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Soil mineralogical characterization of selected carmine alfisols and plinthic inceptisols of Funtua, Nigeria

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ABSTRACT

This study aimed to characterize the mineralogical properties of soils formed over a basement complex parent material in the Northern Guinea Savanna agro-ecology of Nigeria. The selected study site was in Funtua, Funtua Local Government Area of Katsina State, Nigeria. Soil boundaries were delineated, and three soil individuals were identified, namely; Soil-map-unit-red-deep (SMURD) which covered extensive part of the study area occupying 1755.17 ha (66.50 %), soil-map-unit-plinthic-shallow-1 (SMUPS1) occupying 708.70 ha (26.85 %), and soil-map-unit-plinthic-shallow-2 (SMUPS2) occupying 175.60 ha (6.65 %). On each soil individual, a pedon was sited, described, and sampled from genetic horizons. Soil samples collected were prepared and subjected to laboratory mineralogical analysis with the employment of x-ray diffractometer to determine the dominant clay-sized minerals present in the soils. Evaluation of the soil individuals indicate SMURD as very deep (>150 cm) and well-drained; SMUPS1 was shallow (25 - 50 cm) well-drained, and SMUPS2 was well-drained and had a moderate depth of soil materials (71 - 80 cm). It was observed that the soil individuals had mixed mineralogy, which was associated with different rock types and minerals constituting the Basement Complex. The soils were formed under uniform climatic conditions and expected to have undergone a similar rate of weathering. The wide variation in mineral composition of the soils as was attributed to the basement complex characteristics however gave two dominant clay-sized minerals: Kaolinites (and its polymorphs - dickite, clinochrysotile, greenalite) and zeolites.

1.0 Introduction

Identifying minerals is the first step in the mineral analysis. Sometimes, one single analytical method is sufficient to accomplish the job, and sometimes, several analytical techniques have to be employed (Deng *et al.*, 2009). Among commonly-used methods, X-ray diffraction (XRD) has proven to be indispensable (Deng *et al.*, 2009). However, Gold *et al.* (1983) opined that the use of total chemical composition to estimate mineral abundances is a common practice within the basement complex. Kamau (2013) further opined that a comprehensive knowledge of soil mineralogy in Africa is lacking due to poor and incomplete coordinated scientific investigations coupled with the limitations in the traditional analytical tech-

niques. X-ray diffraction spectroscopy (XRD) is a promising method, which directly determines soil mineral composition, but little research has been carried out on this as a tool for quantitative prediction of soil functional properties (Kamau, 2013).

Basement complex is a complex (complicated) rock formed by having two or more different rock types that fixed together (McCurry, 1976) as part of the earth's crust formed of hard igneous or metamorphic rock that lies beneath the soil. The area under basement complex rocks in Nigeria is considerably large, covering over 50 % of total land area, and mostly within Northern Guinea Savanna of the country (Olaniyan *et al.*, 2010). Basement complex as

a soil parent material vary in many characteristics (Brady and Weil, 2013) and are variable both in mineral assemblage and response to soil-forming factors (Maniyunda, 2012). Soil types are influenced broadly by the mineralogical architecture of parent materials as their chemical composition determines the nature of soil reactions and their attendant fertility. These soil mineral types influence their potential for agricultural and non-agricultural use. The soils of the study area formed under a climate (high temperature and moderate rainfalls) that results in deep and shallow weathered soils. The intense weathering causes these soils to be high in clay-sized fractions as corroborated by Niranjane *et al.* (2005) that quartz, its polymorphs, and goethite were additional minerals observed in clay fractions.

X-ray diffraction studies within the basement complex of the Northern Guinea Savanna have shown the presence of significant quantities of amorphous materials, most probably of organic nature as a result of poor crystalline patterns on the diffractogram of pellets analyzed. Moormann *et al.* (1975), Ojanuga (1975), Esu (1987) and Maniyunda (2012) reported a kaolinite dominated clay fraction that has directly influenced the CEC of the soils. They attributed kaolinite dominance to weathering intensity of the soils, concerning its humid climate. Mineralogy is a soil functional property with the potential for predicting soil fertility and by extension, other soil properties (e.g., physical) for both agricultural and other land-use types. It is also used by several classification systems (e.g., USDA Soil Taxonomy)

in recognizing and naming different soil types. Thus, this study aimed to characterize the mineralogical properties of soils formed within the basement complex parent material of the Northern Guinea Savanna of Nigeria.

2.0 Materials and Methods

2.1 The study area

The study area lies between $11^{\circ}25'N$ to $11^{\circ}34'N$ and $7^{\circ}16'E$ to $7^{\circ}22'E$, located in Funtua, Funtua Local Government Area (LGA) of Katsina State, Nigeria. It is bordered by Faskari LGA to the north, Bakori and Danja LGAs to the east and Dandume LGA to the west (Fig. 1). The area has land coverage of 2 639.47 ha.

Geology and Climate

The study area and the central parts are underlain by crystalline rocks of basement complex, (Katsina Diary, 1989). The selected study area has three geological formation types, namely; the migmatite, granite gneiss, and undifferentiated schist. The undifferentiated schist has a limited occurrence. The climate of the study area is typical of that of the Northern Guinea Savanna of Nigeria. It is characterized by a long dry season and a shorter but very conspicuous wet season. It has total annual rainfall figures ranging from 800 mm to 1000 mm. The mean monthly maximum range of temperature was between $28.70^{\circ}C$ and $35.40^{\circ}C$; while the minimum range between $16.89^{\circ}C$ and $32.70^{\circ}C$ (Abaje *et al.*, 2016). Figures 2 and 3 contain long-term (1964-2013) rainfall and temperature data of the study area.

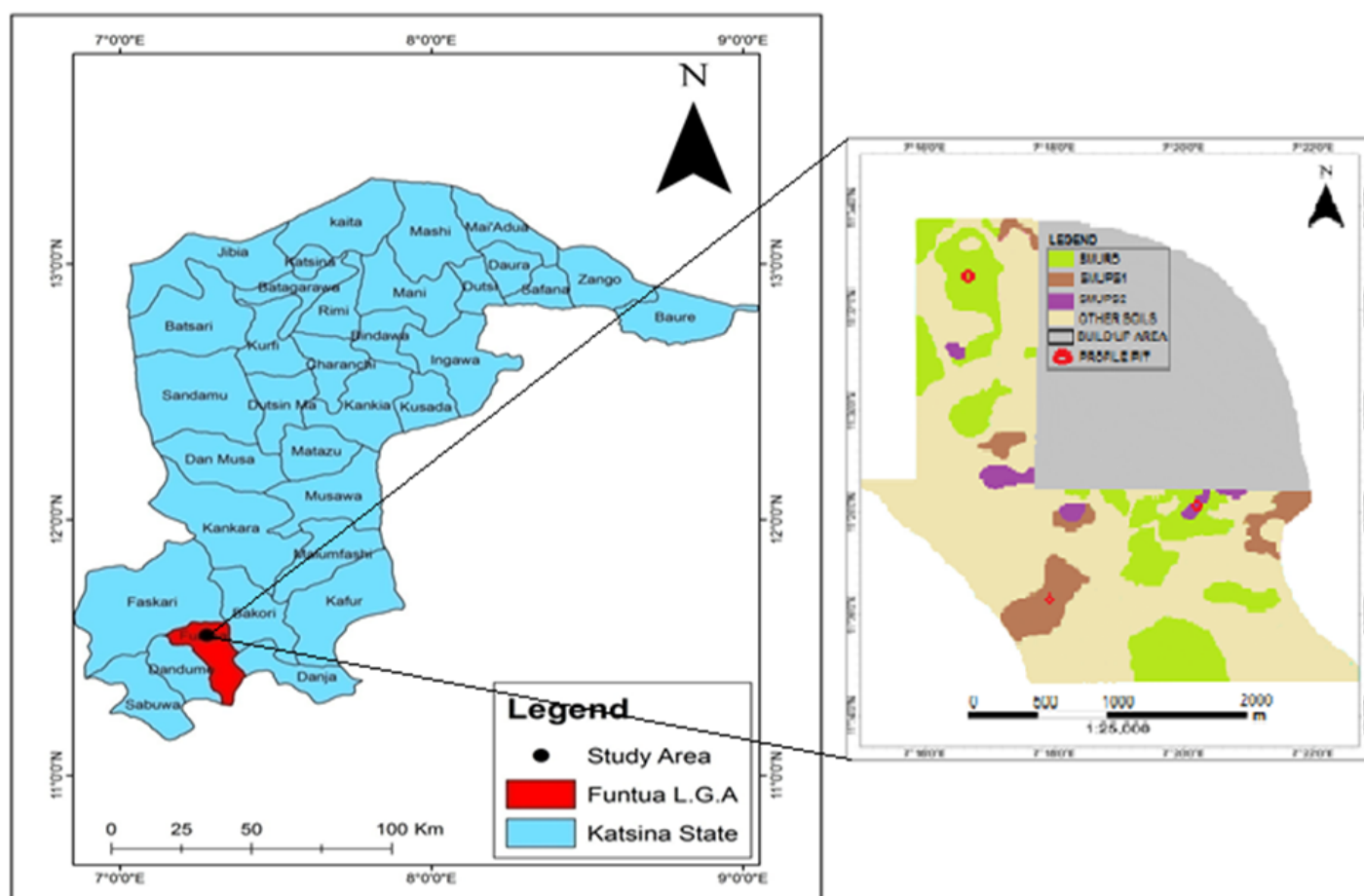


Figure 1 Location map of the study area

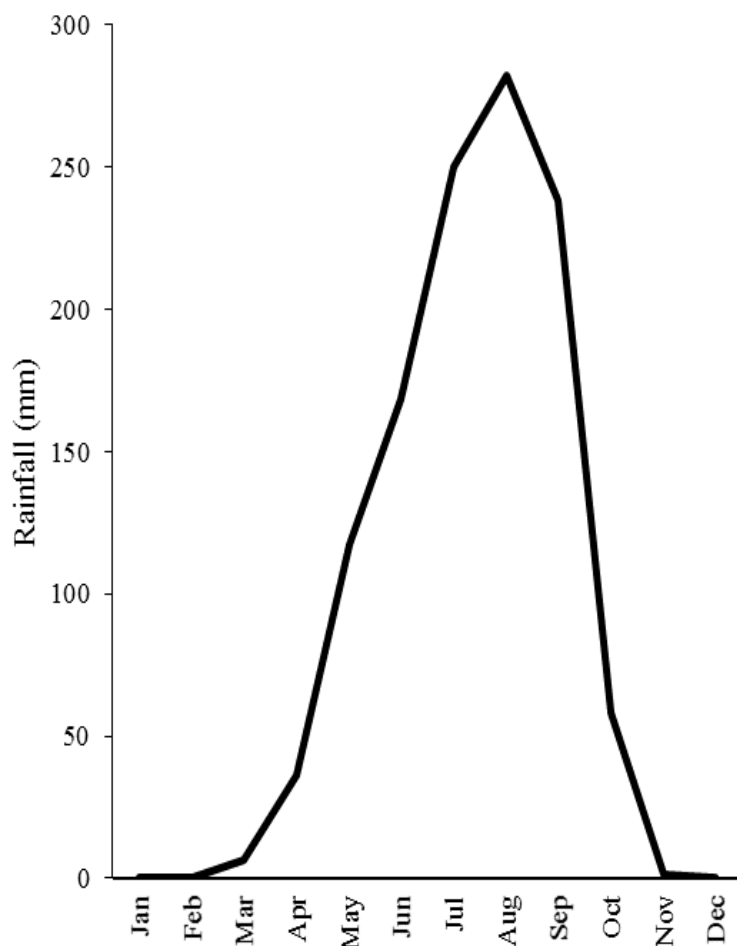


Figure 2: Long-term (1964-2013) rainfall data of the study area

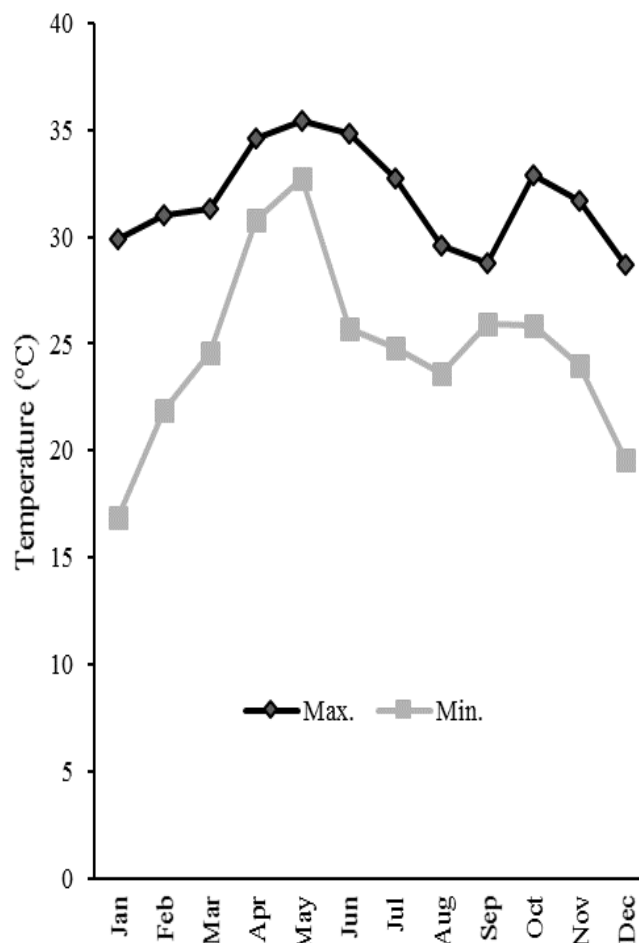


Figure 3: Long-term (1964-2013) temperature data of the study area

2.2 Method of sample collection

Before sample collection, a reconnaissance soil survey was carried out in the study area. This was undertaken to obtain preliminary information as well as the actual land area that was studied (2 639.47 ha); thus, the study enabled for soil mapping. Soil mapping procedures employed was as described by the Soil Science Division Staff (2017). The soil mapping activity identified three soil individuals, namely: Soil-map-unit-red-deep (SMURD), soil-map-unit-plinthic-shallow-1 (SMUPS1), and soil-map-unit-plinthic-shallow-2 (SMUPS2). The concept of the soil mapping or soil individuals was based on soils which shared similar morphological, topographical, and physical characteristics of depth, drainage, the colour of soil matrix, texture, and structure identified. On each soil individual, one soil profile pit was dug, described and sampled from bottom-up, to minimize contamination by falling debris across a horizon's full depth and breadth according to the occurrence of the genetic (natural) horizon for soil mineralogical characterization. Soil samples were air-dried in the laboratory, crushed with porcelain pestle and mortar and sieved to remove materials greater than 2 mm (gravel). The clay mineralogical analysis of the less than 2 mm soil separates carried out.

2.2.1 Mineralogical analysis

The samples were prepared by first removing exchangeable cations, organic matter, and sesquioxides from the samples following the method described by Kunze and Dixon (1986). Particle size separation was determined by the method described by Gee and Or (2002). The gravel content was first removed by direct sieving. Sand, silt, and clay were determined by Bouyoucos hydrometer method, using sodium hexametaphosphate as a dispersant and determining sizes and amount of particles settling by employing progressive time intervals. After obtaining the clay fractions, preparation for an oriented mount for presentation to x-rays continued. About 5 - 10 g of the clay fractions was put into a clean test tube with the aid of spatula. Distilled water was added to dissolve the sample and subsequently placed inside the centrifuge machine. This was allowed to run at 5 rpm for 5 minutes after which it was removed, and the floating material was decanted. Another distilled water was added, mixed thoroughly and again placed inside the centrifuge machine and ran the second time.

This process went on for five times to be sure the individual sample went into a clear suspension. After decanting severally, about 3 - 5 drops of 0.6 % sodium hexametaphosphate solution was added. At this point, a clear suspension of clay was formed above, while the unwanted settled at the bottom of the test tube. A dropper was used to

take some quantity of the suspended clay, saturated with magnesium ions and was applied on a clean labeled glass slide. This was allowed to dry overnight in an oven at 105 °C, and ready for XRD analysis. The x-ray diffraction (XRD) analysis of the clay fraction was done at the Department of Physics, Umaru Musa Yaradua University, Katsina State, Nigeria.

3.0 Results and Discussion

Mineralogy of clay fractions of the soils is discussed below, and their various diffractograms are shown in Figures 4 - 10. X-ray diffractogram of clay fraction revealed three major minerals in surface soils (0 - 9 cm) of SMURD, as shown in Fig. 4. The minerals contained in SMURD as confirmed by the various peaks against corresponding 2Theta Braggs angle were: quartz (peaks: 3.3418 Å, 4.2529 Å, 1.8169 Å, 2.4554 Å, 1.5407 Å), dickite (peaks: 3.5780 Å, 7.1530 Å, 2.2320 Å, 4.1180 Å, 2.5030 Å) and hematite (peaks: 3.6702 Å, 3.6871 Å, 1.6602 Å, 3.7220 Å, 1.4254 Å). The presence and persistence of quartz in the clay-sized minerals could be due to its high resistance to weathering; indicating its inheritance from parent material subjected to intense physical weathering or might have precipitated from Si – supersaturated solutions. The dominance of hematite in surface soils could be responsible for its reddish colour and suggests that the soil is in an advanced stage of weathering. Dickite, also a polymorph of the serpentine subgroup (kaolinite) was found among minerals dominating the soil. Hseu *et al.* (2007) submitted that serpentine minerals are relatively unstable in near-surface conditions and weather quickly into other layer silicates, such as smectite and vermiculite.

At the subsurface soils (50 – 84 cm), hematite (3.6777 Å, 2.7101 Å, 3.5136 Å, 1.4019 Å, 1.4922 Å) and kaolinite (7.1585 Å, 3.5792 Å, 4.3634 Å, 4.1748 Å, 3.8425 Å) dominated (Fig. 5). Kaolinite is one of the most widespread clay minerals in this soil. Appreciable amount of orthoclase feldspar - KAlSi_3O_8 (3.3100 Å, 3.2500 Å, 3.4700 Å, 4.2600 Å, 3.9700 Å) was found at this depth - a member of alkali feldspar which is an excellent source of K in which its relative ease of weathering had contributed to CEC of the soil. At the lower subsurface soils (84 – 200 cm), kaolinite (3.5809 Å, 7.1697 Å, 2.3867 Å, 2.3409 Å, 2.2951 Å) and anatase (3.5014 Å, 1.8855 Å, 2.3575 Å, 1.6601 Å, 1.6868 Å) dominated (Fig. 6). Like quartz, anatase is resistant to weathering; it occurs practically undecomposed in soil (Brookins, 1988). It has low mobility under almost all environmental conditions, mainly due to the high stability of the insoluble oxide TiO_2 , thus considered to be directly derived from the parent material.

X-ray diffractogram of clay fraction revealed three major minerals in surface soils (0 - 31 cm) of soil mapping unit SMUPS1, as shown in Fig. 7. The minerals contained in SMUPS1 as confirmed by the various peaks against corresponding 2Theta Braggs angle were: birnessite (peaks: 7.1384 Å, 3.5692 Å, 2.5191 Å, 2.4236 Å, 2.4315 Å, 1.8673 Å), groutite (peaks: 4.1883 Å, 2.3681 Å, 2.8026 Å, 2.6668 Å, 1.6919 Å, 1.6028 Å) and pyrophyllite (peaks: 4.4571 Å, 9.3330 Å, 4.1598 Å, 3.1110 Å, 4.3164 Å, 4.2181 Å). Birnessite, a phyllosilicate contains a high proportion of manganese (Mn) which might have influenced the enrichment of Mn in this soil mapping unit. Manganese was next to iron in abundance among the soil micronutrients. Its pigmenting effect was low as it occurs in the coarsely dispersed form (plinthite).

The birnessite might have originated as a product of metamorphism from the parent material (basement complex) and may tend to weather to other minerals with time. Its abundance in this soil implies the soil is less weathered as bolstered by the shallow nature of the soil unit; hence their classification as inceptisols. The moderate weathering age of the soil also gave way for the dominance of groutite (diaspore) coupled with the characteristic adhesive property of pyrophyllite which helped in the buildup of plinthic stone lines, Fe-Mn concretions in the soil unit and ultimately high excavation difficulty. Velde (1985) submitted that pyrophyllite does not commonly occur in parent material of low diagenetic or metamorphic grade; but, it is found as a product of high-grade metamorphism through the kaolinite and quartz reaction. Therefore, the dominance of kaolinite alongside analcite might have led to a considerable amount of pyrophyllite that has contributed to the soil's improved consistency.

At the subsurface soils (31 – 50 cm), clay fraction (Fig. 8) was dominated by analcite (peaks: 4.2900 Å, 6.8300 Å, 2.9100 Å, 9.2600 Å, 3.4200 Å) and kaolinite (7.1720 Å, 3.5854 Å, 2.3865 Å, 2.3451 Å, 4.3504 Å). Analcite (a form of zeolite) and kaolinite might be the weathered product of feldspars inherent in the basement complex parent material and increased in relative abundance with soil age. Their dominance also suggests that the soil had been strongly weathered because it was present (analcite) in the clay fraction of soils which were subject to moderate weathering.

X-ray diffractogram of clay fraction revealed three major minerals in surface soils (0 - 13 cm) of soil mapping unit SMUPS2, as shown in Fig. 9. The minerals contained in SMUPS2 as confirmed by the various peaks against corresponding 2Theta Braggs angle were: Zeolite (peaks: 11.8394 Å, 4.4749 Å, 3.9419 Å, 4.1640 Å, 5.9197 Å, 2.5836 Å), kaolinite (peaks: 7.1800 Å, 3.5800 Å, 1.4880 Å, 2.3410 Å, 2.5650 Å) and clinochrysotile (peaks: 7.3500 Å, 3.6600 Å, 4.5400 Å, 2.4600 Å, 1.5370 Å). The occurrence of zeolite in this soil unit appears to be primarily inherited from the parent material rather than of pedogenic process and due to its capacity to absorb water and selectively adsorb ions had contributed to the buildup of plinthite in the soil mapping unit; also, the predominance of clinochrysotile had influenced the formation of Fe-Mg concretions characterizing the soils. The occurrence of kaolinite and clinochrysotile imply the soil was not recently formed and attributed to the soils been well-drained.

At the subsurface soils (31 – 54 cm), clay fraction (Fig. 10) was dominated by dickite (peaks: 7.1588 Å, 2.3219 Å, 2.3281 Å, 3.5794 Å, 4.1230 Å) and muscovite (3.3311 Å, 10.0232 Å, 1.9977 Å, 5.0003 Å, 2.4980 Å). The occurrence of the muscovite mineral is thought to have been produced slowly from weathering of the parent rock. The relative abundance of muscovite found in the clay fractions of this soil mapping unit was attributed to weathering of mica present in the initial material as muscovite formed parts of the residual minerals found in the soils. Dickite, on the other hand, might be expected to develop pedogenically from solutions high in Si and Al. The formation of a zeolite (at the surface soils) in the clay fraction during the genesis of this soil mapping unit (Alfisols) as developed in the basement complex parent material may be attributed to minerals initially present in the sand fraction. Muggler *et al.* (2007) reported that the presence of the product of weathered minerals such as kaolinite and its variant forms (serpentine group - clinochrysotile) indicates advanced weathering.

Horizon	Depth (cm)	
Ap	0-9	Sample ID: UNYU- Katsina 151, Sample name: FIP1-1, Temp: 25.0°C Date: 01/10/18 15:24 Step : 0.030° Integration Time: 0.150 sec Range: 5.000 - 70.000° Cont. Scan Rate: 12.000 [°/min] Vert. Scale Unit: [CPS] Horz. Scale Unit: [deg] 01-085-0795 : Silicon Oxide[Quartz, syn]/Si O2 00-010-0430 : Aluminum Silicate Hydroxide[Diokite]/Al2 Si2 O5 (0 H)4 01-086-1355 : Iron Oxide [Hematite high]/Fe2 O3
<i>Fig. 4: X-ray diffractograms of the clay-sized particle of SMURD 0-9 cm</i>		
B1	50-84	Sample ID: UNYU- Katsina 151, Sample name: FIP1-1, Temp: 25.0°C Date: 01/10/18 14:35 Step : 0.030° Integration Time: 0.150 sec Range: 5.000 - 70.000° Cont. Scan Rate: 12.000 [°/min] Vert. Scale Unit: [CPS] Horz. Scale Unit: [deg] 00-009-0171 : Potassium Aluminum Silicate Oxide/K Al Si2 O8 01-089-6538 : Aluminum Silicate Hydroxide[Kaolinite]/Al2 (Si2 O5) (0 H)4 01-086-1355 : Iron Oxide [Hematite high]/Fe2 O3
<i>Fig. 5: X-ray diffractograms of the clay-sized particle of SMURD 50-84 cm</i>		
B2	84-200	Sample ID: UNYU- Katsina 151, Sample name: FIP1-4, Temp: 25.0°C Date: 01/10/18 15:32 Step : 0.030° Integration Time: 0.150 sec Range: 5.000 - 70.000° Cont. Scan Rate: 12.000 [°/min] Vert. Scale Unit: [CPS] Horz. Scale Unit: [deg] 00-029-1879 : Propiomazine hydrochloride/C20 H24 N2 O S · H Cl 00-058-2028 : Aluminum Silicate Hydroxide[Kaolinite-1A]/Al2 Si2 O5 (0 H)4 01-070-6826 : Titanium Oxide[Anatase, syn]/Ti O2
<i>Fig. 6: X-ray diffractograms of the clay-sized particle of SMURD 84-200 cm</i>		

Horizon	Depth (cm)	XRD Diffractograms of clay samples for soil mapping unit SMUPS1
Ap	0-31	Sample ID: UNYU- Katsina 151, Sample name: F4P1-1, Temp: 25.0°C Date: 01/10/18 13:51 Step : 0.030° Integration Time: 0.180 sec Range: 5.000 - 70.000° Cont. Scan Rate: 10.000 [°/min] Vert. Scale Unit: [CPS] Horz. Scale Unit: [deg] 01-072-7297 : Sodium Manganese Oxide Hydrate[Birnessite, syn]/Na_{0.58}Mn₂O₄ (H₂O)1.5 01-088-0648 : Manganese Oxide Hydroxide[Grothite₈-Mn O (0 H)]/Mn O (0 H) 01-073-4051 : Aluminum Silicate[Pyrophyllite 1A dehydroxylatedTetraAluminum octasilicon oxide]/Al₄Si₈O₂₂
		<i>Fig. 7 X-ray diffractograms of clay-sized particle of SMUPS1 0-31 cm</i>
CBt	31-50	Sample ID: UNYU- Katsina 151, Sample name: F4P1-2, Temp: 25.0°C Date: 01/10/18 14:53 Step : 0.030° Integration Time: 0.150 sec Range: 5.000 - 70.000° Cont. Scan Rate: 12.000 [°/min] Vert. Scale Unit: [CPS] Horz. Scale Unit: [deg] 00-049-0919 : Sodium Aluminum Silicate Hydrate[8LZ-276]/Na_{1.46}Al₁₂Si_{7.67}O_{19.07} · x H₂O 00-038-0055 : Potassium Aluminum Hydrogen Phosphate/K Al H (P₃ O₁₀) 00-058-2004 : Aluminum Silicate Hydroxide[Kaolinite-1A]/Al₂Si₂O₅ (0 H)₄
		<i>Fig. 8 X-ray diffractograms of the clay-sized particle of SMUPS1 31-50 cm</i>

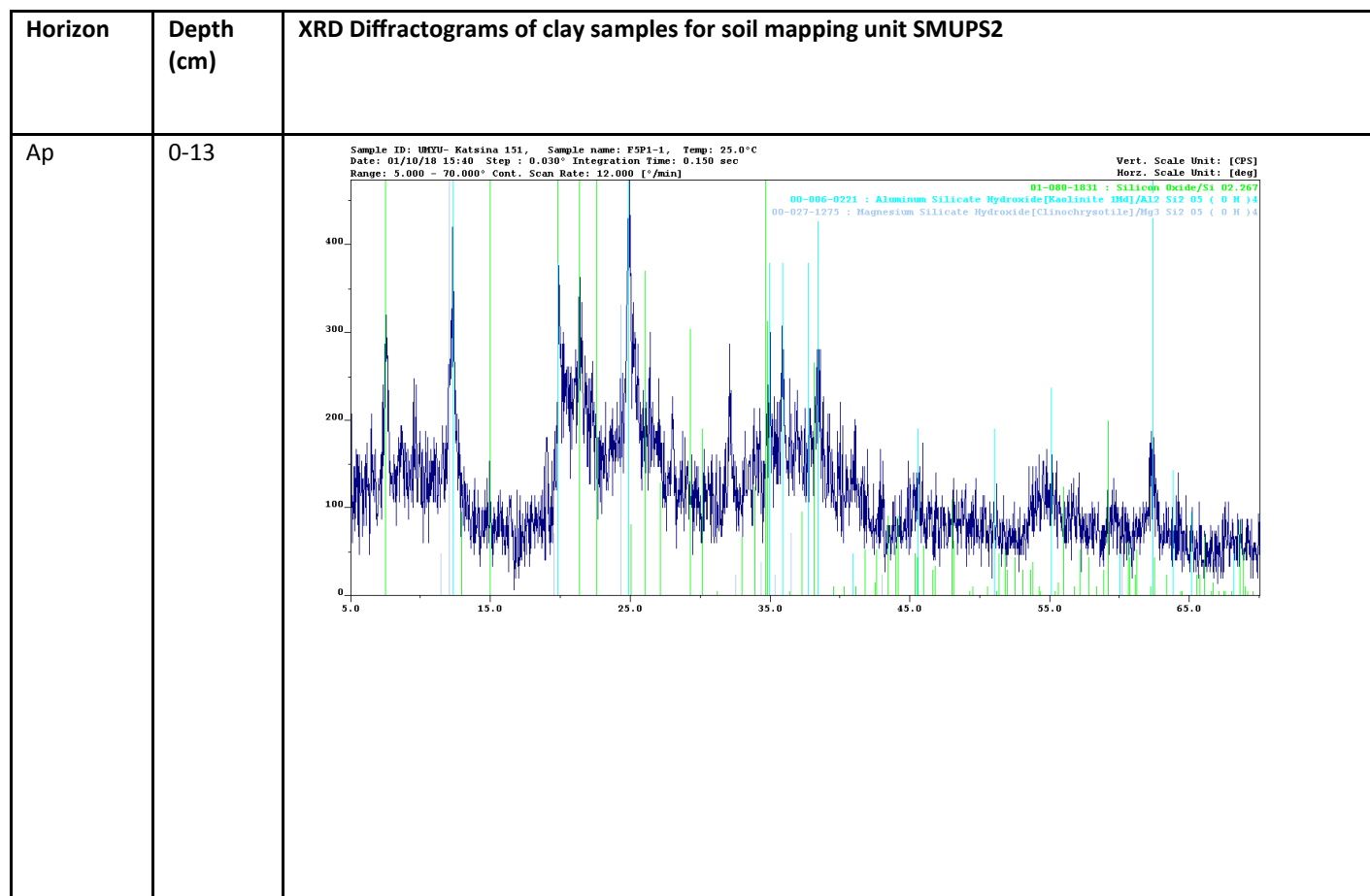


Fig. 9 X-ray diffractograms of the clay-sized particle of SMUPS2 0-13 cm

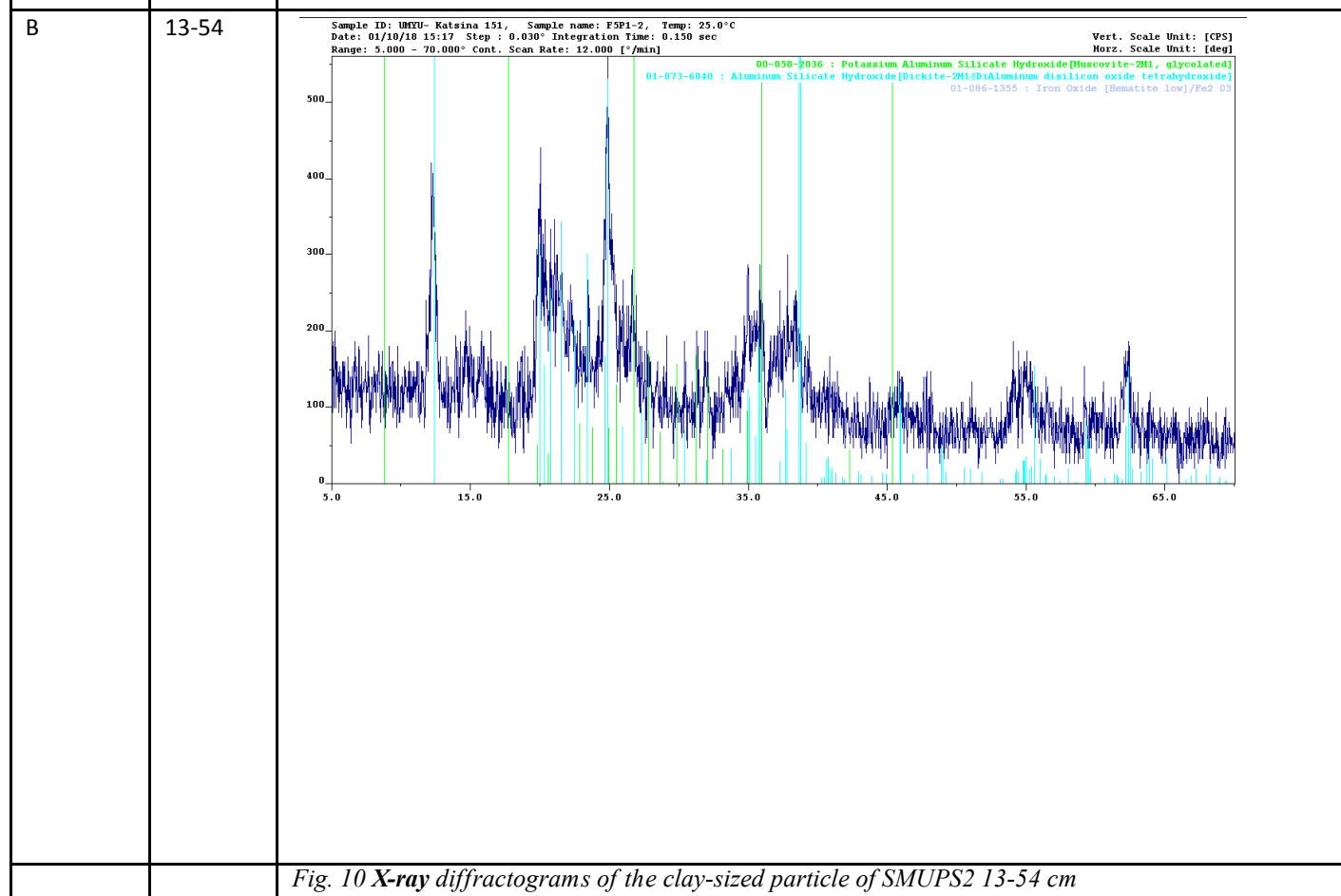


Fig. 10 X-ray diffractograms of the clay-sized particle of SMUPS2 13-54 cm

4.0 Conclusion

Composition and extent of weathering of the basement complex caused variation in the mineralogy of the soils as reflected in their XRD diffractograms of clay samples. The soil individuals have similar mineralogy which was associated with the minerals constituting the basement complex parent material. The same climatic condition of the study area also contributed to the similarity in extent of weathering and types of minerals identified. The wide variation in mineral composition of SMURD, SMUPS1, and SMUPS2 influenced their mineralogical classification to be mixed, mineralogical class. Hematite, kaolinite, quartz, and zeolite dominated the mineralogy of clay fraction of the soils. However, the occurrence of quartz and zeolite even at the subsoils and as parts of clay-sized fraction, though attributed to inheritance from the parent material indicates the soils have been formed mostly in-situ and highly weathered. One could also infer given the dominance of hematite and anatase at lower depth in SMURD as contributor to the red soil colouration, and an indication of an intensively weathered soils that can be managed through addition of organic manure to improve the soil's texture, structure, and acidity. The predominance of kaolinite (and its polymorphs) in SMUPS1 and SMUPS2 with depth implies dominance of low activity clay and inturn low fertile soils. Based on the observed minerals, SMURD, SMUPS1, and SMUPS2 cannot sustain crop production on a long-term basis under continuous crop production. Therefore, high-quality organic residues (such as crop and animal wastes) have to be substantially added through appropriate practice for agricultural use.

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