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Mineralogy and Geochemistry of Soil in Ondo State Bitumen Environment, Nigeria

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Abstract: The geochemistry and bulk mineralogy of surface (0-30 cm) and subsurface (60-90 cm) soil samples in the bitumen environment of Ondo State Nigeria was studied using X-Ray Florescence and X-Ray Diffraction techniques. The bulk minerals were qualitatively studied with EVA software and quantified using Rietveld refinement method. The mineralogy was found to be essentially quartz, kaolinite and feldspars with respective abundances of 83.76-93.76%, 4.38-10.60% and 1.86-3.82%. The geochemistry reveals that the order of abundance of major oxides is $SiO_2 > Al_2O_3 > Fe_2O_3 > TiO_2 \geq K_2O > MgO > CaO > Na_2O \geq P_2O_5 > MnO > Cr_2O_3$. Only Fe_2O_3 shows a little leaching into the subsurface layer while TiO_2 was relatively stable between the two layers. The high quartz, low kaolinite, low feldspar and low gibbsite content may indicate moderate to high degree of weathering; higher contents of silica and alumina as well as alkalis and calcium in the surface layer may equally suggest an aeolian additions and/or relative enrichment of minerals during weathering and nutrient cycling by vegetation.

Keywords: Mineralogy, Geochemistry, Soil, Bitumen, Environment, XRF, XRD

1. Introduction

Southwestern Nigeria lies in the humid tropics and its geology may be broadly divided into basement complex rocks either igneous or metamorphic which are Precambrian (570 M.y.) in age. These occupy most of the northern part of the region. Whereas, the sedimentary rocks that are cretaceous (136 M.y.) to recent in age [1] occupy the southern part. The concentrations of trace and major elements in residual soils depend mainly upon the bedrock type from which the soil parent material is derived [2-4] and pedogenic processes acting upon it [5-8]. The influence of the parent material on trace and major elements tends to decrease with soil development [9]. The most important aspects of pedogenesis relating to the behavior of trace and major elements are those affecting (i) the release of metals from the parent material by weathering, (ii) the translocation

and accumulation of sorbents such as clay minerals, oxides and organic matter. These are controlled by leaching, eluviation, salinization, calcification, podzolization, ferralitization, gleying and organic matter accumulation [10].

Under tropical and sub-tropical climate, geochemical weathering is intense and consequently mineral solubility and elemental redistribution often present different kinds of scenarios [11-12]. Mineralogical analysis may provide information on the relative fate of pollutants and plant nutrients as well as soil physicochemical properties. The understanding of soil mineralogy is therefore recognized as very important in influencing the retention capacity, bioavailability of heavy metals and their mobility in specific environments (soil chemistry and ion exchange reactions) [13-15]. Mineralogy has also been related to the

understanding of forest types and their biogeochemistry [16].

Mineralogy and geochemistry are important soil information governing many physicochemical processes in soil [16] and the end product of physicochemical processes is generally mineralization depending on prevailing climatic conditions [17]. The interrelationships between some important minerals and their elemental status are well studied [9, 18-22]. This is why soil mineralogy is sometimes associated with elemental toxicities and deficiencies of trace and major elements [23-24].

The exploitation of bitumen has attracted various criticisms as a result of environmental pollution that usually accompanies its production. Among the array of possible environmental pollutants are heavy metals and metalloids. The behavior of heavy metals and metalloids in the environment depends on various soil conditions including the physicochemical and mineralogical compositions of soil. The soil conditions have direct effect on the behavior of heavy metals and metalloids either as a pollutant or nutrients. It is therefore beneficial to understand the geochemistry and mineralogical composition of soil. The present research gives the detailed geochemical and bulk mineralogical composition of soil in the bitumen belt of southwestern Nigeria, Ondo State, in order to elucidate the likely factors that may control the behavior of metals and metalloids in such an environment.

2. Materials and Methods

Sampling and Sample Treatment

The Southern part of Ondo State lying between 6°15'N-5°10'E and 7°00'N-4°20'E, wherein lies the bitumen belt, was divided into regular grids of 12.5 X 12 Km^2 and in each of the grid, a soil depth of 0-30 cm and 60-90 cm was sampled in five locations and pooled to represent a composite field sample that represented a density of 1 sample per 150 Km^2 (Figure 1). All samples were georeferenced using Geographic Positioning System (GPS) [25]. The homogeneity of sample distribution in the study area was statistically calculated using Morisita Index 59. This is an estimation of degree of spatial randomness (clustering) of sampling plan. A weighted correlation coefficient, mostly 1, is used to analyze departures of sampling plan from spatial randomness. Morisita Index-MOR 59 was used to do this estimate thus [26]:

$$I = Q \frac{\sum_{i=1}^{Q} ni(ni - 1)}{N(N - 1)}$$

Where Q=number of cells, ni=number of samples in every cell, N=total number of samples

Each sample was air dried in the open laboratory, picked, disaggregated using mortar and pestle, sieved through 2 mm nylon mesh (British Standard) and stored in poly propylene bottles prior to analysis [27].
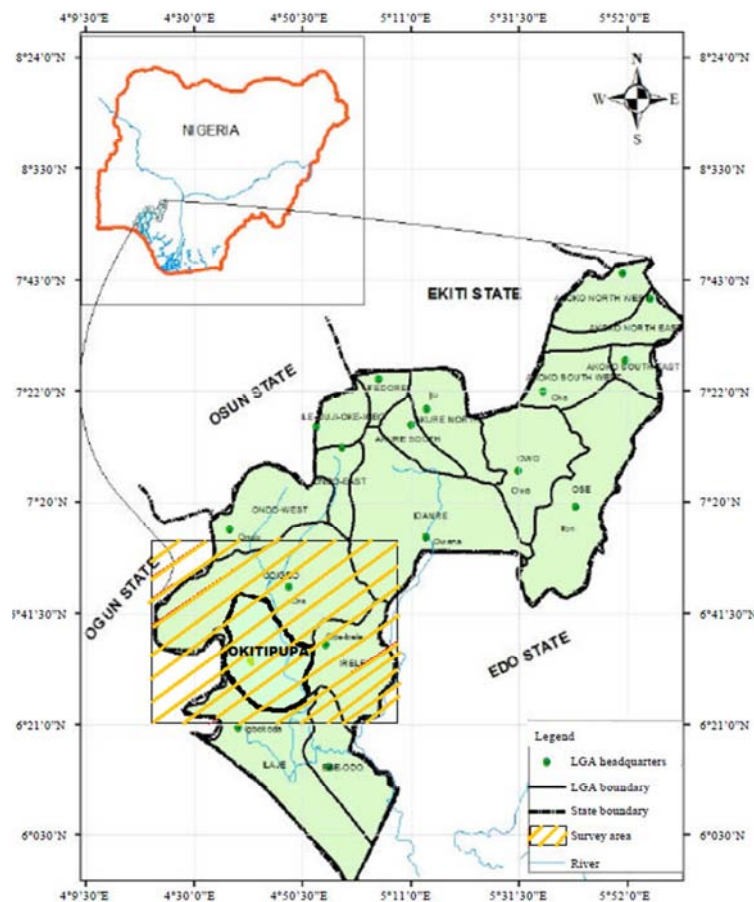

Figure 1. Map Showing the Geographically Referenced Sampling Points within Study Area.

Analysis of Physicochemical Properties of Soil

The pH of 1:2 soil: water and 1:2 soil: $CaCl_2$ solution was measured using a pH glass electrode system model SETRAPHS 25 [28]. Similarly, the conductivity [29] and Electrode Potential [30] of 1:2 soil: water solution was equally measured using a pH glass electrode system. Soil particle size analysis was done using by hydrometer method [31] while analysis of organic matter/soil carbon content of the soil was obtained by wet oxidation method [32]. Soil exchangeable bases was extracted with 1M NH_4OAc (pH 7.0) and the extract analyzed for calcium, magnesium, potassium and sodium. Calcium and magnesium in the extract were analyzed using atomic absorption spectrophotometry while potassium and sodium by flame photometry [33]. Exchangeable acidity was extracted by 0.1 M $BaCl_2$ solution and the extract was titrated with 0.025M NaOH solution using glass electrode pH meter until at pH of 7.8 [34]. Effective cation exchange capacity was obtained by summation [35].

Analysis of Soil Major Oxides (Fused Bead Method)

Exactly 1.0 g. powdered sample was weighed and roasted at 1000°C for "Loss on Ignition (LOI)" determination. An aliquot of 0.50 g was weighed into a platinum crucible and fused with 6.50 g of lithium borate flux (a mixture of 50% lithium tetra-borate and 50% lithium meta-borate) until molten. The molten material was quantitatively transferred to a platinum casting dish and quenched to produce a glass disk that was used to analyse SiO_2, Al_2O_3, CaO, K_2O, P_2O_5, TiO_2, Fe_2O_3, MnO_2, Na_2O and MgO_2 using PANalytical PW-2400 Wavelength Dispersive XRF Spectrometer (at Biotron Research Centre, Western University, London, Ontario, Canada). The net peak intensities were corrected for background, spectral interferences and inter-element matrix corrections. The concentrations were obtained against the calibrations derived from 16-20 international standard reference materials. Based on the quality assurance samples, the analytical errors for major oxides are from 2% to 5% depending on the concentrations [36].

Qualitative and Quantitative Soil Mineralogical Analysis

5 g of air dried soil sample (<2 mm) was ground into fine powder in an agate mortar. An aliquot of the fine powder was deposited on a slide using a sample holder. Few drops of ethanol were added to produce a saturated paste in an etched surface region of the slide. Excess sample smear was removed with a wiper. The slide and content was mounted in the sample holder of a Rigaku DMAX powder X-ray diffractometer (at the Earth Sciences Department, Western University, London, Ontario, Canada) working in θ-2θ geometry with a horizontal goniometer using an incident beam graphite

monochromator and a scintillation counter detector. A routine qualitative scan pattern was collected by focusing CoKα beam on the sample using a 2θ angle step size of 0.02° and a dwelling time of 0.04° per 2θ step scanning between 5° 2θ and 115° 2θ. The experimental data obtained were processed with Diffrac[Plus] EVA Software for qualitative identification of minerals using PDF-4 database of International Centre for Crystallographic Data (ICCD). The identified minerals were quantified by Rietveld method [37] using TOPAS software.

3. Results and Discussion

Morisita Index-MOR 59

Where Q=number of cells=32 (accessible cells), ni=number of samples in every cell=5, N=total number of samples=160. A homogenous process will show a Morisita Index fluctuating around 1 for all scales considered, because of the homogenous distribution of the samples within the boxes at every scale. With the above information the value of Morisita Index calculated is 0.81 showing that the sampling was fairly homogenous.

Some Physicochemical Properties

The physicochemical properties of the soils obtained in the study are shown in Tables 1 and 2 respectively for samples from the surface and subsurface layers. The data shows the soils are slightly acidic with the subsurface soil being more acidic. Both surface and subsurface layers are non-saline and anoxic; the surface soil is principally sandy clay loam while the subsurface soil is clay loam. The organic matter content is generally very low; however, higher values were recorded for the surface soils. The low organic matter content could be due to rapid or high mineralization in the area. Igwe *et al.* (2004) [23] has noted that even in reduced conditions (as in this case), mineralization of organic matter will proceed as rapidly as in aerated conditions provided the mean temperature exceeds 32°C which is often the case in the area under investigation. The values of exchangeable cations (Na, K, Mg and Ca) and that of exchangeable acidity (EA) are very low, with higher values for Ca and Mg in both surface and subsurface soils. The low levels of these exchangeable cations have long been recognized to be typical of West African soils [38] and it was attributed to high leaching process due to intense rainfall and the type of clay minerals present in the soil [23, 38]. Soils in the sub-region are dominated by non-expansive clay minerals with low CEC. Subsurface soils are having lower values compared with surface soils in all these properties. These soil conditions will favour rapid leaching of metals and metalloids with attendant possible underground water infiltration.

Table 1. *Results of Physicochemical Properties of Soil in the Surface Layer of Study Area.*

	n	Mean	Standard Error	Median	Standard Deviation	Sample Variance	Kurtosis	Skewness	Range	Minimum	Maximum
PHw	19	5.85	0.15	5.8	0.69	0.48	-0.67	0.16	2.35	4.87	7.21
pHca	19	5.19	0.13	5.18	0.57	0.33	-0.43	0.35	2.19	4.23	6.41
Cond. (µS/cm)	19	80.77	11.06	66	48.24	2327.85	3.23	1.52	199.1	26.45	225.55
Eh (mV)	19	-105.47	9.86	-99.5	42.98	1847.90	-1.00	0.37	139	-165.5	-26.5
SOM (%)	19	3.35	0.11	3.2	0.51	0.26	1.70	1.23	1.99	2.70	4.68
Sand (%)	19	60.60	2.87	62.26	12.54	157.45	5.28	-1.84	58	20.26	78.26
Clay (%)	19	26.24	1.21	27.24	5.30	28.11	1.22	0.38	24	15.24	39.24
Silt (%)	19	13.16	2.69	10.5	11.74	138.06	12.26	3.26	53	4.5	57.5
Na Exchang. (cmol(+)/kg)	19	0.31	0.02	0.29	0.12	0.02	7.65	2.44	0.57	0.19	0.76
K Exchang. (cmol(+)/kg)	19	0.14	0.01	0.14	0.05	0.00	3.76	1.04	0.25	0.04	0.29
Mg Exchang. (cmol(+)/kg)	19	0.79	0.13	0.54	0.57	0.33	2.56	1.67	2.16	0.25	2.41
Ca Exchang. (cmol(+)/kg)	19	1.14	0.13	0.97	0.57	0.33	5.97	2.12	2.63	0.42	3.04
Sum Exch. Bases	19	2.39	0.17	2.09	0.74	0.55	-0.94	0.66	2.26	1.52	3.78
E.A (cmol(+)/kg)	19	1.38	0.16	1.43	0.70	0.50	-0.81	0.05	2.47	0.23	2.69
ECEC	19	3.78	0.25	3.28	1.09	1.20	-1.24	0.30	3.56	2.17	5.73

Table 2. *Results of Physicochemical Properties of Soil in the Subsurface Layer of Study Area.*

		Mean	Standard Error	Median	Standard Deviation	Sample Variance	Kurtosis	Skewness	Range	Minimum	Maximum
PHw	19	5.24	0.17	5.08	0.74	0.54	2.53	0.87	3.51	3.77	7.28
PHca	19	4.61	0.19	4.30	0.84	0.70	1.61	0.70	3.854	2.92	6.78
Cond. (µS/cm)	19	36.43	6.31	25.9	27.52	757.30	2.43	1.75	100.35	12.4	112.75
Eh (mV)	19	-109.80	9.23	-121.86	40.25	1619.94	2.48	1.53	151.94	-152.11	-0.17
SOM (%)	19	1.52	0.07	1.54	0.29	0.09	2.38	-0.91	1.34	0.71	2.05
Sand (%)	19	45.59	3.37	44.72	14.68	215.55	0.29	0.04	59	16.72	75.72
Clay (%)	19	44.54	2.69	45.28	11.71	137.09	0.35	-0.12	45	21.28	66.28
Silt (%)	19	9.87	1.77	8.5	7.73	59.77	2.86	1.61	31	1	32
Na Exchang. (cmol(+)/kg)	19	0.17	0.01	0.16	0.06	0.00	-0.08	0.90	0.19	0.10	0.30
K Exchang. (cmol(+)/kg)	19	0.12	0.01	0.12	0.05	0.00	-0.75	0.41	0.16	0.05	0.21
Mg Exchang. (cmol(+)/kg)	19	0.56	0.06	0.58	0.28	0.08	-0.51	-0.03	1.03	0.05	1.09
Ca Exchang. (cmol(+)/kg)	19	1.03	0.12	0.98	0.50	0.26	-0.66	0.47	1.74	0.37	2.11
Sum Exch. Bases	19	1.89	0.14	1.73	0.61	0.37	-0.82	0.36	2.16	0.96	3.12
E.A (cmol(+)/kg)	19	1.47	0.15	1.44	0.64	0.42	2.55	1.14	2.96	0.32	3.28
ECEC	19	3.36	0.23	3.26	1.00	1.00	-0.17	0.15	4.00	1.35	5.35

Soil physical properties temporally and spatially change as a result of natural phenomena and human activities which are dependent on seasonal climatic conditions, management practices, crop development and biological activity [39]. The pedological processes occurred in time series of decades and centuries. It is possible to get eluviation of clay to occur in well drained soils which get high amount of precipitation as in the present study. In such cases, eluviation of clay from surface to the subsurface horizon can lead to differences in textural classes of the surface and subsurface horizon especially the clay content [40]. This may account for the observed variations in the clay content of surface and subsurface layers. The work of Tomasic *et al.* (2012) [41] was very comparable to our present findings of higher clay content in subsurface soil relative to surface soil. This can be attributed to high precipitation that favours rapid eluviation of clay from surface to subsurface soil and hence large variation of clay content between the surface and subsurface soil samples.

In general, it is well documented that soil CEC/exchangeable base cations increases with clay or soil organic matter (SOM) [42] but could be deeply affected by anthropogenic activities, such as fertilization, irrigation and reconstruction of plants in terrestrial ecosystems. This

general observation was not obtained in the present study as there seems to be an inverse relation between clay and organic matter content. The increase in soil organic matter (SOM) would increase the base cations/CEC. Exchangeable base cations and CEC vary a lot with different organic matter fractions, soil particle sizes, soil pH, land use change, cation migration characteristics, the eluviation-illuviation processes, alternative reducing-oxidizing conditions, the selective absorption of cations by plants, and some other pedogenic and anthropogenic conditions. Consequently, SOM build-up usually increases soil fertility by providing essential nutrients, enhancing soil biodiversity and improving soil productivity. It is been argued that the increase in SOM with long-term manure application would be a main pathway for improving exchangeable base cations/CEC in soil [43]. This could improve the surface soil fertility relative to subsurface soil with attendant increase in sum exchangeable in the surface soil. The present study area is a forest soil with little or no tillage that could probably mix up layers of soil and as such, litters of leaves and dead wood could return the exchangeable

bases back into the surface soil [44]. All these could account for the observed inverse relationship that was observed in clay content and SOM between surface and subsurface soil samples in the present study.

Soil Geochemistry and Mineralogy

Considering the geochemical composition of soil samples for both surface and subsurface layers (Tables 3-5), it is evident that the leaching of these major oxides has been very moderate since most soluble and resistant minerals were still abundant in the surface layer relative to subsurface layer (Tables 3 and 4). Only Fe_2O_3 shows a little leaching into the subsurface layer while TiO_2 is relatively stable between surface and subsurface layers. Higher contents of silica and alumina as well as alkalis and calcium in the surface layer may be an indication of aeolian additions or relative enrichment of minerals during weathering and nutrient cycling by vegetation [45-47]. Loss on ignition (LOI) shows a slight increase between the surface and subsurface layers indicating probably that the subsurface layer has more volatile components than the surface layer.

Table 3. *Results of Geochemical Properties (Major Oxides) in the Surface Layer of Study Area.*

Sample	SiO₂	TiO₂	Al₂O₃	Fe₂O₃	MnO	MgO	CaO	K₂O	Na₂O	P₂O₅	Cr₂O₃	L.O.I.	Total
Mean (%)	82.12	0.87	7.98	2.66	0.04	0.23	0.14	0.87	0.14	0.06	0.01	4.75	99.86
Standard Error	1.31	0.06	0.73	0.30	0.01	0.02	0.03	0.30	0.04	0.01	0.00	0.30	0.18
Median	83.32	0.83	7.17	2.37	0.03	0.22	0.07	0.13	0.04	0.05	0.01	4.49	99.79
Mode	-	1.03	-	1.71	0.03	0.21	0.06	0.05	0.04	0.06	0.01	4.38	-
Standard Deviation	5.72	0.25	3.17	1.33	0.02	0.08	0.13	1.33	0.19	0.02	0.01	1.31	0.79
Sample Variance	32.74	0.06	10.03	1.76	0.00	0.01	0.02	1.77	0.04	0.00	0.00	1.72	0.62
Kurtosis	2.15	-0.20	0.56	2.69	2.05	0.45	2.90	1.80	5.00	7.91	19	0.24	5.77
Skewness	-1.43	0.07	0.80	1.51	1.65	0.10	1.82	1.74	2.16	2.33	4.36	0.25	0.28
Range	22.21	0.99	12.1	5.39	0.09	0.33	0.47	4.16	0.72	0.11	0.05	5.5	4.36
Minimum (%)	68.24	0.4	2.5	1.1	0.01	0.05	0.04	0.02	0.02	0.03	0.01	2.12	97.75
Maximum (%)	90.45	1.39	14.6	6.49	0.1	0.38	0.51	4.18	0.74	0.14	0.06	7.62	102.11
Count	19	19	19	19	19	19	19	19	19	19	19	19	19

Table 4. *Results of Geochemical Properties (Major Oxides) in the Subsurface Layer of Study Area.*

Sample	SiO₂	TiO₂	Al₂O₃	Fe₂O₃	MnO	MgO	CaO	K₂O	Na₂O	P₂O₅	Cr₂O₃	L.O.I.	Total
Mean (%)	81.78	0.86	7.72	2.84	0.04	0.20	0.13	0.68	0.07	0.06	0.01	5.34	99.73
Standard Error	1.81	0.07	1.05	0.38	0.00	0.02	0.02	0.20	0.01	0.00	4E-19	0.38	0.06
Median	82.64	0.89	6.14	2.51	0.04	0.22	0.11	0.09	0.03	0.06	0.01	5.17	99.71
Mode	-	1.19	-	3.09	0.05	0.24	0.18	0.04	0.02	0.05	0.01	-	-
Standard Deviation	7.91	0.29	4.58	1.66	0.02	0.08	0.07	0.89	0.06	0.02	2E-18	1.65	0.25
Sample Variance	62.52	0.09	21.00	2.76	0.00	0.01	0.00	0.79	0.00	0.00	3E-36	2.73	0.06
Kurtosis	-1.23	-1.57	-1.10	-0.99	0.52	-0.45	-0.36	0.08	-1.54	-0.55	-2.25	-0.10	-0.68
Skewness	-0.27	-0.08	0.59	0.33	0.75	-0.45	0.64	1.22	0.56	0.20	-1.09	0.47	-0.01
Range	24.01	0.89	14.32	5.23	0.07	0.27	0.24	2.54	0.16	0.06	0	6.34	0.91
Minimum (%)	69.13	0.35	1.96	0.4	0.01	0.04	0.04	0.03	0.01	0.03	0.01	2.7	99.24
Maximum (%)	93.14	1.24	16.28	5.63	0.08	0.31	0.28	2.57	0.17	0.09	0.01	9.04	100.15
Count	19	19	19	19	19	19	19	19	19	19	19	19	19

The order of abundance of the major oxides is $SiO_2 > Al_2O_3 > Fe_2O_3 > TiO_2 \geq K_2O > MgO > CaO > Na_2O \geq P_2O_5 > MnO > Cr_2O_3$ for both surface and subsurface layers. This

order follows the general order of soil found in southern part of Nigeria [48] which has $SiO_2 > Al_2O_3 > Fe_2O_3 > TiO_2$ and the relative position of abundance of other oxides depends

strongly on weatherability of parent materials and vegetation.

Geochemical data can also provide an indication of geochemical elements' mobility during intense or moderate weathering in the area. The silica content is very high in all the soil samples together with alumina, iron oxide, titanium oxide and potassium oxide; this weathering regime has thus reduced the soil to SiO_2-Al_2O_3-TiO_2-K_2O system with small amounts of MgO, CaO and Na_2O. TiO_2 has been shown to exist in soil in crystalline forms that are stable and highly insoluble [10]. Their presence in soil suggests ferritisation process in the soil. It is one of the most abundant, thus suggesting a possible advanced weathering process. The lower the TiO_2 content, the more advanced is the weathering process. Surface and subsurface soil samples show similar or comparable TiO_2 content indicating an approximately equal state of weathering. The second and third groups of elements are mainly alkali and alkaline earth with traces of MnO and Cr_2O_3. The concentration of alkali and alkaline earth metals are very small and this could explain the observed low cation exchange capacity (CEC) of soil in the study area. This is not a good soil quality for agricultural production. Buri *et al.* (2000) [38} indicated that the low level of nutrients cations in soils of West Africa is a result of low total basic oxide levels and high Al, Fe and Si oxides. These authors attributed this to prolonged weathering and leaching of the soils, their porous nature and erratic rainfall distribution.

Geochemically, the soil shows a higher depletion of Na relative to K. The Na/K ratios (Table 5) for the area were significantly lower than quoted values for fertile soil and argillaceous sediments [48]. The mean values for SiO_2/Al_2O_3 and SiO_2/Al_2O_3+Fe_2O_3 ratios for surface and subsurface layers show a similar trend (Table 5); the import of iron oxide did not bring any appreciable influence on the trends. This is a result of higher values of silica in the soil samples. The average molar ratio Al_2O_3/Al_2O_3+CaO+K_2O+Na_2O also has a higher value than CaO+MgO/Al_2O_3 ratio (Table 5) for surface and subsurface layers because of higher alumina content. On the basis of the relative abundance of the total geochemical components, the soil samples can be grouped into three for the purpose of discussing their genesis (formation); the most abundant group are Si, Ti, Al and Fe, the second group is moderate Mg, Ca and K and the third group which is least are Mn, P, Cr and Na. The concentration of the first group is high compared with others and this group is responsible for indications of laterization, brownification and kaolinization process in soil [10]. Bello and Adegoke (2010) [49] have shown that high ratios of SiO_2/Al_2O_3 and SiO_2/Al_2O_3+Fe_2O_3 in soil are indicators of strong laterization. In the present study, these ratios are > 2 thus indicating weak lateritic process and/or possibly kaolinization (triangular plots of SiO_2:Al_2O_3:Fe_2O_3). It is, however, very difficult to use these ratios to group the soils according to agricultural productivity since values obtained did not follow a distinct trend. The only seemingly clear trend is that the subsurface soil generally has a higher ratio than that of the surface soil. This, therefore, implies a more pedogenic process in the subsurface than the surface layer. The ratio Al_2O_3/Al_2O_3+CaO+K_2O+Na_2O is high whereas CaO+MgO/Al_2O_3 is low, thus confirming low status of these basic elements in the soil of the present study.

Table 5. *Average Geochemical and Weathering Index of Surface (TS) and Subsurface (SS) Soil Samples.*

Surface Samples						Subsurface Samples					
Samples	Na/K	Si/Al	Si/Al+Fe	Al/Al+Ca+Na+K	Ca+Mg/Al	Samples	Na/K	Si/Al	Si/Al+Fe	Al/Al+Ca+Na+K	Ca+Mg/Al
TS 1_1	0.43	11.7	9.21	0.84	0.1	SS 1_1	0.26	4.25	3.31	0.95	0.02
TS 2_3	0.2	9	7.93	0.65	0.06	SS 2_3	0.05	5.75	4.65	0.82	0.03
TS 3_6	0.08	11.7	8.67	0.65	0.05	SS 3_6	0.05	4.89	3.5	0.83	0.03
TS 4_7	0.31	16.7	10.4	0.96	0.05	SS 4_7	0.21	16.1	11	0.9	0.06
TS 5_8	0.2	10.6	7.14	0.93	0.05	SS 5_8	0.09	8.97	6.22	0.82	0.04
TS 6_9	0.1	4.76	3.28	0.91	0.02	SS 6_9	0.19	10.4	7.88	0.86	0.04
TS 7_11	0.1	4.67	3.55	0.75	0.04	SS 7_11	0.08	6.89	5.01	0.83	0.04
TS 8_15	0.1	6.14	4.97	0.94	0.02	SS 8_15	0.09	34.4	29.9	0.8	0.11
TS 9_16	0.15	9.62	7.79	0.91	0.03	SS 9_16	0.09	11.7	7.76	0.79	0.06
TS 10_18	0.26	12.1	9.7	0.79	0.04	SS 10_18	0.25	19.1	14.8	0.98	0.06
TS 11_20	0.8	12.1	9.72	0.98	0.03	SS 11_20	0.75	18.8	13.1	0.96	0.05
TS 12_23	0.6	11.5	9.25	0.98	0.04	SS 12_23	0.33	16.3	12.5	0.96	0.07
TS 13_24	0.36	10.3	7.84	0.97	0.05	SS 13_24	0.5	29.4	21.7	0.9	0.17
TS 14_27	1	36.2	25.1	0.97	0.04	SS 14_27	0.33	13.7	9.12	0.97	0.05
TS 15_30	0.5	7.59	5.46	0.99	0.03	SS 15_3	0.29	20.2	14.1	0.95	0.11
TS 16_31	0.6	15.9	11.5	0.97	0.09	SS 16_31	0.6	28.4	19.2	0.96	0.1
TS 17_33	0.5	20.9	14.8	0.92	0.13	SS 17_33	1	47.5	37.3	0.93	0.07
TS 18_35	0.4	11.9	8.25	0.98	0.05	SS 18_35	0.29	4.93	3.6	0.99	0.01
TS 19_37	0.4	13.6	9.88	0.98	0.05	SS 19_37	0.4	5.45	3.83	0.99	0.02

The primary minerals (quartz, mica and feldspars) and secondary mineral (kaolinite) are the main mineral components of the soil of the bitumen environment of Ondo state with nakaurite $Cu_8+2(SO_4)_4(CO_3)$, berborite ($BeBO_3OH.H_2O$) and ferrimolybdite $Fe_2(MoO_4)_{3.6}$. $3H_2O$ probably present in small amounts (Figures 2-6). Micas that could be probably present (muscovite and illite) were found in only two samples (surface sample 5_8 and subsurface sample 32_15) (Figures 4 and 5). Illite is micaceous clay mineral with similar chemical and mineralogical composition as muscovite but slightly smaller in particle size. These minerals usually occur in low to medium grade metamorphic and igneous rocks [50]. The alkali feldspars and plagioclase are present in the soils of the study area (Figures 2 and 3). Their significance is their ability to transform into kaolins and smectites under favourable conditions. Kaolin and smectites provide sites for a wide range of physicochemical and chemical reactions especially with ions of heavy metals.

Kaolin minerals (kaolinite, nacrite, halloysite and dickite) (Figures 2-6) are formed from the parent mineral feldspars and micas [46, 51]. Smectites are clay minerals with high aluminium content and are rich in either calcium or sodium regardless of their origin and occurrence.

Conditions of high degree of weathering observed by Yoothong *et al.* (1997) [17] are that: (i). high quartz, low feldspars, high gibbsite, moderate kaolinite and only very low resistant heavy minerals; (ii) high quartz, low feldspars, high gibbsite, low kaolinite, low muscovite and a trace of illite. These conditions could be observed for some of the area under investigation considering the Rietveld refinements (Figures 7 and 8) which gave generally: quartz as 83.76-93.76%, kaolinite group as 4.38-10.60%, feldspars as 1.86-3.82%, albite about 1.82% with traces of other minerals that could not be identified during phase identification. This condition was the same as that observed by Yoothong *et al.*, (1997) [17] as being moderate to intense weathering.
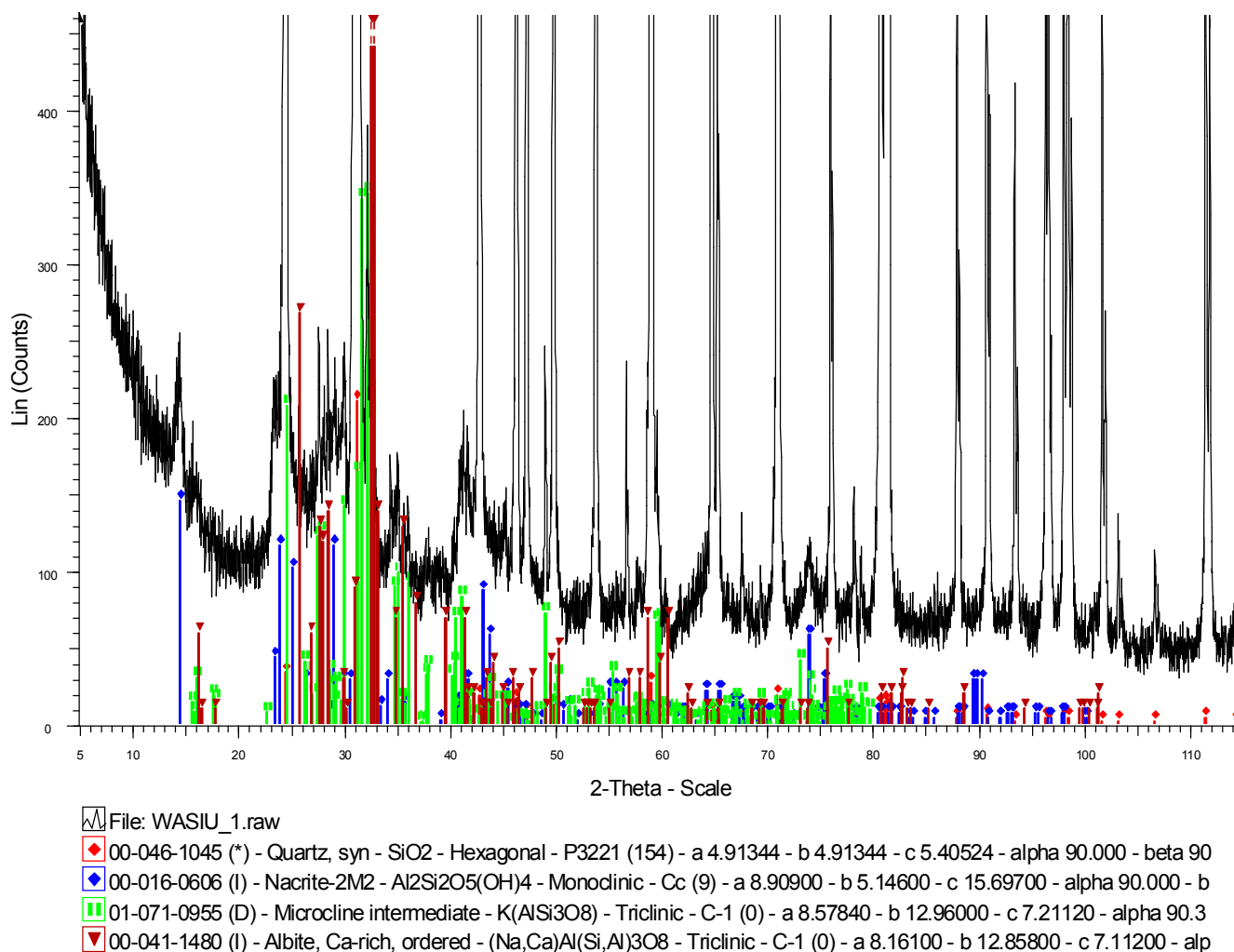

File: WASIU_1.raw

◆ 00-046-1045 (*) - Quartz, syn - SiO2 - Hexagonal - P3221 (154) - a 4.91344 - b 4.91344 - c 5.40524 - alpha 90.000 - beta 90

◆ 00-016-0606 (I) - Nacrite-2M2 - Al2Si2O5(OH)4 - Monoclinic - Cc (9) - a 8.90900 - b 5.14600 - c 15.69700 - alpha 90.000 - b

▯ 01-071-0955 (D) - Microcline intermediate - K(AlSi3O8) - Triclinic - C-1 (0) - a 8.57840 - b 12.96000 - c 7.21120 - alpha 90.3

▼ 00-041-1480 (I) - Albite, Ca-rich, ordered - (Na,Ca)Al(Si,Al)3O8 - Triclinic - C-1 (0) - a 8.16100 - b 12.85800 - c 7.11200 - alp
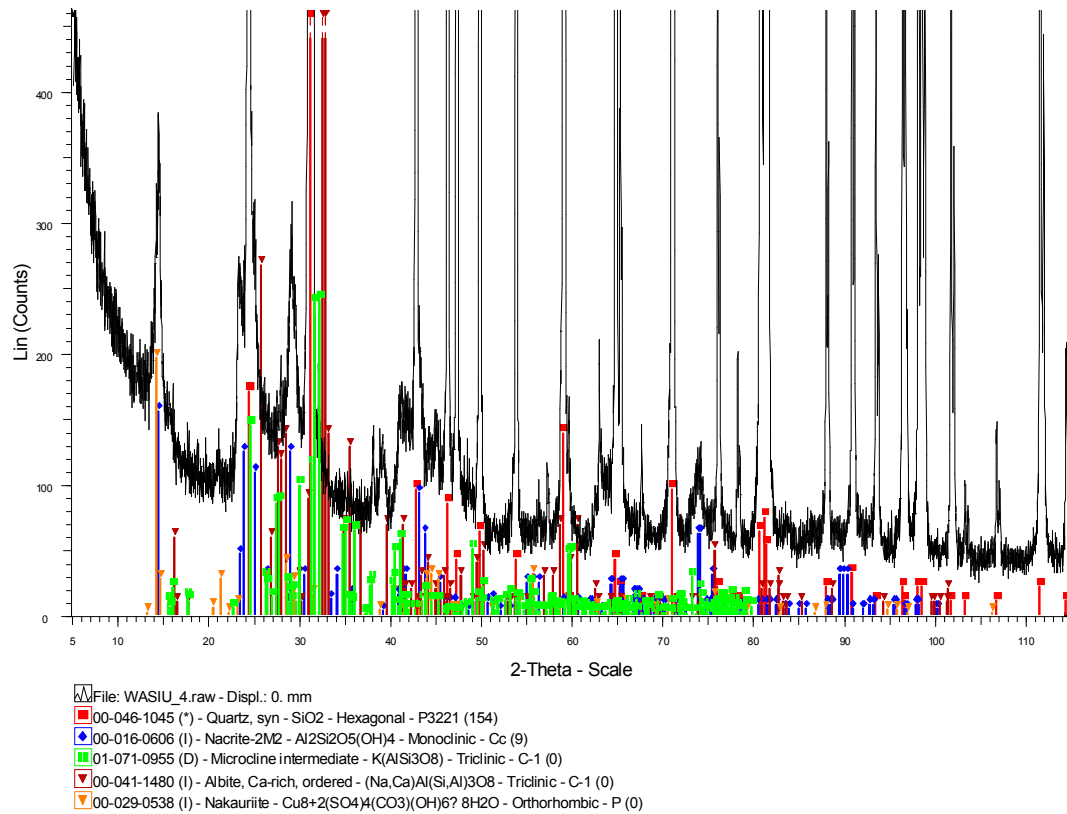
***Figure 2.** Diffractogram for Mineralogical Phase Identification of Sample 1_1.*

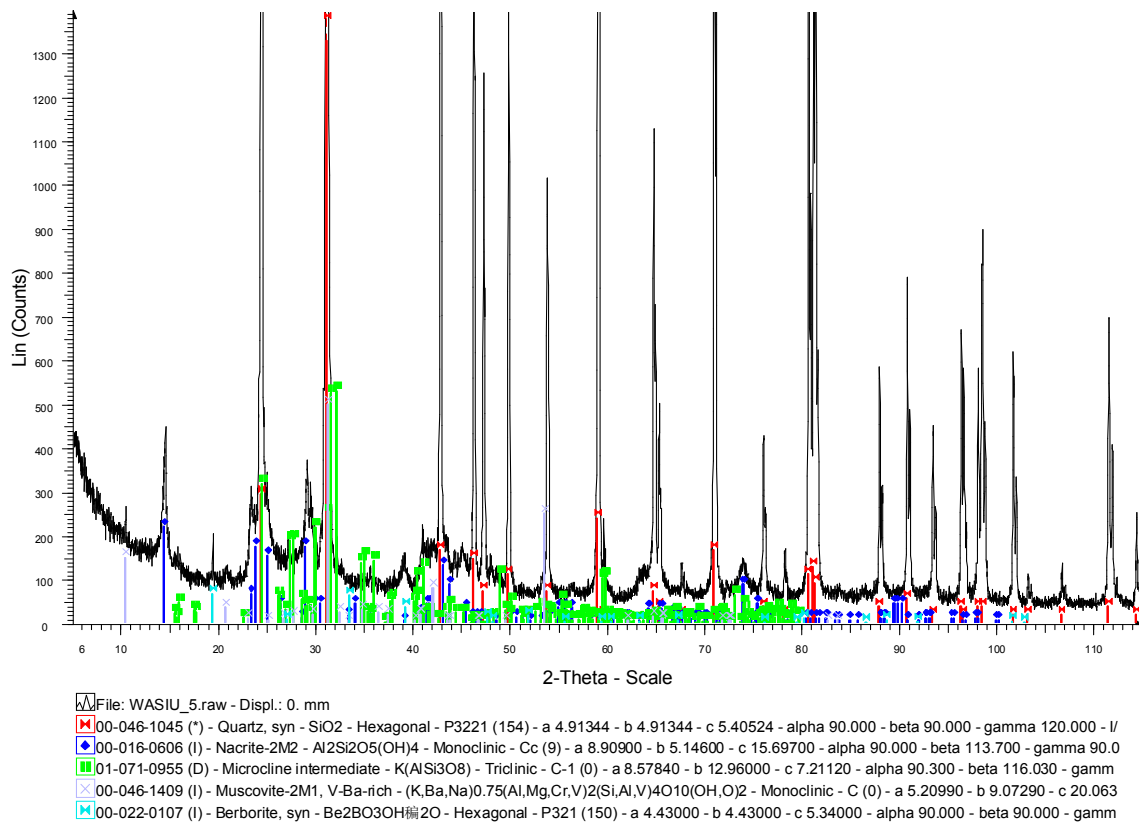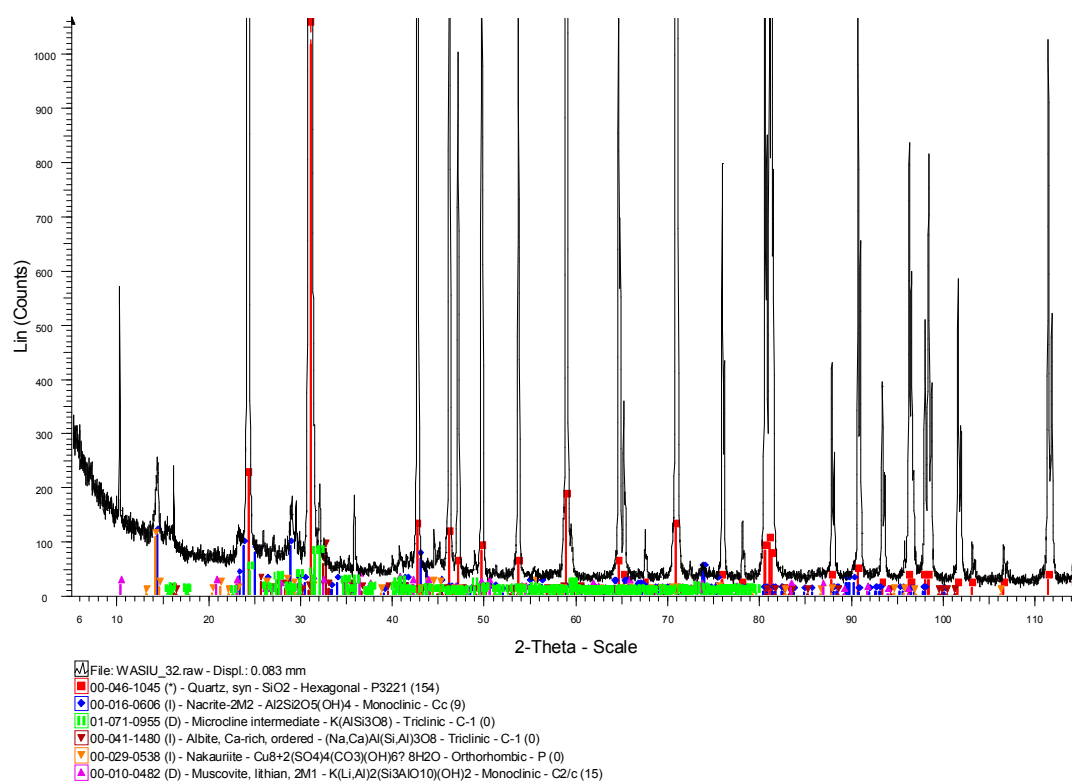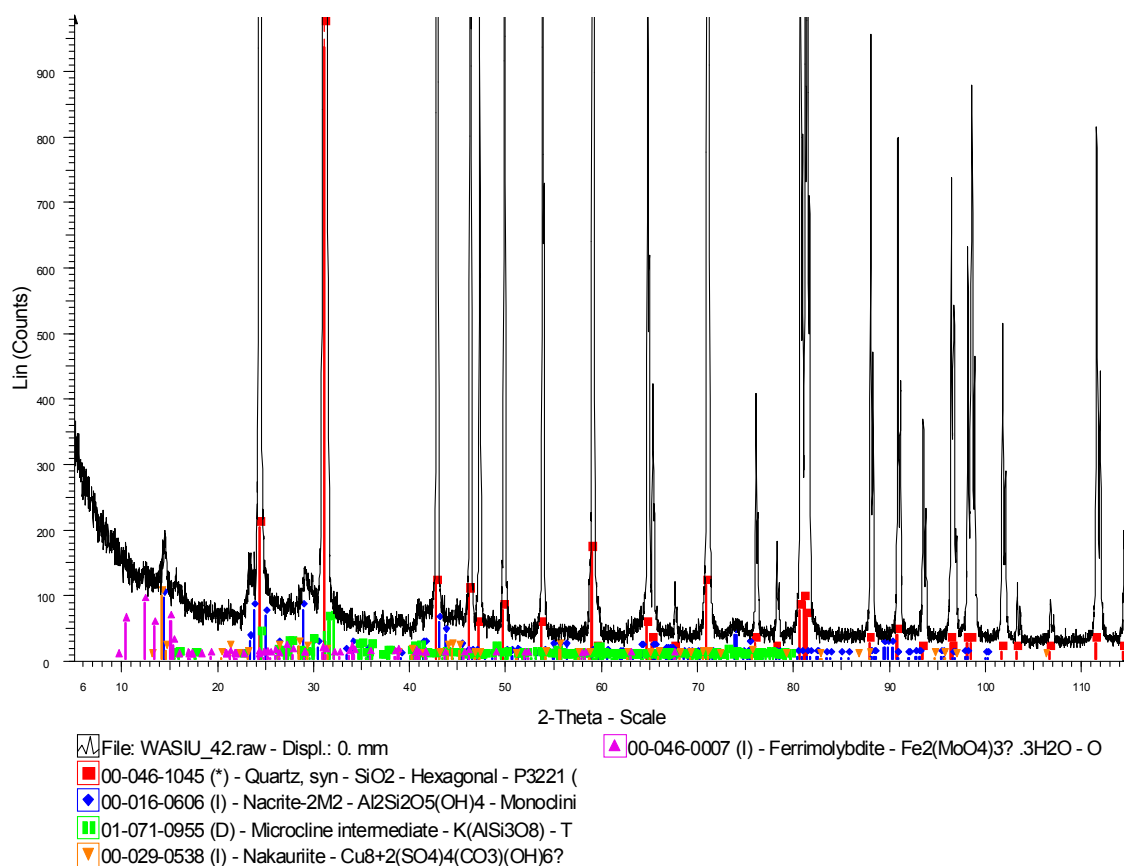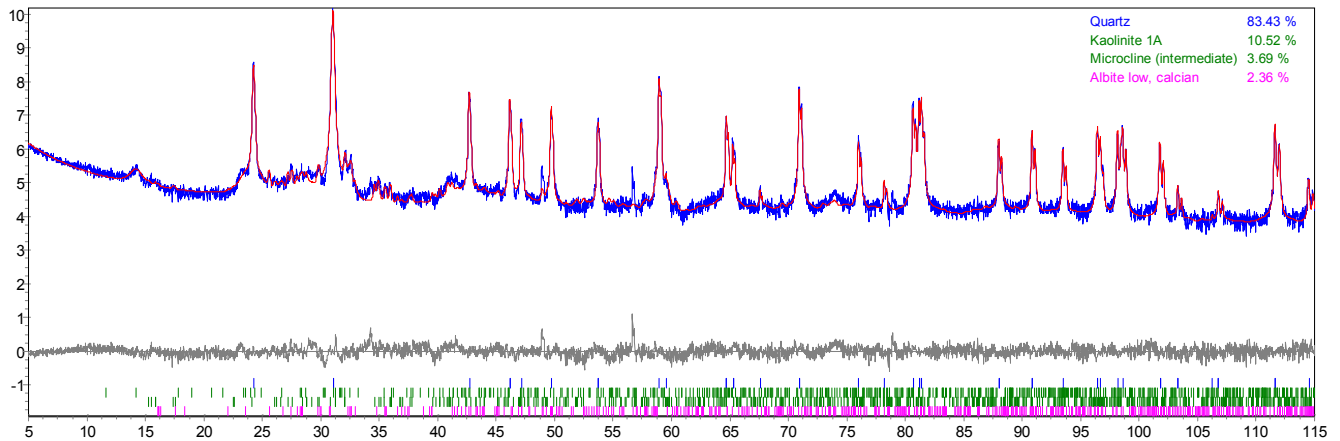**Figure 3.** *Diffractogram for Mineralogical Phase Identification of Sample 4_7.*

File: WASIU_4.raw - Displ.: 0. mm
■ 00-046-1045 (*) - Quartz, syn - SiO2 - Hexagonal - P3221 (154)
◆ 00-016-0606 (I) - Nacrite-2M2 - Al2Si2O5(OH)4 - Monoclinic - Cc (9)
■ 01-071-0955 (D) - Microcline intermediate - K(AlSi3O8) - Triclinic - C-1 (0)
▼ 00-041-1480 (I) - Albite, Ca-rich, ordered - (Na,Ca)Al(Si,Al)3O8 - Triclinic - C-1 (0)
▼ 00-029-0538 (I) - Nakauriite - Cu8+2(SO4)4(CO3)(OH)6? 8H2O - Orthorhombic - P (0)

File: WASIU_5.raw - Displ.: 0. mm
⋈ 00-046-1045 (*) - Quartz, syn - SiO2 - Hexagonal - P3221 (154) - a 4.91344 - b 4.91344 - c 5.40524 - alpha 90.000 - beta 90.000 - gamma 120.000 - I/
◆ 00-016-0606 (I) - Nacrite-2M2 - Al2Si2O5(OH)4 - Monoclinic - Cc (9) - a 8.90900 - b 5.14600 - c 15.69700 - alpha 90.000 - beta 113.700 - gamma 90.0
■ 01-071-0955 (D) - Microcline intermediate - K(AlSi3O8) - Triclinic - C-1 (0) - a 8.57840 - b 12.96000 - c 7.21120 - alpha 90.300 - beta 116.030 - gamm
✕ 00-046-1409 (I) - Muscovite-2M1, V-Ba-rich - (K,Ba,Na)0.75(Al,Mg,Cr,V)2(Si,Al,V)4O10(OH,O)2 - Monoclinic - C (0) - a 5.20990 - b 9.07290 - c 20.063
⋈ 00-022-0107 (I) - Berborite, syn - Be2BO3OH・2O - Hexagonal - P321 (150) - a 4.43000 - b 4.43000 - c 5.34000 - alpha 90.000 - beta 90.000 - gamm

Figure 4. *Diffractogram for Mineralogical Phase Identification of Sample 5_8.*

File: WASIU_32.raw - Displ.: 0.083 mm
■ 00-046-1045 (*) - Quartz, syn - SiO2 - Hexagonal - P3221 (154)
◆ 00-016-0606 (I) - Nacrite-2M2 - Al2Si2O5(OH)4 - Monoclinic - Cc (9)
▥ 01-071-0955 (D) - Microcline intermediate - K(AlSi3O8) - Triclinic - C-1 (0)
▼ 00-041-1480 (I) - Albite, Ca-rich, ordered - (Na,Ca)Al(Si,Al)3O8 - Triclinic - C-1 (0)
▽ 00-029-0538 (I) - Nakauriite - Cu8+2(SO4)4(CO3)(OH)6? 8H2O - Orthorhombic - P (0)
▲ 00-010-0482 (D) - Muscovite, lithian, 2M1 - K(Li,Al)2(Si3AlO10)(OH)2 - Monoclinic - C2/c (15)

Figure 5. *Diffractogram for Mineralogical Phase Identification of Sample 32_15.*

File: WASIU_42.raw - Displ.: 0. mm
■ 00-046-1045 (*) - Quartz, syn - SiO2 - Hexagonal - P3221 (
◆ 00-016-0606 (I) - Nacrite-2M2 - Al2Si2O5(OH)4 - Monoclini
▥ 01-071-0955 (D) - Microcline intermediate - K(AlSi3O8) - T
▽ 00-029-0538 (I) - Nakauriite - Cu8+2(SO4)4(CO3)(OH)6?
▲ 00-046-0007 (I) - Ferrimolybdite - Fe2(MoO4)3? .3H2O - O

Figure 6. *Diffractogram for Mineralogical Phase Identification of Sample 42_31.*

Figure 7. Rietveld Refinement for Identified minerals in sample 1_1.

Figure 8. Rietveld Refinement for Identified minerals in sample 4_7.

4. Conclusion

The soil under investigation is slightly acidic, non-saline, anoxic with low organic matter and CEC. The surface soil is principally sandy clay loam while the subsurface soil is clay loam. The low organic matter is due to rapid mineralization. The low levels of exchangeable cations have long been recognized to be typical of West African soils attributable to high leaching process. These soil conditions will favour rapid leaching of metals and metalloids with attendant possible underground water infiltration. The order of abundance of the major oxides is $SiO_2 > Al_2O_3 > Fe_2O_3 > TiO_2 \geq K_2O > MgO > CaO > Na_2O \geq P_2O_5 > MnO > Cr_2O_3$ for both surface and subsurface layers. This order follows the general order of soil found in southern part of Nigeria which has $SiO_2 > Al_2O_3 > Fe_2O_3 > TiO_2$ and the relative position of abundance of other oxides depends strongly on weatherability of parent materials and vegetation. Higher contents of silica and alumina as well as alkalis and calcium in the surface layer may be an indication of aeolian additions or relative enrichment of minerals during weathering and nutrient cycling by vegetation. The primary minerals (quartz, mica and feldspars) and secondary mineral (kaolinite) are the main mineral components of the soil of the bitumen environment of Ondo state. These minerals are undergoing high degree of weathering evidence by high quartz, low feldspars, high gibbsite, moderate kaolinite and only very low resistant heavy minerals; and/or high quartz, low feldspars, high gibbsite, low kaolinite, low muscovite and a trace of illite.

Acknowledgement

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