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Clay Mineralogy of Selected Soils in Southern Nigeria[1]

A. GALLEZ, A. S. R. JUO, A. J. HERBILLON, AND F. R. MOORMANN[2]

ABSTRACT

Clay minerals in eight soil profiles from southern Nigeria were investigated by means of X-ray diffraction, infrared spectroscopy, differential thermal analysis, and electron microscopy. These soils are derived from basement complex rocks, arenaceous sedimentary rocks and basalts.

Kaolinite is the most predominant clay mineral for all the soils studied. A pronounced variation in clay mineralogy was found in the soils derived from basement complex rocks sampled at various locations along a toposequence. Halloysite occurs in freshly weathered materials, while smectite is found in poorly drained, lower members of the toposequence.

Gibbsite occurs in soil derived from cretaceous arenaceous rocks in the high rainfall area. Among all soils studied, the highest amounts of amorphous Al silicate and extractable Fe and Al oxides were found in those derived from basalts. In all cases, Fe oxides exist predominantly in crystalline forms.

Additional Index Words: kaolinite, halloysite, smectite, gibbsite, extractable Fe and Al, amorphous Al silicates, electron micrograph of soil clays.

THE physico-chemical properties as well as the management of tropical soils depend to a high degree on the kind and amount of clay minerals and Fe and Al oxides present in the soil. Published information on clay minerals in Nigeria soils is scarce. Jungerius and Levelt (1964) reported that kaolinite was the most abundant clay mineral in some soils from Eastern Nigeria. Based on the results of X-ray analysis, Nye (1955) briefly reported the clay minerals present in the soils from a catena over granitic gneiss in Western Nigeria and found that "kaolin" and mica were the predominant minerals in these soils and "montmorillonoid" was present in the valley soils. Ogunwale (1973)[3] showed the presence of spheroidal form of halloysite in some Nigerian soils derived from sandstones. Juo et al. (1974) studied the forms of extractable Fe oxides in some well-drained Nigerian soils derived from basement complex rocks and arenaceous sedimentary rocks and found that Fe oxides and hydrous oxides in these soils exist almost entirely in crystalline forms.

The objectives of this study are to establish the clay mineralogy of some representative soils from southern Nigeria and to relate the occurrence of clay minerals to parent materials and soil weathering conditions.

SOILS

The locations of the eight soil profiles selected for this study are shown in Fig. 1. They are representative for three broad groups of parent materials and cover several agroclimatic zones of the lowland humid tropics.

Profiles 1 to 4, located at the International Institute of Tropical Agriculture (IITA) near Ibadan are formed on materials derived from Pre-Cambriam basement complex rocks, in this case of intermediate crystalline rocks (quartz-biotite-plagioclase-hornblende paragneiss) (Freeth, 1971).[4] They represent various positions in the topography. The Ekiti series (No. 1) is a shallow young soil close to a rock outcrop of banded gneiss; this soil occurs on crests and on steeper slopes. The Egbeda profile (No. 2) is a characteristic and widespread deep soil on the flat and convex parts of the pediment land form. The Gambari profile (No. 3) occurs on various places along the slope, usually on slope breaks in narrow strips, indicating fossil or active spring levels. The Iregun profile (No. 4) is common on the middle and lower parts of the concave lower slopes, bordering the valley bottoms in this physiographic region.

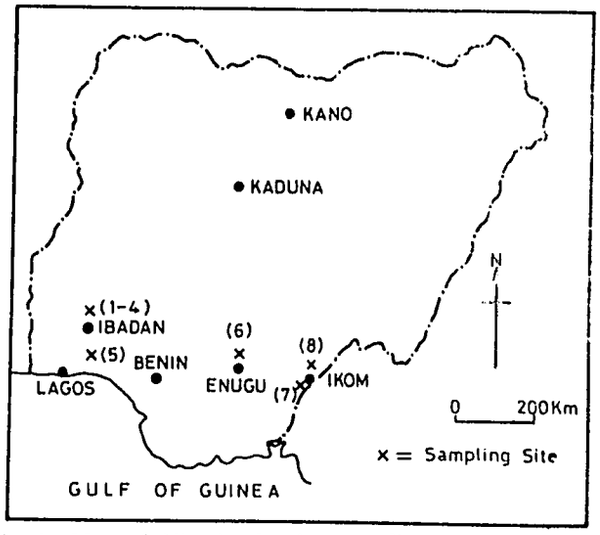

Fig. 1—Map of Nigeria showing sampling sites. Figures in parentheses designate the profiles as subsequently referred to in the text and tables.

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[2] Research fellow, IITA; Soil Scientist, IITA; Research Scientist, M.R.A.C. Tervuren and Associate Professor, University of Louvain and Soil Scientist, IITA, respectively.

[3] J. O. Ogunwale. 1973. Ph.D. thesis, University of Ibadan.

[4] S. J. Freeth. 1971. Ph.D. thesis, University of Ibadan.

The relative position of the profiles in the toposequence has been described by Nye (1954 and 1955), Smyth and Montgomery (1962) and Folster (1971). Rainfall of the area is bimodal, with an average annual rainfall of 1,230 mm. The area is under semideciduous tropical rain forest which, in the case of IITA is secondary due to widespread shifting cultivation.

Profiles 5 and 6 are formed on parent materials, derived from arenaceous sedimentary rocks, respectively of Tertiary-Pleistocene and Cretaceous age. The Alagba profile (No. 5) is representative for the gently undulating to flat, well drained and deeply weathered coastal terrace area. The Nkpologu profile (No. 6) is found on an undulating plateau with a similar predominance of well drained and deeply developed soils. The vegetation in the area of Alagba profile (No. 5) is medium-wet tropical rainforest, with moderately intensive shifting cultivation. Rainfall is bimodal averaging 1700 mm annually.

The present vegetation type in the area of profile 6 is derived savanna due to intensive cultivation. Rainfall is approximately 1760 mm annually and is bimodal.

Profiles 7 and 8 from Ikom are formed on parent materials, derived from olivine-basalt (probably Tertiary). Weathering in profile 7 took place under free drainage, whereas drainage in the case of profile 8 was less free due to its position in a flat or slightly depressed part of the terrain. Both profiles were formed on a gently undulating to nearly flat lava plateau, with occasional volcanic push ridges. The original vegetation on the plateau was dense tropical forest but the area is now extensively used for cultivation of tree and food crops and for forestry. The bimodal annual rainfall averages about 2,700 mm.

The classification of the profiles is given in Table 1, (Soil Survey Staff, 1975). Complete soil profile descriptions are available at IITA (unpublished).

ANALYTICAL METHODS

Soil samples were air dried and passed through a 2-mm sieve. Mechanical analysis was done by the hydrometer method of Bouyoucos (1951). The pH determinations were made on soil paste in water and in 1*N* KCl on a Beckman Expandometric pH meter. The cation exchange capacity was measured by the sum of exchangeable cations extracted with a 1*N* ammonium acetate for exchangeable bases and with 1*N* KCl for exchangeable Al and H according to the procedure given by McLean (1965). The Al in the KCl extract was determined colorimetrically according to the modified aluminon method (Hsu, 1964).

For clay mineralogical analysis, the clay fraction was separated from the soil by ultrasonic dispersion in distilled water using the Biosonic III probe type sonic disperser at 52 W/cm^2 for 3 to 5 min. The $< 2\mu$m fraction was then siphoned into another container and flocculated with $MgCl_2$ and the residue was washed with distilled water until free of chloride. The clay samples were then freeze dried. In some cases, the soil particles were not fully dispersed by ultrasonic vibration in water suspension. It was necessary to raise the pH of the suspension by addition of dilute NaOH to pH 7.0.

For X-ray diffraction analysis, oriented clay specimens were made by depositing clay suspensions onto glass slides. Random clay specimens were prepared according to Niskamen (1964). The X-ray diffraction patterns were obtained on a Philip diffractometer using Ni-filtered Cu-radiation. Identification of minerals from the diffractograms was made according to procedures and criteria given by Brown (1961). Kaolinite, mica, and smectite were identified from Mg-saturated and ethylene-glycol solvated clay specimens after organic matter and free Fe oxides removal. Goethite, hematite, and gibbsite were identified on the diffractograms of the untreated clay samples.

Infrared spectra were recorded on a Beckman IR-20A double-beam spectrometer. Clay samples were prepared in the form of KBr pellets with samples to KBr ratios of 1:1000 for the frequency range between 300 cm^{-1} to 2000 cm^{-1} and 1:300 for the region between 2000 cm^{-1} to 4000 cm^{-1}. Sample pellets were heated at 110C for 12 hours to remove adsorbed water prior to scanning.

Differential thermal analyses of clays were made in a nitrogen atmosphere using a Du Pont model 900 Thermal Analyser with a high temperature DTA Cell (1200C) at a heating rate of 30C/min. The clay samples were Mg-saturated and dried under a relative humidity of 60 to 70%.

A semiquantitative estimation of the kaolinite content was made by measuring the surface area under the endothermic peak of 550C and compared with a standard curve obtained from pure kaolinite (Barshad, 1965 and Dixon, 1966). The estimation of other minerals was made as follows: mica and smectite by comparing the intensity of X-ray diffraction peaks and chemical analysis; goethite and hematite by X-ray diffraction and extractable Fe; and gibbsite by the characteristic DTA endothermic peak area and IR absorption bands due to OH stretching vibrations (Jackson, 1969; Barshad, 1965; and Mejia et al., 1968). The amount of tubular-shaped halloysite present in the clay fraction of the Ekiti soil (No. 1) was estimated from electron microscopic observations.

Electron microscopic observations were made on a AEI EM6G electron microscope. A drop of the clay suspension was dried on the carbon support film after ultrasonic dispersion.

Amorphous aluminosilicate in clay was determined according to the procedure given by Jackson (1965). A sample of soil clay pretreated with H_2O_2 and dithionite-citrate-$NaHCO_3$ (DCB) was boiled with 0.5*N* NaOH for 2.5 min and the dissolved Al and Si were determined colorimetrically. The amount of Al and Si extracted by NaOH was used to estimate the amorphous aluminosilicate.

Free Fe and Al oxides were letermined according to Mehra and Jackson (1960) using a dithionite-citrate-$NaHCO_3$ system. Amorphous Fe and Al were extracted from soils by NH_4-oxalate according to the procedure described by Schwertmann (1959).

RESULTS AND DISCUSSION

General properties of the soils, extractable Fe and Al oxides and a summary of the clay minerals present in the soil profiles used in this study are given in Table 2.

Soils from Basement Complex Rock

X-ray, IR, and DTA analyses indicate that kaolinite is the most abundant type of clay mineral present in these soils. Goethite is also a commonly occurring mineral in the clay fraction throughout the four profiles studied. This is indicated by the X-ray diffraction peak at 4.18Å and the

Table 1—Classification of selected profiles in southern Nigeria

Profile no.	Location	Group	Subgroup	Family	Series
1	Ibadan	Ustropept	Paralithic*	Loamy-skeletal, shallow	Ekiti
2	Ibadan	Paleustalf	Oxic	Clayey (Skeletal) Oxidic	Egbeda
3	Ibadan	Plinthustalf	--	Loamy skeletal, mixed	Gambari
4	Ibadan	Haplustalf	Aquic	Clayey, mixed	Iregun
5	Shagamu	Paleustalf	Oxic	Clayey, kaolinitic	Alagba
6	Nsukka	Paleustult	Ustoxic*	Loamy, siliceous	Nkpologu
7	Ikom	Tropudalf	Oxic*	Clayey, very fine, (oxidic) - Kaolinitic	--
8	Ikom	Tropudalf	Oxic* Ultic	Clayey, very fine, kaolinitic	--

* Subgroups marked are not mentioned in soil taxonomy and are therefore tentative.

Table 2—Physical, chemical, and mineralogical data of soils derived from basement complex rocks (Profiles 1–4), arenaceous sedimentary rocks (Profiles 5 & 6), and from basalt (Profiles 7 & 8)

Horizon	Depth	Mechanical analysis			Org. C	pH		CEC	Base sat.	Fe_2O_3 in soil		Al_2O_3 in soil		Clay Minerals*
		Sand	Silt	Clay		H_2O	KCl			Oxalate	Dithionite	Oxalate	Dithionite	
	cm	%			%			meq/100 g	%	%		%		
						Profile No. 1 (Ekiti)								
A1	0-16	66.3	18.4	15.3	1.56	6.78	6.26	8.16	96	0.20	1.45	0.17	2.39	$K_2 H_2 M_1 Mt_1 Gh_1 F_4$
B	16-46	64.3	16.0	19.7	0.74	6.50	5.75	5.05	94	0.19	1.09	0.17	2.46	$K_2 H_2 M_1 Mt_1 Gh_1 F_4$
C	46-66	55.3	14.0	30.7	0.35	5.95	4.90	4.89	92	0.20	2.26	0.21	3.12	$K_1 H_2 M_1 Mt_1 Gh_1 F_4$
						Profile No. 2 (Egbeda)								
A1	0-6	52.2	23.8	24.0	1.80	6.19	5.60	8.73	91	0.27	5.65	0.17	1.19	$K_1 M_1 Gh_1 Hm_1$
HA3	6-16	58.2	11.8	30.0	0.90	6.55	5.67	8.97	89	0.30	5.63	0.20	1.01	$K_1 M_1 Gh_1 Hm_1$
HB2t	16-63	36.2	10.8	53.0	0.78	5.53	4.88	4.67	83	0.36	7.79	0.20	1.17	$K_1 M_1 Gh_1 Hm_1$
HHB2t	63-103	30.2	20.8	49.0	0.12	5.92	5.80	3.79	87	0.32	11.61	0.19	1.29	$K_1 M_1 Gh_1 Hm_1$
HHB3t	103-152	30.2	22.8	47.0	0.02	6.16	6.09	3.89	87	0.27	13.95	0.28	1.51	$K_1 Gh_1 Hm_1$
HHBC	152-170	34.2	28.8	47.0	nil	6.14	5.92	4.16	88	0.27	11.70	0.15	1.13	$K_1 Gh_1 Hm_1$
						Profile No. 3 (Gambari)								
A1	0-18	66.3	12.7	21.0	1.84	6.49	5.68	9.34	96	0.31	2.31	0.14	4.07	$K_2 M_1 Q_3 Gh_1 I_4$
A3cn	18-36	70.3	10.7	19.0	0.44	6.30	5.38	4.48	89	0.18	2.54	0.14	3.75	$K_2 M_1 Gh_1 I_4$
B21tcn	36-65	53.7	14.0	32.3	0.36	6.05	5.20	5.98	93	0.21	4.26	0.20	3.76	$K_2 M_1 Gh_1 I_4$
B22tcn	65-87	43.0	13.7	43.3	0.36	5.80	4.92	7.96	94	0.21	5.07	0.20	3.85	$K_2 M_1 Gh_1 Hm_1 I_4$
B3t	87-127	35.0	18.1	46.9	0.32	5.73	4.80	9.38	95	0.22	3.96	0.20	3.73	$K_2 M_1 Gh_1 Hm_1 I_4$
HC	127-187	47.0	22.7	30.3	0.12	5.56	4.55	10.91	95	0.21	2.83	0.17	3.56	$K_2 M_1 Gh_1 Hm_1 I_4$
						Profile No. 4 (Iregun)								
A1	0-18	58.3	16.7	25.0	1.46	6.25	5.42	9.81	98	0.29	1.93	0.16	0.51	$K_2 S_2 M_1 Gh_1$
Bt	18-50	54.3	11.7	31.0	1.36	5.88	4.73	7.66	99	0.39	2.79	0.18	0.74	$K_2 S_2 M_1 Gh_1$
B2tg	50-93	46.3	7.7	46.0	--	6.13	5.06	18.50	99	0.31	3.10	0.14	0.65	$K_2 S_2 M_1 Gh_1 Hm_1$
Cg	93-165	48.3	14.7	37.0	--	6.66	5.19	19.79	99	0.41	3.90	0.13	0.77	$K_2 S_2 M_1 Gh_1 Hm_1$
						Profile No. 5 (Alagba)								
Ap	0-13	75.0	7.6	17.4	1.41	6.81	6.01	5.68	94	0.25	1.84	0.19	1.80	$K_2 Gh_1 Hm_1 Q_3 I_4$
A3	13-36	71.0	6.7	22.3	1.43	6.40	5.35	3.15	89	0.26	2.32	0.21	1.59	$K_1 Gh_1 Hm_1 Q_3 I_4$
B1	36-68	57.0	4.7	38.3	0.32	6.13	5.22	3.42	95	0.27	4.31	0.30	2.40	$K_1 Gh_1 Hm_1 I_4$
B21t	68-122	47.0	4.7	48.3	0.28	6.11	5.28	3.12	95	0.17	4.89	0.32	1.70	$K_1 Gh_1 Hm_1 I_4$
B22t	122-183	45.0	2.7	52.3	0.20	5.79	5.01	2.73	94	0.17	5.31	0.21	2.86	$K_1 Gh_1 Hm_1 I_4$
						Profile No. 6 (Skpologu)								
Ap	0-6	67.2	6.5	26.3	1.23	4.60	3.83	1.87	20	0.21	3.17	0.39	1.13	$K_1 Gh_1 G_1 Hm_1 Q_3 I_4$
AB	6-43	67.5	6.8	25.7	0.94	4.60	3.86	1.74	17	0.19	2.85	0.39	1.31	$K_1 Gh_1 G_1 Hm_1 Q_4 I_4$
B21t	43-70	64.2	6.5	29.3	0.61	4.76	3.92	1.78	16	0.23	3.86	0.43	1.20	$K_1 Gh_1 G_1 Hm_1 Q_4 I_4$
B22t	70-93	58.2	5.5	36.3	0.43	4.81	3.90	2.32	14	0.23	4.60	0.42	1.18	$K_1 Gh_1 G_1 Hm_1 Q_4 I_4$
B23t	93-170	54.2	4.5	41.3	0.32	5.15	3.97	2.15	16	0.20	5.80	0.61	1.17	$K_1 Gh_1 G_1 Hm_1 Q_4 I_4$
						Profile No. 7 (Ikom I)								
A1	0-12	32.4	27.6	40.0	3.63	5.44	4.90	7.33	98	1.28	12.63	0.91	3.06	$K_1 Gh_1 Hm_1 H_1 Q_3$
A3	12-27	24.4	23.6	52.0	2.13	5.52	4.91	6.06	97	1.15	13.43	0.74	2.58	$K_1 Gh_1 Hm_1 H_1 Q_3$
B1	27-40	16.4	17.6	66.0	1.40	5.71	5.15	5.17	98	0.93	13.18	0.71	2.71	$K_1 Gh_1 Hm_1 H_1 Q_3$
B2t	42-110	12.4	11.6	76.0	0.80	5.92	5.57	3.64	99	0.72	13.17	0.58	2.74	$K_1 Gh_1 Hm_1 H_1$
B2t	at 180	11.4	9.6	79.0	0.39	5.92	4.89	2.10	93	0.50	12.12	0.55	2.93	$K_1 Gh_1 Hm_1 H_1$
B2t	at 200	23.4	7.6	69.0	0.45	6.02	5.12	1.91	94	0.54	14.87	0.56	2.69	$K_1 Gh_1 Hm_1 H_1$
						Profile No. 8 (Ikom II)								
Ap	0-7	28.4	29.6	42.0	4.70	5.91	5.04	4.02	97	1.10	8.95	0.65	2.61	$K_1 Gh_1 H_1 Q_3$
B1	7-26	14.4	21.6	64.0	0.94	5.35	4.34	3.87	62	1.21	10.04	0.74	2.88	$K_1 Gh_1 H_1 Q_4$
B21t	26-29	12.4	13.6	74.0	0.60	5.77	4.35	2.93	47	0.65	10.32	0.65	3.14	$K_1 Gh_1 H_1 Q_4$
B22t	69-107	11.4	9.6	79.0	1.05	5.55	4.22	3.93	46	0.54	10.39	0.67	2.94	$K_1 Gh_1 H_1 Q_4$
B23t	107-199	9.2	6.4	84.4	0.53	5.92	4.30	2.96	44	0.47	10.82	0.58	3.30	$K_1 Gh_1 H_1 Q_4$

* Abbreviations of mineral names: K - kaolinite; H - halloysite (tubular form); M - mica (dioctahedral); Mt - mica (trioctahedral); S - smectite (montmorillonite); Q - quartz; G - gibbsite; Gh - goethite; Hm - hematite; F - feldspar; I - interstratified materials. Indication of quantity: 1 - >60%; 2 - 10 to 60%; 3 - <10%; 4 - possible trace amount.

DTA endothermic peak at about 320C. The presence of several other types of minerals in the clay fraction of these soils demonstrates an interesting relationship between the degree of soil weathering, the movement of parent materials, and the chemical weathering environments.

The X-ray diffraction pattern of the clay fraction (ethylene glycol solvated) of the shallow Ekiti profile (No. 1) situated at the upper part of the toposequence is characterized by strong peaks at 7.14Å and 10Å indicating the presence of kaolinite and mica (Fig. 3). The presence of both dioctahedral and trioctahedral micas in the clay fraction of the Ekiti soil was observed by the presence of the 060 lines at 1.50Å and 1.53Å, respectively (not shown). A tubular-shaped clay mineral was also observed in the electron micrograph (Fig. 4). The similarity between this tubular mineral and the electron micrograph of "tubular halloysite" given by Bates et al. (1950) and Grim (1968) indicates the presence of halloysite in the Ekiti soil.

A differential thermogram of the clay sample (not shown) also shows the presence of halloysite in the Ekiti soil. The strong endothermic peak at 150C is largely due to halloysite since the sample only contains a small amount of amorphous material which alone would give a weaker and broader peak at the same temperature. The presence of halloysite cannot be identified on the X-ray diffractogram since the soil contains a considerable amount of mica in the clay fraction. Hence, the characteristic 10Å peak for the halloysite in the ethylene glycol solvated sample overlaps with the 10Å peak due to mica. The absence of a peak at 7.3 seems to rule out the presence of metahalloysite in this soil. Moreover, the poor geometry for diffracting X-rays in preferred orientation for the tubular and spheroidal halloysites would make the X-ray identification of these minerals extremely difficult in a mixture containing predominantly kaolinite. (Askenasy et al. 1973).

In the Egbeda profile (No. 2), the clay from the upper horizons (A1, HA3, and HB2t) contains considerable mica (Fig. 5 and Fig. 3). The 060 line of X-ray diffractograms (not shown) indicated that only dioctahedral mica presents in this profile. The absence of mica and the increase in free iron oxide content in the lower horizons suggests that the upper horizons of this profile were influenced by recently weathered colluvial material from shallow soils of the upper part of the slope while the lower horizons of the profile

were weathered *in situ*. The Gambari profile (No. 3) is the only profile of this toposequence to contain large amounts of laterite concretions as well as plinthite. Kaolinite and goethite again are the most abundant clay minerals present. The profile contains dioctahedral mica throughout the profile. X-ray diffraction data show possible presence of a trace amount of smectite and/or mica-vermiculite interstratified material. Quartz exists in the clay fraction of the surface layer but not the lower layers of the profile.

The X-ray diffraction pattern (Fig. 3) of the oriented natural clay specimen of Iregun profile (No. 4) after Mg-saturation and ethylene glycol solvation shows peaks at 14.7Å and 15.7Å. However, after the removal of free Fe and Al oxides by treating the clay with dithionite, citrate, and bicarbonate (DCB), the X-ray diffraction pattern of the Mg-saturated and ethylene glycol solvated clay samples gives a strong 17Å peak and concurrently shows the disappearance of the 14.7Å and 15.7Å peaks. This suggests the presence of a moderate amount of smectite (montmorillonite) rather than vermiculite or interstratified materials in the Iregun profile (No. 4). The presence of coatings of free Fe and Al oxides and possibly the interlayer polyvalent ions such as Al^{3+} and Fe^{3+} in the clay may prevent full expansion of the basal spacing of the smectite to 17Å when treated with ethylene glycol (Walker, 1958). The presence of moderate amounts of smectite is also indicated by the diffuse pattern of the particules shown in the electron micrograph (Fig. 6). The Bg and C horizons of this soil contain more than 30% of smectite as estimated on the basis of X-ray diffraction, DTA, and CEC data of the clay samples. Dioctahedral mica also exists in small amount throughout the profile (Table 2).

The above results clearly show the variations in clay mineralogy of the soils under different weathering environment at various locations along a toposequence in function of age and drainage. Pedogenetic aspects of similar toposequences in West Africa have been described by Nye (1954), Ségalen (1969), and Folster (1971).

The presence of halloysite and trioctahedral mica, as well as the presence of traces of feldspar in the clay fraction clearly confirm the pedogenetic youthfulness of the

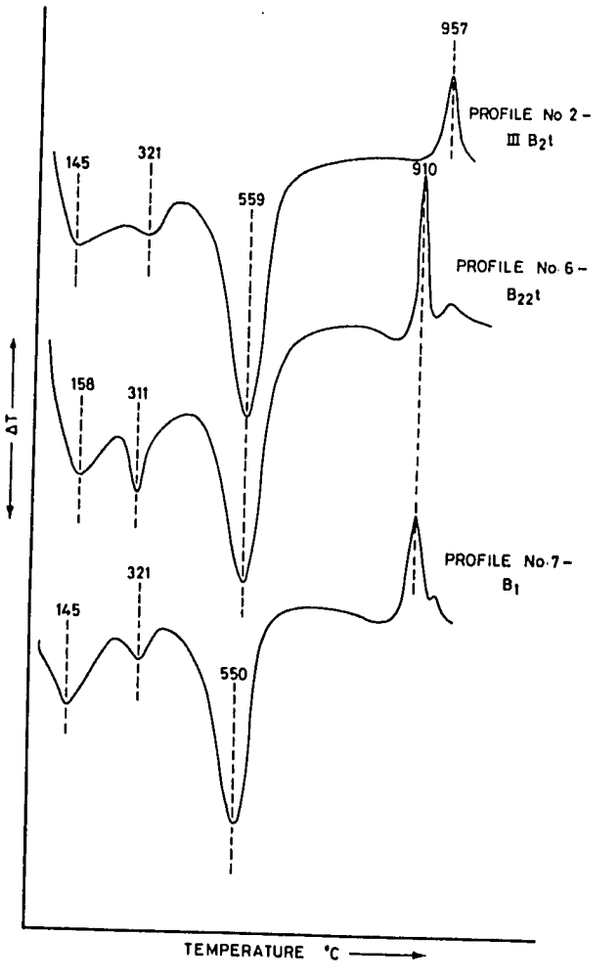

Fig. 2—DTA curves of < 2 μm fraction of Ikom profile (No. 7), Nkpologu profile (No. 6) and Egbeda profile (No. 2).

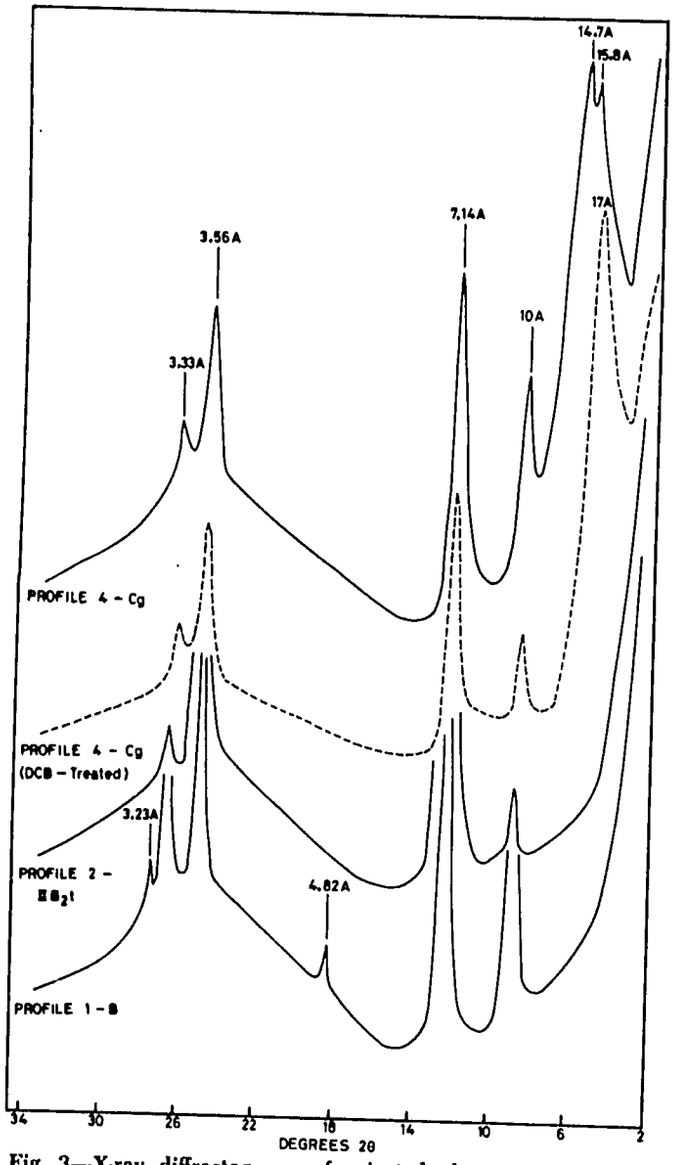

Fig. 3—X-ray diffractograms of oriented clay samples from Ekiti profile (No. 1), Egbeda profile (No. 2) and Iregun profile (No. 4). Samples were Mg-saturated and ethylene glycol solvated. Diffractogram in dotted line showing clay sample treated with dithionite-citrate-$NaHCO_3$ (DCB).

Ekiti profile (No. 1). The deeply developed and well drained older Egbeda profile (No. 2) has a characteristic dominance of kaolinite and crystalline Fe oxides, typical for tropical soils. Nevertheless, the occasional presence of clay-size mica in these profiles indicates a rejuvenation of the landscape and hence of the soils. The poor drainage condition and the enrichment with Ca, Mg, and silica (unpublished data) as a result of interflow favors the formation of smectite in the Iregun profile.

Soils From Arenaceous Sedimentary Rocks

Two representative soil profiles from this group (profiles No. 5 and 6) contain predominantly kaolinite. Goethite is also present throughout the profiles. The Nkpologu soil (No. 6) contains an appreciable amount of gibbsite as shown by both DTA and IR analyses (Fig. 2 and 7). Infrared spectra (Fig. 7) of the Nkpologu clay show the characteristic OH stretching vibrations for gibbsite between 3530 and 3390 cm^{-1}. The pronounced endothermic peak between 300C and 360C (Fig. 2) also indicates the presence of gibbsite in addition to goethite. An electron micrograph (Fig. 8) of the clay fraction for the profile No. 6 (Nkpologu series) shows fine particles of well shaped kaolinite with an average diameter of approximately 0.2 μm. The Alagba profile (No. 5) did not contain any detectable amount of gibbsite.

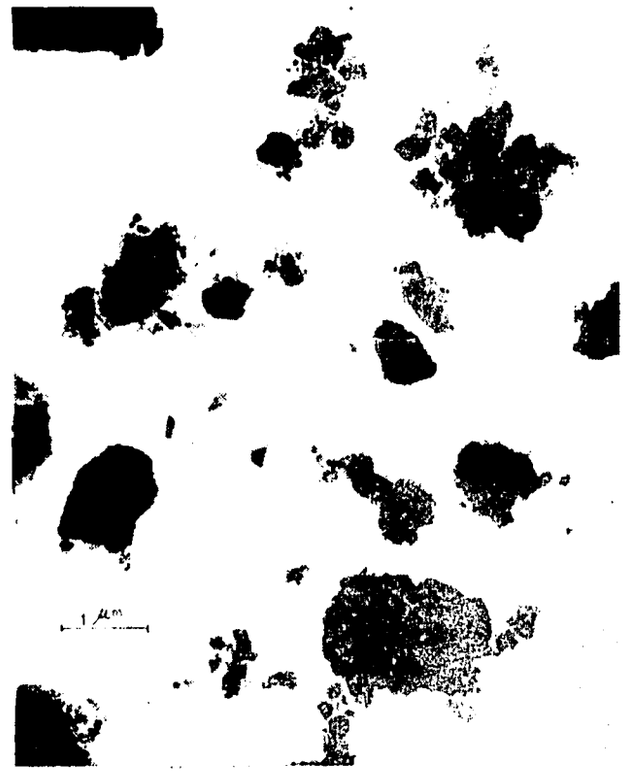

Fig. 5—A1 horizon, Egbeda profile (No. 2), H_2O_2 treated, (electron micrograph of < 2 μm fraction).

Fig. 4—C horizon, Ekiti profile (No. 1), H_2O_2 treated, (electron micrograph of < 2 μm fraction).

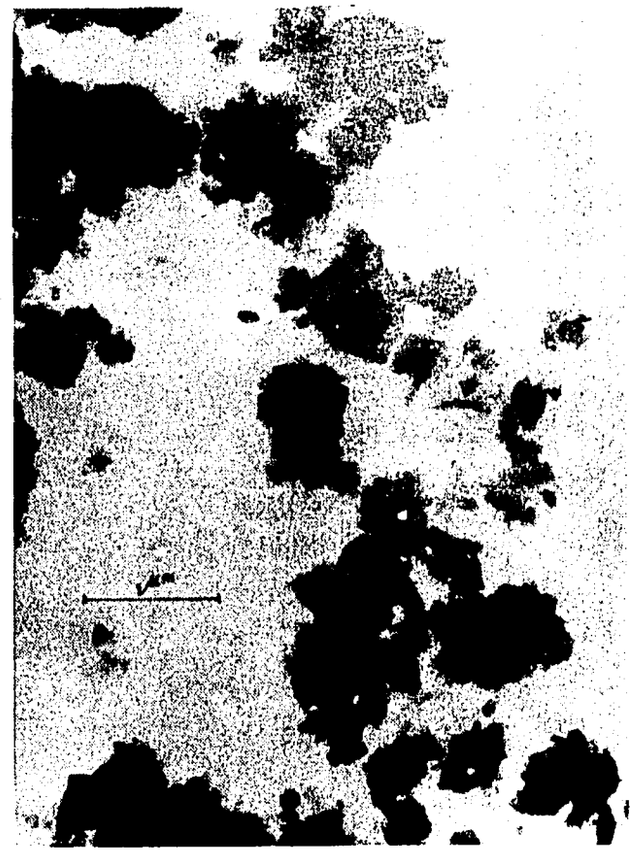

Fig. 6—Cg horizon, Iregun profile (No. 4), H_2O_2 treated, (electron micrograph of < 2 μm fraction).

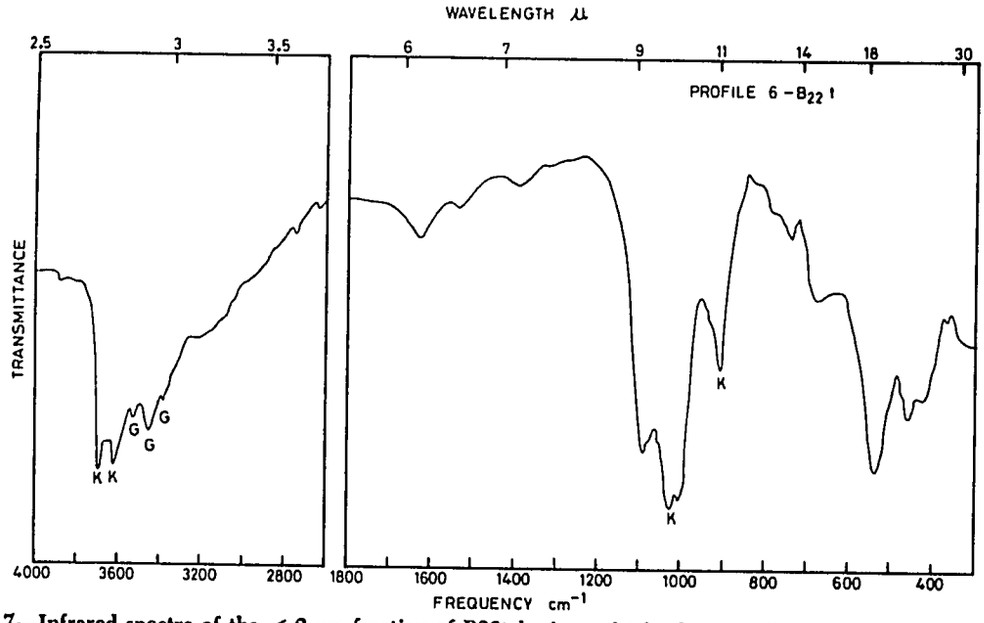

Fig. 7—Infrared spectra of the < 2 μm fraction of B22t horizon of Nkpologu profile (No. 6) H_2O_2 treated.

Fig. 8—B22t horizon, Nkpologu profile (No. 6), H_2O_2 treated, (electron micrograph of < 2 μm fraction).

The presence of gibbsite in the Nkpologu profile is related to the low base saturation (20–25%) associated with the specific parent material (Upper Senonian Sandstones).

Soils From Basalts

Soils derived from volcanic materials comprise only a small area in the Southeastern part of Nigeria near the Cameroun border. The reddish brown color of profile No. 7 and the yellowish brown color of the profile No. 8 coincide with the presence of hematite in the former though both soils contain goethite (Table 2). The absence of hematite in the clay fraction of profile No. 8 may be related to an impeded drainage during its in situ formation. Kaolinite again, is the most abundant clay mineral. Electron micrographs (Fig. 9 and 10) of the clay samples show the presence of well-shaped kaolinite and goethite. The high degree of dispersion of the clay particles after treating with the dithionite-citrate-bicarbonate system (Fig. 11) as compared with the untreated sample (Fig. 10) might be due to the removal of amorphous materials, which hold the crystallized clay particles together in addition to Fe oxides removal. Electron microscopic observations by Jones and Uehara (1973) recently showed the amorphous coatings of kaolin particles from a Hawaiian soil by suspending the bridging particles over holes in the supporting substrates. They also indicated that the coatings could not be detected by mounting samples on conventional carbon substrate. The amorphous gel coatings are believed to be noncrystalline and positively charged aluminosilicate. The electron micrograph (Fig. 9) also shows the presence of a trace amount of tubular halloysite in profile No. 8.

Field observations show that these soils have excellent physical properties, such as structure, aggregation and infiltration. This again suggests the presence of amorphous coatings around the clay particles to form microaggregates in soils derived from volcanic materials.

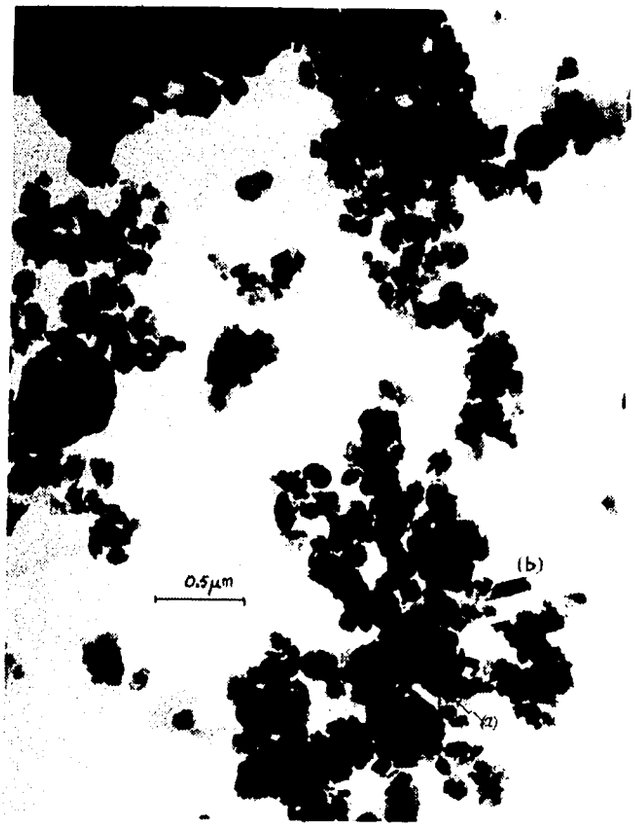

Fig. 9—B1 horizon, Ikom profile (No. 8), H_2O_2 treated, (*a*) goethite, (*b*) halloysite, (electron micrograph of < 2 μm fraction).

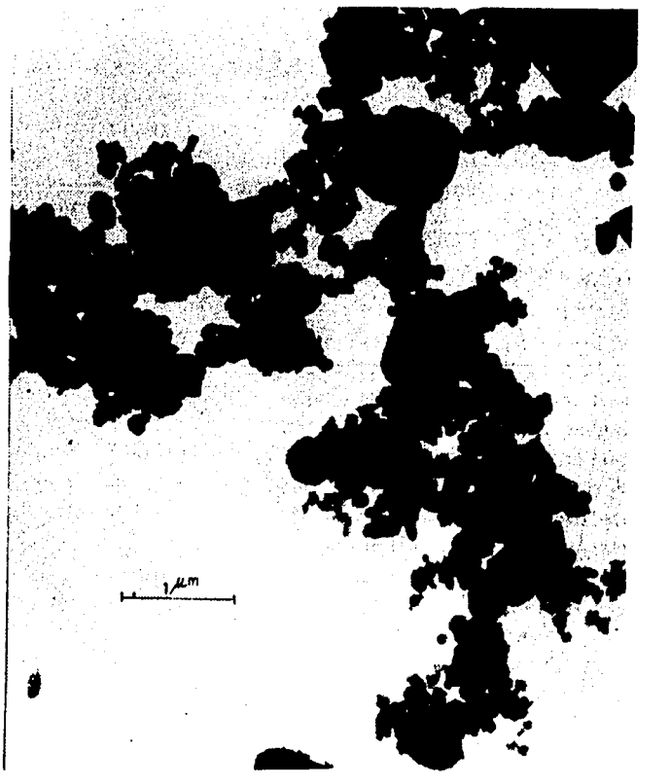

Fig. 10—A3 horizon, Ikom profile (No. 7), H_2O_2 treated, (electron micrograph of < 2 μm fraction).

Amorphous Aluminosilicates and Extractable Fe and Al Oxides

The DCB-treated clay samples of the Ikom profiles (No. 7) contain 8 to 13% of amorphous aluminum silicates while that of Egbeda profile (No. 2) contain approximately 6% throughout the profile. This seems to indicate that the major portion of the silicates in the clay fraction of these soils exists in crystalline forms, even though a small fraction of the amorphous Al silicate may have been removed during pretreatment of clay samples by DCB.

The contents of oxalate and dithionite-citrate-bicarbonate (DCB) extractable Fe and Al oxides are given in Table 2. The values of active Fe ratio

$$\left(\frac{\text{oxalate-Fe}_2\text{O}_3}{\text{DCB-Fe}_2\text{O}_3}\right)$$

for all soils studied are very low and generally decreases with depth within each profile. This is in agreement with a previous study by Juo et al. (1974).

In the soils derived from basement complex rocks, the oxalate-Fe_2O_3 content is very similar between the different profiles and remains constant with depth. However, the values of the DCB-Fe_2O_3 content, the DCB-Fe_2O_3/clay ratio, and the active Fe ratio show interesting variations. The young Ekiti profile shows the lowest DCB-Fe_2O_3 content and the highest active Fe ratio. The highest DCB-Fe_2O_3 content is found in the intensively weathered Egbeda pro-

Fig. 11—A3 horizon, Ikom profile (No. 7), H_2O_2 and DCB treated, (electron micrograph of < 2 μm fraction).

file (No. 2) subsoil where the active Fe ratio is also the lowest. The increase in DCB-Fe_2O_3 content (total free iron oxide) with depth in the Egbeda profile coincides with the decrease in magnitude of the negative delta pH (pH KCl — pH H_2O) (Table 2). This suggests the increase in positive charges in the lower horizons though the soil colloids still bear net negative charge (Mekaru and Uehara, 1972). The high value of DCB-Fe_2O_3 to clay ratio (0.24) in the IIIB2t horizon of Egbeda profile indicates the oxic characteristic of the soil (USDA Soil Taxonomy, 1970). The low DCB-Fe_2O_3 content and relatively high active Fe ratio are also found in the hydromorphic Iregun Soil.

In the young Ekiti profile (No. 1), the DCB-Al_2O_3 content is some what higher than in the other profiles and higher than the DCB-Fe_2O_3 content. This difference may be related to the fact already reported by Harrison (1933) that during the first stage of tropical weathering, on acid rocks, the breakdown of ferromagnesian minerals is delayed with respect to the weathering of primary aluminosilicates such as feldspars. The high DCB-Al_2O_3 values found in the plinthitic Gambari profile (No. 3), which represents a location of an absolute accumulation of iron, are surprising. This suggests that aluminum also could participate in this accumulation. In contrast, the hydromorphic Iregun profile (No. 4) contains the lowest DCB-Al_2O_3. This indicates that the process of neoformation of clays by silification occurs.

In the soils over arenaceous sedimentary rocks, the content and distribution of oxalate-Fe_2O_3 are comparable to those on the soils over basement complex rocks. The presence of gibbsite in the Nkpologu profile (No. 6) is not reflected in the DCB-Al_2O_3 content which is somewhat lower than in the gibbsite-free Alagba profile (No. 5).

Among all soils studied the two Ikom profiles (No. 7 and 8) developed from basalt contain the highest amounts of oxalate-Fe_2O_3 and DCB-Fe_2O_3 throughout the profile. The higher DCB-Fe_2O_3 values in the Ikom I profile (No. 7) as compared to the Ikom II profile (No. 8) are probably due to the better internal drainage of the former. The oxalate-Fe_2O_3 content is essentially the same in the two profiles. These results do not support the observation of Ségalen (1969) who reported that the contents in amorphous iron oxide in tropical soils were systematically higher in the red soils when compared to the yellow ones. The constant clay/DCB-Fe_2O_3 ratio found within the profiles developed from basement complex rocks and from arenaceous sedimentary rocks indicates the comigration of clay and iron oxides from A horizon into B horizon (Juo et al. 1974). However, this relationship was not found in the two basaltic profiles.

In all soils studied, values of DCB-Fe_2O_3 and DCB-Al_2O_3 are considerably higher than the oxalate-Fe_2O_3 and oxalate-Al_2O_3, respectively. For iron, a considerable fraction of sesquioxides is present in crystalline forms.

For aluminum, no crystalline oxides or hydroxides can be detected except in the Nkpologu profile (No. 6) which contains moderate amount of gibbsite. The results obtained in this study are clearly in contrast with those reported from soils of temperate zone where the DCB-Al_2O_3 content are either equal or only slightly higher than the oxalate-Al_2O_3 values (Blume and Schwertmann 1969, McKeague et al. 1971).

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