8221

Yasuo Kitagawa and Maria Regina Freire Möller

> EMBRAPA-CPATU 1978

EMBRAPA



CONTENTS

ABSTRACT	1
1- INTRODUCTION	2
2- EXPERIMENTAL METHODS	4
2.1- PREPARATION OF CLAY SAMPLES	4
2.2 - X-RAY DIFFRACTION	5
2.3 - DIFFERENTIAL THERMAL ANALYSIS	6
2.4 - CHEMICAL ANALYSIS OF CLAY FRACTION	6
2.5 - ELECTRON MICROSCOPY	7
3- <u>SAMPLES AND RESULTS</u>	7
3.1- CLAY MINERAL COMPOSITION OF THE SOILS WITH OXIC B HORIZON.	7
3.1.1- Yellow Latosols	7
3.1.2- <u>Red-Yellow Latosols</u>	9
3.1.3- <u>"Latossolo Roxo" soil</u>	11
3.2 - CLAY MINERAL COMPOSITION OF THE SOILS WITH TEXTURAL B HORIZON.	12
3.2.1- <u>Red-Yellow Podzolic soils</u>	12
3.2.2- <u>"Terra Roxa Estruturada" soils</u>	15

3.3- CLAY MINERAL COMPOSITION OF LOWLAND SOILS	17
3.3.1- Low Humic Gley soils	17
3.3.2- Ground-Water Laterite soils	19
3.3.3- <u>Alluvial soils</u>	21
4- GENERAL DISCUSSION AND CONCLUSIONS	22
ACKNOWLEDGMENTS	25
<u>REFERENCES</u>	26
SINOPSE	29

CLAY MINERALOGY OF SOME TYPICAL SOILS IN THE BRAZILIAN AMAZON REGION

Yasuo Kitagawa¹

and

Maria Regina Freire Möller²

ABSTRACT

The outline of the mineral composition in the clay fraction of some typical soils occurring in the Brasilian Amazon region is as follows:

In the soils with oxic B horizon; Yellow Latosols, Red-Yellow Latosols and "Latossolo Roxo" Soil, kaolinite was predominant, goethite and hematite were found in general, and gibbsite was frequently detected. A small amount or trace of mica minerals occurred in several lateritic soils. The presence of the other 2:1-type clay minerals was rare in the lateritic soils.

In Red-Yellow Podzolic soils, kaolinite was also predominant, and iron-oxide minerals were always identified. Considerable amount of gibbsite and small amounts of mica minerals and dioctahedral vermiculite were present in some of these soils.

 National Institute of Agricultural Sciences, Nishigahara, Kita-ku, Tokyo 114, Japan. Cooperation scientist dispatched to CPATU by Japan International Cooperation Agency, Tokyo 160, Japan.

2) CPATU, Caixa Postal 48, Belém, Pará, Brasil.

EMBRAPA

In the so-called "Terra Roxa Estruturada" soils, kaolin minerals were dominant, but considerable amounts of iron-oxide minerals were found in the clay fraction, so that hematite was ' especially rich. Metahalloysite was a dominant clay mineral in a "Terra Roxa Estruturada" Soil. A small amount of dioctahedral vermiculite was present in the other soils.

The clay mineral composition of the low land soils was a little complicated. Montmorillonite/dioctahedral-vermiculite interstratified mineral and mica minerals were dominant in two Low Humic Gley soils and a Ground-Water Laterite soils, respectively, although kaolin minerals were predominant in many lowland soils. Small amounts of 2:1-type clay minerals were frequently detected in the other lowland soils.

Quartz existed in the clay fraction of all the soil samples.

1 - INTRODUCTION

The Amazon region is located in the humic tropical zone, where soils develop under the drastic condition of high temperature and heavy rainfall. The primary silicates are quickly weathered, and alkalines and alkaline earths are taken away from soil horizons by rain water. Organic materials are rapidly decomposed, and little accumulated in soil. Soils are enriched with aluminum and iron because of the relatively high mobility of silica with water.

The Amazon region is extremely vast, and many types of soils have developed under the various conditions of soil genesis, i.e., lateritic soils and Red-Yellow Podzolic soil in the uplands, and Alluvial soils, Low Humic Gley soil and Ground-Water Laterite soil in the lowlands. These soils were described by SOMBROEK (18), FALESI (4), and VIEIRA (20). About 70% of the Brazilian Amazon region is covered with the lateritic soils according to FALESI.

2

The study on the clay mineral composition of the soils distributed in the Amazon region is very interesting and important problem for the genesis, classification, fertility and management of the soils. It is generally known that kaolin minerals are predominant in the lateritic soils developed under the drastic conditions of weathering. Kaolin minerals have low values of specific surface area and cation exchange capacity, so that the lateritic soils have low fertility. SOMBROEK (18) reported that more than 80% of crystalline minerals is kaolinite in the clay fraction of Yellow Latosol distributed in the Amazon region. CHIBA (3) also reported the predominance of kaolin minerals in three samples of Yellow Latosol. IWASA (7) studied the clay mineral composition of fourteen lateritic soils in the Transamazon Highway zone, and concluded that kaolin minerals are dominant although five soils contained small amounts of 2:1-type clay minerals. According to KNOX . (GRIM, 6), "Kaolinite was the only mineral reported in more than half of a total of over 20 Red and Yellow Podzols. In the remainder, kaolinite was the dominant, but small amounts of illite and smectite were also reported." NYUN and MCCALEB (16) reported that kaolinite is the most abundant clay mineral in the Red-Yellow Podzolic soils called Davidson and Hiwasse series in the North Carolina Piedmont region in the U.S.A. On the other hand, RICH and OBENSHAIN (17) reported that a dominant clay mineral in a Red-Yellow Podzolic soil derived from a muscovite schist in Virginia, U.S.A. is dioctahedral vermiculite which had been already reported by BROWN (1). Considerable amounts of 2:1-type clay minerals such as montmorillonite, vermiculite and mica minerals were found in the Red-Yellow Podzolic soils in the Brazilian Amazon region by SOMBROEK (18) and IWASA (7).

The lowland soils should be less uniform in the clay mineral composition than the upland soils, because they are composed of complicated parent materials which had been deposited recently by river waters, and the soil weathering under the always or seasonally flooded condition is not so rapid as the upland soils (MATSUI, 14). SOMBROEK (18) stated that the clay fraction of a Low Humic Glay soil in the Low Amazon Floodplain called "várzea" is composed of quartz, kaolinite, feldspar, illite, intermediate mineral between kaolinite and illite, swelling illite and chlorite, and the content of kaolin minerals is less than 30% in it, while kaolinite is a dominant clay mineral in a Ground-Water Laterite soil in Caeté-Maracassuné area although a small amount of mica minerals is found in the silt fraction. IWASA (7) reported the complexity of clay mineral composition of an Alluvial soil in Armaça island, Amazonas, which contained large amounts of montmorillonite and illite besides kaolinite.

In this report, the clay mineral composition of nineteen soils of the Brazilian Amazon region is discussed; the soils with oxic B horizon, three Yellow Latosols, three Red-Yellow Latosols and a "Latossolo Roxo" soil; the soils with textural B horizon, three Red-Yellow Podzolic soils and two "Terra Roxa Estruturada" soils; and the lowland soils, three Low Humic Gley soils, two Ground-Water Laterite soils and two Alluvial soils. Results of X-ray diffraction, differential thermal analysis, electron microscopy and chemical analysis are presented for the discussion.

2 - EXPERIMENTAL METHODS

2.1 - PREPARATION OF CLAY SAMPLES

The clay fraction was separated from the air-dried soil less than 2mm in diameter by the following method:

At first, organic materials in soil sample were decomposed with 10% of hydrogen peroxide untill its dark color disappeared, then the soil sample was stirred vigorously in distilled water EMBRAPA

by using an electric stirrer owing to make suspension, and its pH value was adjusted to 8.5 with a NaOH solution. The suspension of clay, the fracton less than 2 microns, was collected from that of the soil according to the Stokes' Law. To the collected suspension, CaCl₂ was added for aggregation of the clay particles, and the aggregate was separated by centrifugation, washed successively with distilled water, aceton-water mixture and aceton, dried at room temperature, and pulverized by using an agate mortar. This is the Ca²⁺ saturated clay sample, and was employed for X-ray diffraction, differential thermal analysis, chemical analysis and electron microscopy.

The clay sample saturated with K^+ was prepared from the Ca²⁺ -saturated sample by washing with 1 N KCl and distilled water, successively, and used for X-ray diffraction.

2.2 - X-RAY DIFFRACTION METHOD

The X-ray diffraction patterns were obtained with Co-K α radiation using a Rigaku Denki Ltd, Geigerflex diffractometer. The condition of measurement was as follows: voltage and current of X-ray tube, 30 kV, 15 mA; radius and slit system of goniometer, 190mm and 1° of divergence slit, 0.30mm of receiving slit, 1° of scatter slit; filter for Co-k α radiation, Fe; counter, argon-sealed-off proportional counter, type PR-250A; scanning speed, 1 to 2°/min; count full scall, 1000 to 4000 cps; time constant, 1 to 2 sec. A powder specimen was put in a 18mm x 20mm rectangular openning of an aluminum sample holder on the measurement. A specimen oriented on the glass slide of 50mm x 35mm was used to emphasize the basal reflection (001) of clay minerals, in addition to the random powder specimen.

Two types of the specimen saturated with ${\rm Ca}^{2+}$ and ${\rm K}^+$ were

5

prepared for examining the change of basal spacing of 2:1-type clay minerals. Moreover, Ca^{2+} -saturated specimen was treated with 10% glycerol solution in ethanol for the determination of montmorillonite, and K⁺-saturated clay was heated at 300 and 600°C for 2 hr in order to confirm gibbsite, vermiculite, chlorite and kaolin minerals. Some samples were treated with a dithionite-citrate-bicarbonate system (MEHRA et. al., 15), and measured by powder method, for the purpose of confirming the reflection of iron-oxide minerals such as hematite, goethite and lepidocrocite.

2.3 - DIFFERENTIAL THERMAL ANALYSIS

The differential thermal analysis (DTA) curves were obtained by using a Mitamura, thermal analyzer, at a heating rate of 10° C/min from room temperature to 1000° C in an ordinary atmosphere.

2.4 - CHEMICAL ANALYSIS OF CLAY FRACTION

Silicon in the clay sample was determined by colorimetry, molybdenum blue method, after fusion with NaOH. The other elements were determined after the dissolution of the sample with a $\mathrm{HF-H_2SO_4}$ system treatment. Hydrogen peroxide and o-phenanthroline method was used for the colorimetric determination of titanium and iron, respectively. Aluminum was determined by the titration with sodium ethylen-diamine-tetraacetic acid (Na-EDTA). Manganese, magnesium and calcium contents were measured by means of atomic absorption method, and that of sodium and potassium by flame-photometry. The content of structural water (H₂O+) in the clay samples was determined by heating at 800°C for a day in a muffle furnace.

The contents of these elements were based on the weight dried at 110° C for 24 hr in an oven.

2.5 - ELECTRON MICROSCOPY

The electron micrograph was taken by using a Siemens, ELMISKOP 101, electron microscope, at accelating voltage of 80 kV and direct magnification of x10000. The specimens for the observation were treated beforehand with dithionitecitrate-bicarbonate system, to prevent the influence of iron-oxide minerals.

3 - SAMPLES AND RESULTS

3.1 - CLAY MINERAL COMPOSITION OF THE SOILS WITH OXIC B HORIZON
3.1.1 - <u>Yellow Latosols</u>.

Samples:

Three profiles of Yellow Latosols in the States of Acre, Amazonas and Pará were used, and the outline of location, original material, relief, declivity, erosion, drainage, vegetation and actual use, in addition to physical and chemical properties of the soils, are presented in Table 1 to 3. Each three horizons of the samples were used in the experiment, because the clay mineral composition is not so different among horizons, in general.

These soils have very low pH value, low cation-exchange capacity (CEC) value and extremely low exchangeable-cation percentage (ECP). Available phosphorus is also very poor except in the A₁ horizon of LA-2.

Chemical analysis:

Chemical composition of the clay fractions of three Yellow Latosols is shown in Table 4. The low values of the ratio of silica to alumina, and high content of iron in LA-1 and LA-2 suggests high content of kaolin minerals and free iron oxides, respectively. The contents of MgO and K₂0 were low in LA-1 and LA-2, which indicates the rare presence of 2:1type clay minerals such as montmorillonite, vermiculite and mica minerals. An unusually high content of CaO in the A₁ horizon of LA-2 should be caused by its precipitation with oxalate which is an intermediate product during the composition of organic materials with warmed hydrogen peroxide.

X-ray diffraction:

In Fig. 2, the X-ray diffraction patterns of the clay fraction of Yellow Latosols by a powder method are presentend, and all of the charts had a very strong diffraction peak at 7.24 and 3.58 Å associated with kaolinite (KITAGAWA, 12). This result shows that kaolinite is a dominant clay mineral in Yellow Latosols, and coincides with that of previous studies (18, 3, 7) as mentioned before. Judging from the intensity the diffraction peak, the kaolinite content of LA-3 was the highest of the three. The presence of a very weak peak at 10 Å in LA-2 suggests the occurrence of a small amount of mica minerals left behind from the weathering process. The content of K_2^0 as an indicator of occurrence of mica minerals was about 0.7 % and slightly high in LA-2 (Table 4).

A small amount of gibbsite was found in all the horizons of LA-1 because of the occurrence of a diffraction peak at $4.85 \stackrel{0}{\text{A}}$. LA-2 also contained trace of gibbsite.

Considerable amounts of goethite at 4.17 Å and a small amount of hematite at 2.69 Å were present in LA-1 and LA-2. The content of goethite in LA-3 was low for the low intensity of the diffraction peak. The subsoil of LA-2 contained a small amount of lepidocrocite whose diffraction peak is at

6.30 Å. The diffraction peaks of these iron-oxide minerals disappeared by the treatment with a dithionite-citrate-bicarbonate system after MEHRA, et.al. (15) as shown in Fig. 23. This result agreed with the high contents of $Fe_2^0a_3$ in the clay fraction of LA-1 and LA-2 (Table 4).

The weak diffraction peak at 3.35 Å found in all the samples was associated with the presence of a small amount of quartz.

DTA:

The DTA curves of all the clay fraction of Yellow Latosols (Fig. 3) had a large endothermal peak near $550^{\circ}C$ and a sharp exothermal peak near $900^{\circ}C$, and showed the occurrence of a large amount of kaolin minerals. An endothermal peak near $300^{\circ}C$ in all the horizons of LA-1 and the A₁ of LA-2 was originated in gibbsite. This supports the result of the X-ray diffraction method.

3.1.2 - Red-Yellow Latosols

Samples:

Three samples of Red-Yellow Latosols from Acre, Amazonas and Pará were employed, and their properties are shown in Table 5 through 7. The pH value, CEC value, ECP, as well as the contents of organic carbon and available phosphorus are very low in these soils.

Chemical analysis:

The ratio of silica to alumina was rather high in LVA-1, very low in LVA-2, and relatively low in LVA-3 (Table 8).

The contents of MgO and K_2^0 were a little high in LVA-1, and the structural water (H_2^{0+}) content was relatively low, which were presumed to be a co-existence of mica minerals and other 2:1-type minerals in LVA-1. On the other hand, this table also shows the very high content of H_2^{0+} in LVA-2. The abundant structural water and low values of the ratio of silica to alumina in the clay fraction suggest the presence of gibbsite, $Al(0H)_3$, of which water content is 34.65 % in weight. The Fe₂0₃ content was high in LVA-1.

X-ray diffraction:

X-ray diffraction patterns of the powder specimens of three Red-Yellow Latosols are shown in Fig. 4. In the clay fraction of all three soils, kaolinite, having the basal spacing of 7.24 Å, was a dominant clay mineral. All the horizons of LVA-1 contained mica minerals because a 10 Å peak was noticed in the diffraction charts. A small amount of montmorillonite or vermiculite called 14 Å minerals was found in the subsoil of LVA-1. The presence of 2:1-type minerals in LVA-1 had been already presumed by the chemical analysis.

The strong diffraction peak at 4.85 and 4.39 Å in LVA-2 suggest that a considerable amount of gibbsite exists in all the horizons, as assumed above. But gibbsite is not a dominant mineral in LVA-2 considering the intensity of the diffraction peak. The absolute peak intensity of pure gibbsite is extremely high.

Small amounts of hematite (2.69 Å) and goethite (4.17 Å) were found in LVA-1 and LVA-3, while, only a small amount of goethite was found in LVA-2 and hematite was not detectable.

The diffraction peak at 3.35 and 4.25 $\overset{\circ}{A}$ in LVA-1 indicates the presence of quartz. The other two soils had very small

amount of quartz. In LVA-2, a small amount of feldspar was detected through the occurrence of a small peak at 3.20 Å.

DTA:

The DTA curves of the clay samples of Red-Yellow Latosols are drawn in Fig. 5. It was confirmed that kaolinite was a dominant mineral in all the samples, and considerable amount of gibbsite was present in LVA-2, judging from the occurrence of the DTA peake near 550 and 900°C, and near 300°C, respectively. In LVA-1, the peaks associated with kaolin minerals were relatively weak because of the co-existence of 2:1-type minerals. The content of kaolinite was very high, so that the intensity of the DTA peak was very high in LVA-3.

3.1.3 - "Latossolo Roxo" soil

Samples:

A "Latossolo Roxo" soil found in the State of Pará was used, and the properties of the soil are represented in Table 9. The reaction of the soil is moderately acid. ECP is considerably high although the CEC value is not high, and the later is dependent on the content of organic matter. Exchangeable Ca^{2+} is relatively high in the A₁ horizon. Available phosphorus is extremely poor in the subsoil.

Chemical analysis:

Table 10 shows the chemical composition of the clay fraction of "Latossolo Roxo" soil. The ratio of silicate to alumina was low, and the contents of bases were low, while, the Fe_20_3 content was very high. This result suggests the occurrence of kaolin and iron-oxide minerals.

EMBRAPA

X-ray diffraction:

The X-ray diffraction patterns of the powder specimens of "Latossolo Roxo" soil are drawn in Fig. 6. The diffraction peak at 7.24 and 3.58 Å originated in kaolinite, which was regarded as a dominant clay mineral for the high peak intensity.

A small amount of gibbsite was detected by the occurrence of the diffraction peak at 4.85 $\stackrel{\text{O}}{\text{A}}$ in all the horizons.

Enough hematite with 2.69 Å peak and goethite with 4.17 Å were found as presumed from the chemical composition.

Trace of quartz (3.35 Å) occurred in the clay fraction of all the horizons.

DTA:

The DTA curves of the clay specimens of "Latossolo Roxo" soil shown in Fig. 7 confirmed the presence of kaolinite as a dominant mineral. They had a small endothermal peak near 300[°]C associated with gibbsite.

3.2 - CLAY MINERAL COMPOSITION OF THE SOILS WITH TEXTURAL B HORIZON

3.2.1 - Red-Yellow Podzolic soils

Samples:

Three Red-Yellow Podzolic soils were collected in Acre, Amazonas and Pará, and listed in Table 11 to 13. The soil reaction is very strongly acid in PVA-1 and PVA-2, and extremely acid in PVA-3. The CEC values are relatively low, ECP is extremely low in PVA-2 and PVA-3, and available phosphorus is very low in all the soil samples.

Chemical analysis:

The chemical composition of the clay fraction of three Red-Yellow Podzolic soils is shown in Table 14. The ratio of silica to alumina was slightly high in PVA-1, and low in PVA-2 and PVA-3. A moderately high content of K_2^0 and a slightly low content of H_2^{0+} presumed the co-existence of mica minerals in PVA-1 as in the case of LVA-1. In the other samples, the base contents were very low. The content of H_2^{0+} was relatively high in PVA-2, which should indicate the occurrence of gibbsite as mentioned in LVA-2. The Fe₂0₃ content was high in all the samples, especially in PVA-2.

X-ray diffraction:

The results of the X-ray diffraction method in the clay fraction of the Red-Yellow Podzolic soils are shown in Fig. 8 and 9. Kaolinite was a dominant mineral in all the samples judging from the occurrence of a strong diffraction peak at 7.24 Å. Mica mineral with 10 Å basal spacing was found in PVA-1 as presumed from the chemical composition in Table 14. A small amount of dioctahedral vermiculite was present in PVA-2, which was detected by observing the changes of 14 Å basal spacing with several treatment. This diffraction peak was not changed by glycerol and K⁺ saturation, and shifted toward 10 Å by heating at 300 and 600°C after the clay specimen was saturated with K⁺ (Fig. 9), as described by BROWN (1).

Considerable amount of gibbsite was noticed in PVA-2 by the presence of 4.85 and 4.39 Å diffraction peaks, as well as in the chemical analysis.

Hematite with 2.69 Å peak and goethite with 4.17 Å were

found in all the samples of Red-Yellow Podzolic soils. The diffraction peak at 4.17 Å disappeared with the treatment by MEHRA, et. al. (15) (Fig. 23). The occurrence of iron-oxide minerals was coincident with the high content of Fe_20_3 in the clay fraction of the soils.

The diffraction charts of PVA-1 had the peaks at 3.35 and 4.25 Å associated with quartz, and its content in the upper horizon was higher than in the subsoil. Trace of quartz also existed in PVA-2 and PVA-3. Feldspar with the peak at 3.20 Å was detectable in PVA-1 and PVA-2.

DTA:

The DTA curves of the specimens of Red-Yellow Podzolic soils drawn in Fig. 10 supported the occurrence of kaolinite in all the samples and gibbsite in the clay fraction of PVA-2. The content of kaolinite in PVA-3 was very high, judging from the high intensity of an endothermal and an exothermal peak near 550 and 900[°]C, respectively.

Electron microscopy:

The electron micrograph of the specimen from the B₂₁ horizon of PVA-3 (Plate 1) shows the occurrence of small formless- or hexagonal-plate particles which were associated with soil kaolinite (KITAGAWA, 9). A very small amount of metahalloysite or halloysite particles of which shape is tubular (KITAGAWA, 9) was also found in this photograph. It is generally thought that a small amount of metahalloysite or halloysite should be co-existed even if kaolinite is predominant in soils because of the similarity between their structures.

3.2.2 - "Terra Roxa Estruturada" soils.

Samples:

Two samples of the so-called "Terra Roxa Estruturada" soils were used, and their properties are shown in Table 15 and 16. These soils were obtained from the States of Mato Grosso and Pará. The reaction of the soils is slightly acid. The CEC value, exchangeable Ca²⁺ and ECP are very high in the Ap horizon of TRE-1. The CEC values of the subsoil of TRE-2 are higher than those of TRE-1, in spite of a rather high content of organic carbon in the latter and the similarity of their clay content. This fact suggests a difference in the clay mineral composition in TRE-2 and TRE-1. ECP is considerably high in connection with the relatively high content of exchangeable Ca²⁺ and Mg²⁺ except in the Ap horizon of TRE-1. Available phosphorus is extremely low in TRE-2.

Chemical analysis:

The chemical composition of the clay samples of the soils called "Terra Roxa Estruturada" is presented in Table 17. The result of the chemical analysis was characterized by the extremely high content of Fe_20_3 . About one third of their clay fraction was occupied by Fe_20_3 in TRE-1, because the soil originated from basic rocks as shown in Table 15. The ratio of silica to alumina in TRE-1 was extremely low, while in TRE-2 was similar to the lateritic soils. The base contents of these soils were not so high.

X-ray diffraction:

The X-ray diffraction charts of the powder specimens of "Terra Roxa Estruturada" soils are shown in Fig. 11. The diffraction peak at 7.24 Å suggested that kaolinite is a dominant clay mineral, because the peak intensity of layer silicates is relatively low in the case of the powder method. A small amount of dioctahedral vermiculite was detected by looking over the changes of basal spacing at 14 Å (Fig. 12). The presence of metahalloysite in TRE-2 attracted attention in particular, which confirmed from the presence of the diffraction peak at 7.34 Å (KITAGAWA, 9). The peak intensity also suggested that metahalloysite is predominant in this soil.

In the TRE-1, a large amount of hematite connected with the diffraction peak at 2.69 Å which disappeared by the dithionite-citrate-bicarbonite system (Fig. 23), was found in all the horizons. A small amount of lepidocrocite with 6.30 Å peak was identified only in the Ap horizon, and goethite was not confirmed in any of the horizons. The presence of abundant iron-oxide minerals was already noticed in the chemical composition. Considerable amount of gibbsite was present in TRE-1, because the strong diffraction peaks occurred at 4.85 and 4.39 Å. Fair amounts of hematite and goethite with 4.17 Å peak existed in all the horizons of TRE-2.

Traces of quartz with the diffraction peak at 3.35 Å was found in all the clay samples.

DTA:

The DTA curves of the clay specimens of "Terra Roxa Estru turada" soils (Fig. 13) showed the occurrence of an endothermal peak near 550°C and an exothermal peak near 900°C associated with kaolin minerals, and an endothermal peak near 300°C associated with gibbsite.

Electron microscopy:

In the electron micrograph of the specimen from the Ap horizon of TRE-2 shown in Plate 2, thin-plate particles of which edges are bent were found, and they should be associated with metahalloysite (TAKAHASHI, 19). The tubular particles of metahalloysite were also present in this plate.

3.3 - CLAY MINERAL COMPOSITION OF LOWLAND SOILS

3.3.1 - Low Humic Gley soils

Samples:

Three samples of Low Humic Gley soils occurring in the States of Acre, Amazonas and Pará were employed in the experiments, and their properties are presented in Table 18 to 20. The soil reaction is strongly acid in GPH-1 and GPH-3, and extremely acid in GPH-2. The CEC value is extremely high in GPH-1, and rather high in GPH-3. The content of exchangeable Ca²⁺ and Mg²⁺ in GPH-1 is extremely high and slightly high, respectively, so that ECP is very high in GPH-3. GPH-2 has high exchangeable Al³⁺, low exchangeable bases and extremely low ECP as in the latosols.

Chemical analysis:

Table 21 shows the chemical composition of the clay fraction of Low Humic Gley soils. The ratio of silica to alumina was very high in GPH-1 and GPH-3, and slightly high in GPH-2. The Mg0, k_2^0 and H_2^{0+} contents in GPH-1 and GPH-3 were considerably high, slightly high and slightly low, respectively. This result suggests the occurrence of 2:1-type clay minerals. The K_2^0 content was slightly high in GPH-2.

X-ray diffraction:

The X-ray diffraction charts of the clay fraction in Low Humic Gley soils by the powder method, and the changes of basal spacing by glycerol and heating treatments are shown in Fig. 14 and 15, respectively. The very strong diffraction peak at 15 Å in GPH-1 and GPH-3 was associated with montmorillonite/ dioctahedral-vermiculite interstratified minerals (MACEWAN, et.al., 13), because the peak was shifted to 18 Å by glycerol retention of Ca^{2+} -saturated specimen, to 12.5 Å by K⁺ saturation, and to 10 Å by heating at 600°C, but this shift was imperfect by 300°C heating (Fig. 15). This agreed with the results of the chemical analysis from the viewpoint of the dominance of 2:1-type mineral in the clay fraction. Kaolinite was also a dominant mineral in GPH-3, while only a small amount of it existed in GPH-1. On the other hand, kaolinite was predominant, and a small amount of montmorillonite or vermiculite was detectable, in GPH-2.

A small amount of lepidocrocite was found in GPH-2, and its peak at 6.30 Å disappeared by the treatment with a dithionite-citrate-bicarbonate system as shown in Fig. 23.

All the profiles contained a small amount of mica minerals and quartz. Trace of gibbsite was found in the clay fraction of GPH-2.

DTA:

The DTA curves of GPH-2 showed the mode of kaolinite (Fig. 16). The curves of GPH-1 was montmorillonite-like, because an endothermal peak between 100 and 200[°]C was double (Fig. 16). The DTA curves of GPH-3 has the characteristics of their two minerals.

Electron microscopy:

The electron micrograph of the specimen from the Cg horizon of GPH-1 (Plate 3) shows the characteristics of

montmorillonite, because its particle shape is like to paper (TAKAHASHI, 19).

3.3.2 - Ground-Water Laterite soils

Samples:

Two profiles of Ground-Water Laterite soil in the State of Pará are shown in Table 22 and 23. The soil reaction is very strongly acid in both. The exchangeable H^+ and Al^{3+} are rather high, and ECP are low. In LH-2, the CEC value of the A_2 horizon is lower than in the other horizons. The contents of available phosphorus are slightly high, compared with the other Amazon soils.

Chemical analysis:

The result of the chemical analysis of Ground-Water Laterite soils is shown in Table 24. The ratio of silica to alumina was high in LH-1 except the C_2 horizon, and relatively low in LH-2. Especially in the A_2 horizon of LH-2, the ratio was low as in the latosols. The K_2^0 . Mg0 and H_2^{0+} content of LH-1 was very high, slightly high and low, respectively. This results suggest the presence of considerable amount of mica minerals. The clay mineral composition of the A_2 horizon of LH-2 should be different from the other horizons as mentioned in the paragraph under samples, because of the low ratio of silica to alumina, the low contents of Mg0, Ca0 and K_2^0 , and the high Fe₂0₃ content.

X-ray diffraction:

The X-ray diffraction patterns of Ground-Water Laterite soils (Fig. 17 and 18) showed that kaolin and mica minerals were the dominant minerals in LH-1. Kaolinite was very high in the A_2 horizon of LH-2, judging from the peak at 7 and 10 Å. In LH-1, the diffraction peak of kaolin minerals was situated at 7.29 Å where the middle between kaolinite and metahalloysite is (KITAGAWA, 9), and it is assumed that the mineral is a mixture or an intermediate of kaolinite and metahalloysite. This will be discussed in the observation of electron microscope.

A small amount of 2:1-type clay minerals was found in LH-2, but montmorillonite or vermiculite were not identified. The minerals in the Ap horizon were similar to dioctahedral vermiculite as shown in Fig. 18. The 2:1-type minerals were not detected, and considerable amounts of hematite and goethite were recognized in the A_2 horizon of LH-2, as discussed in the chemical composition of the clay fraction. A small amount of hematite occurred in all the horizons of LH-1.

DTA:

The DTA curves of the clay fractions of Ground-Water Laterite soils (Fig. 19) supported the presence of mica minerals in LH-1, and a large amount of kaolinite in the A_2 horizon of LH-2 in connection with the intensity of an endothermal peak near 550 °C and an exothermal peak near 900 °C.

Electron microscopy:

The plate in the electron micrograph of the specimen from the A₁ horizon of LH-1 (Plate 4) should be associated with mica minerals (TAKAHASHI, 19). The small particles of soil kaolinite were also found but the particles associated with metahalloysite were not found, in this photograph. Consequently, the kaolin minerals discussed in the paragraph of X-ray diffraction should be kaolinite.

3.3.3 - Alluvial soils

Samples:

Two Alluvial soils occurring in the Territory of Rondonia and the State of Pará were employed in the experiments, and shown in Table 25 and 26. The reaction of these soils is extremely acid in the surface soils and strongly acid in the subsoils, and the CEC value of the subsoils is very low, because they have sandy texture. Exchangeable H^+ and Al^{3+} are fairly high, and ECP is very low in these soils. The available phosphorus is low in SA-2.

Chemical analysis:

The result of the chemical analysis of the clay fractions of Alluvial soils (Table 27) shows that SA-1 had the low ratio of silica to alumina and the low contents of MgO and K_2O , while, SA-2 had the slightly high ratio of silica to alumina and relatively high contents of MgO and K_2O . This suggests the co-existence of 2:1-type clay minerals in SA-2.

X-ray diffraction:

The X-ray diffraction patterns of the clay specimens of Alluvial soils are shown in Fig. 20 and 21. Kaolinite with 7.24 Å peak was predominant in all the samples as in the upland soils. A small amount of mica minerals with the diffraction peak at 10.0 Å was detected in all the horizons of SA-2 and the surface soil of SA-1. Moreover, SA-2 contained a small amount of montmorillonite of which basal spacing at 15 Å was shifted to 18 and 10 Å by the glycerol saturation and 300° C heating, respectively (Fig. 21).

Small amounts of gibbsite with 4.85 Å peak and quartz

with 3.35 Å were found in both soils. Goethite with 4.17 Å peak was detected in SA-1.

DTA:

The DTA curves of the clay specimens of Alluvial soils are drawn in Fig. 22. These curves showed the mode of kaolin minerals in all the samples. A large endothermal and an exothermal peak occurred near 550 and 900°C, respectively. A very small endothermal peak at 300°C was associated with gibbsite.

4 - GENERAL DISCUSSION AND CONCLUSIONS

The clay mineral composition of nineteen soils occurring in the Brazilian Amazon region was examined by means of chemical analysis, X-ray diffraction method, DTA and electron microscopy. Results are summarized in Table 28.

In the clay fraction of the soils with oxic B horizon such as Yellow Latosol, Red-Yellow Latosol and "Latossolo Roxo" soil, kaolinite was predominant, gothite was detected, hematite was found except in one profile of Red-Yellow Latosol, and gibbsite was frequently present. The previous reports by SOMBROEK (18), CHIBA (3) and IWASA (7) also concluded the predominace of kaolin minerals in the lateritic soils of the Amazon region. A small amount or trace of mica minerals existed in several lateritic soils. These mica minerals should be very stable, and not be weathered under the drastic condition of the soil genesis in the tropics. KITAGAWA, et.al. (11) pointed out that mica minerals in soils are more stable under a chemical treatment than the deposit minerals such as muscovite and illite. A small amount of montmorillonite or vermiculite was found only in the subsoil of a Red-Yellow Latosol. In the soils with textural B horizon, the clay mineral composition was as follows:

Kaolinite was predominant, and iron-oxide minerals such as hematite and goethite were present in all the samples of Red-Yellow Podzolic soils. A small amount of mica minerals and dioctahedral vermiculite was found in some of these soils. The vermiculite in the weathered upland soils should be originated in dioctahedral micas, of which probability was presented by KITAGAWA, et.al. (12). Red-Yellow Podzolic soils in the Amazon region should fall clay-mineralogically under the category of the lateritic soils, and be different from the namesake in Virginia, U.S.A. reported by RICH, et.al. (17). A dominant clay mineral of Gley-Brown Podzolic soils distributed in the subfrigid zone is montmorillonite-like minerals in the A, horizon, and dioctahedral vermiculite in B horizons (KITAGAWA, 8; BRYDON, et.al., 2). The podzolic soils in the Amazon region were also mineralogically diferrent from Gley-Brown Podzolic soils, consequently.

In the soils called "Terra Roxa Estruturada", kaolin minerals were dominant. Considerable amounts of iron-oxide minerals were found in the clay fraction, and hematite content was especially high, because they were originated from basic rocks. A "Terra Roxa Estruturada" soil from Mato Grosso contained kaolinite, hematite and gibbsite, but goethite was absent. A small amount of dioctahedral vermiculite was also detected in this soil. In the other "Terra Roxa Estruturada" soil, metahalloysite was dominant in spite of the predominance of kaolinite in the other upland soils occurring in the Amazon regicn. The presence of metahalloysite in the lateritic soils was reported in an Indonesian soil derived from old "volcanic ash" by KITAGAWA, et.al. (10).

The clay mineral composition of the lowland Low Humic Gley, Ground-Water Laterite and Alluvial soils in the Amazon

region was a little complicated as SOMBROEK (18) and IWASA (7) pointed out. Although kaolinite was predominant in many soils, montmorillonite/dioctahedral-vermiculite interstratified and mica minerals were dominant in two Low Humic Gley soils and a Ground-Water Laterite soil, respectively. The dominant component of the interstratified minerals should be montmorillonite, judging from the mode of the changes of basal spacing by the treatments with glycerol and heating. GJEMS (5) reported the occurrence of a dioctahedral-vermiculite/montmorillonite interstratified mineral in a Scandinavian Podzolic soil, but it was a vermiculitic mineral. Mica and 2:1-type clay minerals were frequently found in the lowland soils, even if kaolinite was dominant.

Quartz existed more or less in the clay fraction of the Amazon soils. Accerding to KITAGAWA, et.al. (10), quartz is not always found in some tropical volcanogenous soils of Indonesia. Instead α -cristobalite occurs more frequently.

Kaolin minerals were dominant in the upland soils of the Amazon region, and the fertility of the soils was low from the viewpoint of clay mineralogy, in general. The soil called "Terra Roxa Estruturada" which is a kind of the upland soil have high fertility, but a dominant clay mineral was kaolin minerals. It is important to solve this problem, and will be discussed in following studies. Some of the lowland soils of this region contained a large amount of montmorillonite-like clay minerals, and were regarded as clay-mineralogically fertile, because montmorillonite have high CEC value and large specific surface area, so that its existence leads to high buffer action and high nutrients holding-capacity of the soils.

ACKNOWLEDGMENTS

We wish to thank Dr. Hermínio Maia Rocha, ex-director of CPATU, Dr. Cristo Nazaré Barbosa do Nascimento, director of CPATU, and Mr. Kenji Ishikawa, consul general of Japan at Belém, for their strong encouragement; Dr. Ítalo Cláudio Falesi, CPATU, Dr. Benedito Nelson Rodrigues da Silva, CPATU, Dr. Emmanuel de Souza Cruz, CPATU, Dra. Gladys Ferreira de Souza Morrill, CPATU, Dr. Emanuel Adilson de Souza Serrão, CPATU, and Prof. Lúcio Salgado Vieira, College of Agricultural Sciences of Pará, for their helpful advices; and Dr. Ronaldo Araujo, Nucleus of Phatology and Hygine, The Medicine Faculty, Federal University of Pará, for taking electron micrographs.

The collection and description of the soil samples were carried out by scientists in charge of EMBRAPA's and RADAM's research projects.

REFERENCES

- 1- BROWN, G. Dioctahedral analogue of vermiculite. Clay Miner. Bull. 2:64-70, 1953.
- 2- BRYDON, J. E., KODAMA, H., and ROSS, G. J. Mineralogy and weathering of the clays in Orthic Podzols and other podzolic soils in Canada. Trans. 9th Int. Cong. Soil Sci. (III):41-51, 1968
- 3- CHIBA, M. Report on the Japan-Brazil Technical Cooperation for the Investigation of Soils and Fertilizers in the Amazon Region, OTCA Tokyo 1970. 1-87. (In Japanese).
- 4- FALESI, I. C. O estado atual dos conhecimentos sôbre os solos da Amazônia Brasileira. Bol. Téc. IPEAN, Belém (54):17-67, 1972.
- 5- GJEMS, O. A swelling dioctahedral clay mineral of a vermiculite-smectite type in the weathering horizons of Podzols. Clay Miner. Bull. 5:183-193, 1963.
- 6- GRIM, R. E. Origin and occurrence of the clay minerals. Clay Mineralogy, MacGraw-Hill N.Y. 1968. 479-527.
- 7- IWASA, Y. Report on the Japan-Brazil Technical Cooperation for the Investigation of Soils and Clay Minerals in the Amazon Region, JICA Tokyo 1976. 1-177. (In Japanese).
- 8- KITAGAWA, Y. Clay minerals of a podzolic soil in Sarufutsu, Hokkaido. Pedologist 10:11-17, 1966. (In Japanese).
- 9- KITAGAWA, Y. Identification of kaolinite and metahalloysite in tropical soils. JARQ 10:58-62, 1976.



- 11- KITAGAWA, Y., and WATANABE, Y. An aspect on interlayer potassium of mica minerals in soils. Soil Sci. Plant Nutr. 16:167-172, 1970.
- 12- KITAGAWA, Y., and WATANABE, Y. Preparation of dioctahedral vermiculite from muscovite. Clay Sci. 4:31-36, 1970.
- 13- MACEWAN, D. M. C., RUIZ AMIL, A., and BROWN, G. Inter stratified clay minerals. The X-Ray Identification and Crystal Structures of Clay Minerals (ed. by BROWN, G.), Mineral. Soc. London 1961. 393-445.
- 14- MATSUI, T. Soils of Japan and their clay minerals. Clay Handbook, Gihodo Tokyo 1967. 152-158. (In Japanese).
- 15- MEHRA, O. P., and JACKSON, M. L. Iron oxide removal from soils and clays by a dithionite-citrate system bufferred with sodium bicarbonate. Clays Clay Miner. 7:317-327, 1959.
- 16- NYUN, M. A., and MCCALEB, S. B. The Reddish Brown Lateritic soils of the North Carolina Piedmont region: Davidson and Hiwasse series. Soil Sci. 80:27-41, 1955.
- 17- RICH, C. I., and OBENSHEIN, S. S. Chemical and clay mineralogical properties of a Red-Yellow Podzolic soil derived from muscovite schist. Soil Sci. Soc. Amer. Proc. 19:64-70, 1955.
- 18- SOMBROEK, W. G. Amazon Soils: A recnnaissance of the soils of the Brazilian Amazon region, Center Agr. Pub. Doc. Wagenningen 1966. 76-95.

EMBRAPA

- 19- TAKAHASHI, H. Electron microscopy in Mineralogical properties of clay minerals. Clay Handbook, Gihodo Tokyo 1967. 48-63. (In Japanese).
- 20- VIEIRA, L. S. Os solos da Amazônia. Manual da Ciência do Solo, Edi. Agron. Cer. Ltda. S. Paulo 1975. 381:440.

KITAGAWA, Y. e Möller, M. R. F. Mineralogia de Argila de Alguns Solos Típicos na Amazônia Brasileira.

SINOPSE: — A composição mineralógica da fração argila de alguns solos típicos ocorrentes na Amazônia Brasileira é a seguinte:

Nos solos com B latossólico; Latossolo Amarelo, Latossolo Vermelho Amarelo, Latossolo Roxo, encontrou-se predominância de caolinita, geralmente acompanhada de goetita, hematita e frequentemente gibsita. Pouca quantidade ou traços de micas ocorreram em alguns solos lateríticos. A presença de outros minerais tipo 2:1 foi rara.

Nos solos com B textural; Podzólico Vermelho Amarelo, também houve predominância de caolinita acompanhada de óxidos de ferro. Consideráveis quantidades de gibsita e pouca de mica e vermiculita dioctaedral estiveram também presentes em alguns destes solos.

Em Terra Roxa Estruturada, predominaram as caolinitas, principalmente a metahaloisita, com quantidade considerável de óxidos de ferro, especialmente hematita. Identificou-se ainda traços de vermiculita dioctaedral em um perfil.

A composição da argila em solos de baixadas evidenciou minerais 2:1 em quantidade mais significativa, assim é que em dois Glei Pouco Húmico e uma Laterita Hidromórfica o mineral interestratificado montmorilonita/vermiculita-dioctaedral e minerais de mica foram dominantes. Já em outros solos, a dominância foi de caolinita, aparecendo pouca quantidade de argila 2:1.

O quartzo esteve presente nas frações de argila de todos os solos.