey minerals, which improves the laterization process.

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Due to the different conditions of laterization in zones A and B, the factors of concentration of $Al_2O_3$, $Fe_2O_3$, $TiO_2$, and $SiO_2$ are somewhat different in both zones (Table V).

TABLE V

*Factors of Concentration:*

|  | Zone A | Zone B |
|---|---|---|
| $Al_2O_3$ ............ | 2.18 | 1.70 |
| $Fe_2O_3$ ............ | 2.52 | 2.74 |
| $TiO_2$ ............ | 2.50 | 2.11 |
| $SiO_2$ ............ | 0.036 | 0.033 |

During the process of laterization – till the development of ferruginous bauxite – *1030 kg.* of Si, Mg, Ca, Alk. are carried away from and *480 kg.* of $H_2O^+$ (320 kg) and other substances (160 kg, connected to the migration of Fe and Al) are introduced into one $m^3$ of diabase.

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## B. ŠINKOVEC

## LATERITI PODRUČJA SERRANIA DE LOS GUAICAS (VENEZUELA) I NJIHOVE ISHODNE STIJENE

Područje Serrania de los Guaicas leži 230 km južno od Ciudad Bolivar i 12–17 km zapadno od Canaima vodopada. Teren je blago brdovit. Iznad zaravnjene površine izdižu se grebeni dijabaza, visine 50–200 metara.

Istraživanje laterita vršeno je na južnom dijelu grebena los Guaicas na dužini od 5 km (zona A) i na grebenu, koji se nalazi zapadno od grebena los Guaicas na dužini od 6 km (zona B). Istraživanja su vršena sa istražnim oknima i plitkim bušenjem, po profilnim linijama okomitim na pružanje grebena.

Na istraživanom području nalaze se sedimenti Roraima formacije i magmatske stijene Roraima magmatske provincije.

Roraima formacija sastoji se od klastičnih sedimenata, pretežno pješčenjaka. Starost formacije nije tačno utvrđena. Na osnovu korelacije s drugim susjednim slojevima smatra se najvjerojatnijim, da je Roraima formacija kredne starosti.

Roraima magmatska provincija spada u post-Roraima ciklus magmatske aktivnosti, koji je razvijen u sjevernim dijelovima brazilsko-gvajanskog štita i koji formira intruzive hipoabisalnog tipa. Glavni tipovi stijena su hiperstenski, olivinski i toleitski dijabazi i mirmekitski i kvarcni gabro.

Na istraživanom području nalaze se dva sila dijabaza, koji grade na terenu dva jasno uočljiva grebena: zonu A (Fila los Guaicas) i zonu B. Debljina silova dijabaza iznosi 70–120 metara.

Na shematskoj geološkoj karti vidi se da istraživani teren predstavlja dio antiklinale pružanja SE–NW, koja blago tone prema NW. Ta antiklinala je markirana silovima dijabaza, koji su konkordantno utisnuti u Roraima pješčenjake. Pad slojeva je prema istoku i sjeveroistoku oko 20°, osim u krajnjem zapadnom dijelu terena, gdje je pad slojeva prema zapadu.

Toleitski dijabazi zona A i B strukturno i mineraloški međusobno se razlikuju, a također se razlikuju lateriti tih zona. Dijabazi zone A izgrađeni su od relativno krupnozrnih, uglavnom idiomorfno razvijenih prizmatskih kristala plagioklasa, koji čine oko 60% stijene. Između plagioklasa nalaze se pretežno izolirane nakupine mineralnih agregata piroksena. Struktura stijene je subofitska.

Plagioklasi dijabaza zone B oko 40% stijene. Također su idiomorfno razvijeni, ali su manjih dimenzija, tako da je ta stijena ofitske strukture.

Glavni minerali dijabaza su labrador, piroksen i hornblenda, a sporedni i sekundarni minerali su ortoklas, kvarc, klorit, apatit, sericit, leukoksen, biotit, kalcit, epidot, ilmenit, magnetit, pirit, halkopirit, pirhotin, hematit i kovelin.

Minralni sastav dijabaza zona A i B je gotovo isti; međutim zapaža se veća razlika u međusobnom količinskom odnosu pojedinih minerala (Tabela I). Kemijske analize dijabaza date su u Tabeli II, a normativni sastav po CIPW i Nigglieve vrijednosti u Tabeli III.

Mineraloške, strukturne i kemijske razlike dijabaza zona A i B uslovljene su magmatskom diferencijacijom.

Lateriti područja Serrania de los Guaicas nastali su lateritizacijom dijabaznih silova, te su vezani za izdanke dijabaza. Silovi dijabaza izgrađuju jasno uočljive grebene, na čijim se blago zaobljenim vrhovima nalaze lateriti. Širina lateritnog pokrova varira od 200–500 metara; prosječna širina je 400 metara. Debljina gornjeg željezovito-boksitnog dijela laterita varira od 2–14 m, srednja debljina je 7 metara. Debljina donjeg glinovitog dijela laterita varira od 3–9 metara (Slika 2).

Postoji nekoliko teksturnih varijeteta laterita. Tvrdi, porozno-granularni laterit smeđe crvene boje (željezovita kora) nalazi se na vrhu i prekriva porozni žutosmeđi laterit sa svijetlim pjegama (u zoni A) ili mekani zemljasti laterit sa tvrdim konkrecijama (u zoni B). U najnižoj zoni nalazi se zemljasti, glinoviti laterit.

U željezovitoj kori sadržaj $Fe_2O_3$ često je iznad $50\%$, a sadržaj $Al_2O_3$ ispod $20\%$. U srednjoj zoni (zona obogaćenja) sadržaj $Al_2O_3$ je $25–45\%$, a sadržaj $Fe_2O_3$ je $30–45\%$. Sadržaj $SiO_2$ u prvoj i drugoj zoni je $0,1–5\%$. U donjoj zoni sadržaj $SiO_2$ naglo se povećava iznad $5\%$, $Al_2O_3$ je $20–30\%$, i $Fe_2O_3$ je $20–40\%$.

Srednji kemijski sastav željezovitog boksita (gornja i srednja zona) u zoni A je $Al_2O_3 = 34,5\%$, $Fe_2O_3 = 37,0\%$, $SiO_2 = 1,73\%$, $TiO_2 = 3,7\%$, a u zoni B je $Al_2O_3 = 31,0\%$, $Fe_2O_3 = 43,5\%$, $SiO_2 = 1,42\%$, $TiO_2 = 5,5\%$.

U lateritima je utvrđen slijedeći mineralni sastav: džipsit, kaolinit, haloazit, kvarc, getit, »amorfni limonit«, hematit, ilmenit, leukoksen.

Džipsit je uz getit glavni mineral željezovitog boksita. Predstavljen je dvjema formama: kriptokristalastom i mikrokristalastom. Kriptokristalasti džipsit se nalazi zajedno s getitom i »amorfnim limonitom« u neizdiferenciranim neprozirnim masama ili ima kolomorfnu strukturu. Pretežno je nastao od feromagnezijskih silikata. Mikrokristalasti džipsit je bezbojan i u vidu mikrozrnatih agregata zamjenjuje plagioklase. Veličina čestica džipsita varira od $< 10$ do 150 mikrona i raste prema površini željezovito-boksitne zone.

Kaolinit je glavni mineral donje glinovite zone laterita. Ostali spomenuti minerali imaju sporedno značenje.

Na osnovu proučavanja kemijskog i mineraloškog sastava laterita i dijabaza područja Serrania de los Guaicas, utvrđeno je da mineralni sastav i struktura matične stijene ima važnu ulogu u formiranju laterita. Da bi odnos $Al_2O_3 : Fe_2O_3$ u lateritu bio povoljniji, odnos Sal : Fem minerala u dijabazu mora biti što veći. Povoljnija je krupnozrnija struktura matične stijene (subofitska, doleritska), jer takove stijene daju visoko porozne laterite, u kojima je moguća jača cirkulacija vodenih otopina, što pogoduje formiranju kvalitetnijeg laterita.

## PLATE – TABLA I

1. *Subophitic texture of diabase; plagioclase (f), pyroxene (p), hornblende (h). Zone A. One Nicol, 30 ×*
   Subofitska struktura dijabaza; plagioklas (f), piroksen (p), hornblenda (h). Zona A. Jedan nikol, 30 ×

2. *Same as fig. 1., but croissed Nicols.*
   Isto kao sl. 1., ali ukršteni nikoli.

3. *Ophitic texture of diabase; white-plagioclase, grey-pyroxene and amphibole, black-ilmenite. Zone B. One Nicol, 30 ×*
   Ofitska struktura dijabaza; bijelo-plagioklas, sivo-piroksen i amfibol, crno-ilmenit. Zona B. Jedan nikol, 30 ×

4. *Laterite, pseudomorphosis of gibbsite after plagioclase; white-gibbsite, black-»limonite« – gibbsite cryptocristalline mass.*
   *Zone A. One Nicol, 60 ×*

   Laterit, pseudomorfoza džipsita po plagioklasu; bijelo-džipsit, crno – »limonitno« – džipsitna kriptokristalasta masa. Zona A. Jedan nikol, 60 ×
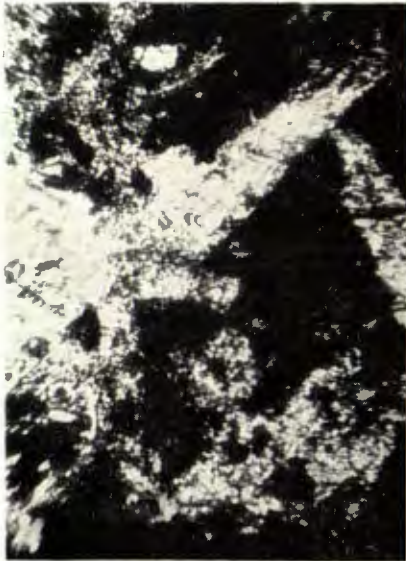
1



2



3



4

5



6



7



8

Fig.3 THERMOGRAVIMETRIC AND DIFFERENTIAL-THERMIC CURVES OF
THE LATERITE SAMPLES FROM THE ZONES A AND B

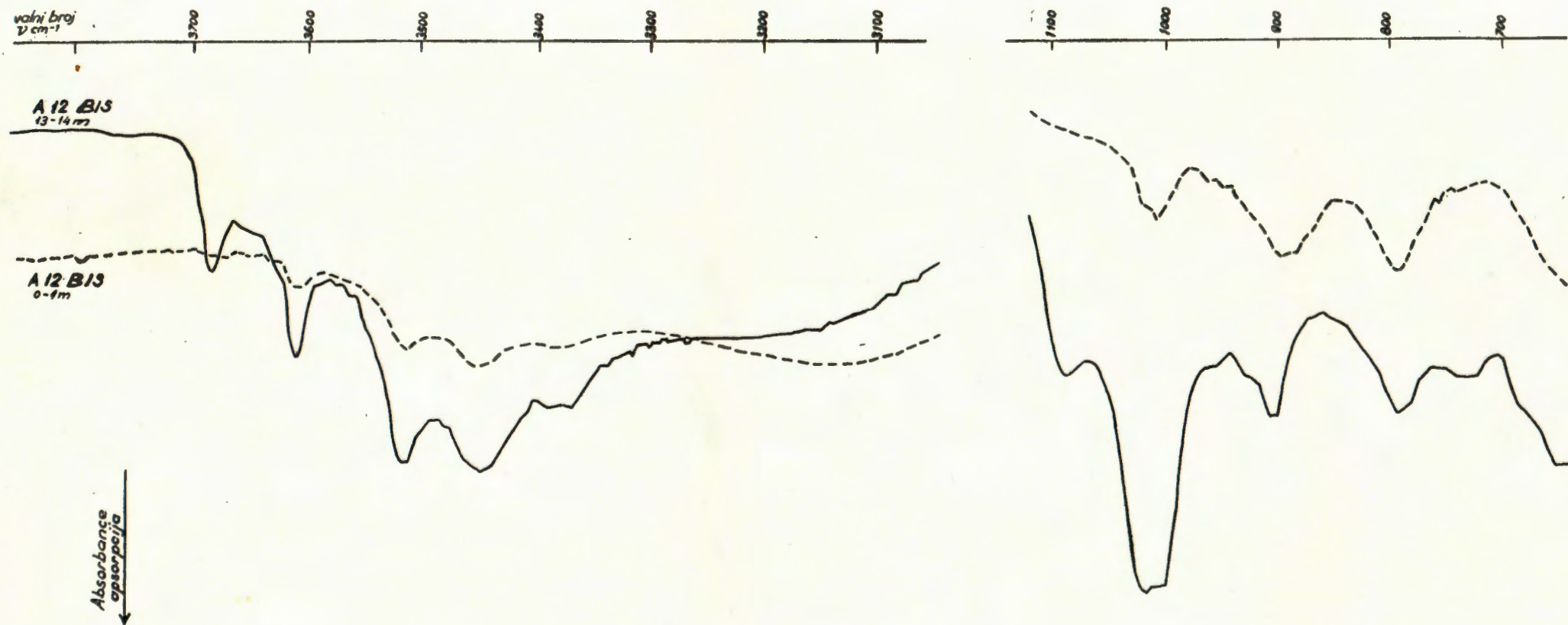DIJAGRAMI TERMOGRAVIMETRIJSKIH i DIFERENCIJALNO-TERMIČKIH ANALIZA LATERITA

Fig. 4. Absorption spectra of laterit.
Sl. 4. Apsorpcioni spektar laterita.

ZONE B

☐ Camp 3
30°

ZONE A

Los. Guaicas

☐ Camp 2

ESTRECHURA

CARONI →

Cucurital

Caruo

A                      B

f

?

| | Diabase sill |
| | diabaz |
| | Roraima sandstone |
| | roraima pješčanjak |
| | axis of anticline |
| | os antiklinale |
| | fault |
| | rasjed |

SERRANIA DE LOS GUAICAS

*GEOLOGICAL MAP*

*GEOLOŠKA KARTA*

0      1      2 km

B. ŠINKOVEC