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RESEARCH ARTICLE

CHARACTERIZATION AND UTILIZATION OF CLAYS FROM ORIGO AND AWO SOUTHWESTERN NIGERIA

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ABSTRACT

This study discusses the possible industrial applications of clay from south western Nigeria based on mineralogy and chemical composition. Qualitative and quantitative X-ray Diffractometric Studies (XRD) was performed on 10 clay samples, while X-ray fluorescence (XRF) spectrometric analysis was performed on 15 clay samples. The XRD was carried out on both unoriented and oriented samples. Mineralogically, kaolinite is the dominant clay mineral while smectite occurs in small amount, and the non-clay mineral identified include quartz, mica, feldspar, goethite, and gibbsite. The concentrations of SiO_2 range from 42.45 % to 71.56 %, Al_2O_3 from 14.00 % to 36.73 %, Fe_2O_3 from 0.18 % to 12.43 %, K_2O from 0.23 % to 7.24 % and H_2O from 1.21 % to 6.5 %. The percentages of K_2O, CaO, and MgO are in consonance with the relative chemical mobility of the elements during the process of chemical weathering which accounts for the high percentage of kaolinite. The clays are residual in nature which is obtained as a result of chemical weathering of pegmatite. The high kaolinite content makes the clay suitable for refractory composite.

KEYWORDS

Kaolinite, refractory, pegmatite, X-ray Diffraction, feldspar.

1. INTRODUCTION

The demand for tiles and bricks is presently on the increase in Nigeria as an average Nigerian can now afford to build brick houses with floor tiles instead of concrete floor, hence the need to explore for more clay. The term "clay mineral" refers to phyllosilicate minerals and other minerals which impart plasticity to clay by making it hard after it has been dried or fired [1-3]. Clay is an important raw material found across Nigeria; it is also an important industrial raw material needed to manufacture a wide variety of products like, bricks, fillers, coaters, drilling mud, poetry, paper, paint, ink, sorbents and cosmetics [4, 12-15]. The difference in different clay types is accounted for by the arrangement of the octahedral and tetrahedral structure in the clay [16]. The industrial utilization of clay depends on its geological disposition, mineralogy and chemical properties.

Clays are divided into two classes:
1. Residual clay – found in the place of origin
2. Transported clay – also known as sedimentary clay, is removed from the place of origin by an agent of erosion and deposited in a new and possibly distant position.

Residual clays are most commonly formed by surface weathering, which gives rise to clay in three ways:
1. Chemical decomposition of rocks such as granite, containing silica and alumina.
2. Solution of rocks such as limestone, containing clayey impurities which being insoluble, are deposited as clay.
3. Disintegration and solution of shale.

Clay minerals could result from the chemical weathering of rocks [17]. Traditionally, most analysis of clay usually involves X-ray diffraction (XRD) method to determine the mineralogy [18-27]. More recent work has been carried out on both the qualitative and quantitative analyses of clay [27]. For chemical analysis, X-ray fluorescence (XRF) has been used for the elemental composition analysis [28-30]. Several authors have characterized clay in different parts of Nigeria using different methods [6, 8, 10, 11, 31-32].

1.1 Geological Setting

The rocks of Origo, Awo and Ede belong to the Nigerian basement complex which forms part of the mobile belt that lies between the Archean to Early Proterozoic West African and Congo craton. Four of the six lithological groups recognized by Rahaman [33-34] are present in the study area. These are:
i) The migmatite gneiss - quartzite complex.
ii) Members of the Schist Belt
iii) Charnockitic rock
iv) Members of the Older Granite Suite.

1.2 Older Granite

The detailed mapping of the area shows that the clay deposits occur on the pegmatite and pegmatite is a member of the Older granite. There is the exhibition of graphic texture in the granite (Figure 1), which is a common constituent of pegmatite. The graphic pegmatite shows interlocking grains of quartz and feldspars. Graphic granite occurs only in restricted zones of the pegmatite [35]. In the graphic granite observed, the quartz appears embedded in the feldspar (Figure 1).

Figure 1: A field photograph from Ede (1 km from Awo) showing graphic texture in granite. It is the 1st phase of (earliest) the pegmatite. Grains of feldspar (f) interlock with that of quartz (q).

On the pegmatite are crystals of garnet (Figure 2) which are reddish-brown in colour and are seed-like in shape. The colouration might be due to the presence of Fe which makes it almandine garnet. There is the occurrence of xenolith of pegmatite (earlier formed pegmatite) in pegmatite in the study area (Figure 3), which shows phase relationship within the pegmatite. There are occurrences of crystals of microcline of up to 4 cm in length oriented in different directions. A partially weathered pegmatite with books of mica (Figure 4) still standing out was observed on the clay at Ede (1 km from Awo). The mica is still occurring as books because it is more resistant to weathering than the feldspar which has been weathered into clay. A dyke of weathered pegmatite can be seen in a weathered host rock (Figure 5). The occurrence of the weathered pegmatite as dykes shows its intrusive nature.

2. MATERIALS AND METHODS

Samples of clay for unoriented analysis were done at the Central Analytical facility (CAF) Stellenbosch University while oriented analysis was carried out at Agricultural Research Council Pretoria (ARC), both in South Africa. The modal abundances of minerals in the raw clay samples were calculated using Reference Intensity Ratio (RIR) method. A geochemical analysis using XRF was done at CAF Stellenbosch University.

2.1 X-ray diffraction analysis (unoriented sample)

2.2.1 Sample preparation

A representative portion of the clay sample was air dried and milled into powder using agate mortar. The milled sample was later pressed into an aluminum sample holder forming a reflective surface. This was analyzed as pressed or unoriented samples.

Figure 2: A field photograph of pegmatite from Ede (1 km from Awo) showing crystals of brown garnet.

Figure 3: A field photograph from Ede (1 km from Awo), showing xenolith of pegmatite in pegmatite. The coarse-grained portion 'A' is the first phase while 'B' is the 2nd phase of the pegmatite with microcline 'M' crystals of about 4cm in length.

Figure 4: A field photograph from Ede (1 km from Awo) showing books of mica embedded in clay.

Figure 5: A field photograph from Origo showing a discordant weathered pegmatite dike 'P'. The weathered pegmatite is discordant to a weathered rock which is likely to be schist 'S' based on its structure.

2.2.2 Data collection and treatment

Ten samples were submitted in powdered form and measurements were performed under ambient conditions (Table 1). Data was collected using PANalytical Data Collector Software and analyzed in PANalytical High Score Plus. All raw data were treated and analysed in the same manner to ensure consistency. The background was determined using smoothed data, a derivative method with a bending factor of 0 and a granularity of 13. The $K\alpha_2$ wavelength from the Cu tube was stripped from the scan data using Rachinger method and a $\left(\frac{K\alpha 2}{K\alpha 1}\right)$ = 0.5, as tabulated below. Using the Minimum second derivative method to achieve maximum peak resolution as recommended for multi-phase samples, peaks were identified in the scans with tips broader than 0.05 2θ but narrower than 1.00 2θ, and a base width less than 2.00 2θ.

2.2 X-ray diffraction analysis (oriented sample)

2.2.1 Pre-treatment of samples

The clay fraction (< 2um) was extracted by decantation and centrifugation. This fraction was treated with ethylene-glycol under solvation and thereafter, thermal treatment. The prepared samples were then scanned with XRD at ARC (Agricultural Research Council) South Africa, using a Philips 1840 XRD instrument with a Co lamp over a range of 2 – 35^{o}θ, which is an adaptation of the method of Bühmann *et al.* [36].

2.3 X-ray fluorescence spectrometric analysis (XRF)

The X-ray fluorescence spectrometric analysis was employed for the chemical analysis of the clay samples. A total of fifteen samples were analyzed for both the major and trace elements.

Table 1: Scan Conditions

Anode material	Cu
K-Alpha1 wavelength	1.540598 Å
K-Alpha2 wavelength	1.544426 Å
Ratio K-Alpha2/K-Alpha1	0.5
Generator voltage	45 kV
Tube current	40 mA
Scan axis	Gonio
Scan range	2.499999996° - 74. 99348°
Scan step size	0.0167113°
No. of points	4338
Scan type	Continuous
Time per step	50.8 s

XRF is ideal for rapid and accurate whole bulk elemental analysis in rock or soil samples. The instrument is an AXIOS 2.4 KWatt with a Rh X-ray tube. Element settings vary from 50 - 50 to 60 - 40 to 25 - 100 mA KV, depending on the fluorescence yield of the element. A range of international reference material was used to set up the major and trace element analytical methods (for example NIM-G, -S, P, -N and the full range of South African Reference Materials). Major elements are analysed on fused beads after a H_20^- loss is performed at 110°C and a LOI is determined at 950°C for one hour for each sample. The L.O.I. is made of contributions from the volatile compounds' H_2O^+, OH^-, CO_2, F, Cl, S; in parts also K, Na (if heated for too long); or alternatively added compounds O_2 (oxidation, e.g. FeO to Fe_2O_3), later CO_2 (CaO to $CaCO_3$). Trace elements were analysed on pressed powder pellets after the material has been milled to ~50 micrometer with Zibb mill. For Major elements analysis 5 g of the milled sample was used while for the Trace elements analysis 100 g was used.

3. RESULTS AND DISCUSSION

3.1 Mineralogy

The X-ray diffraction analysis was carried out for the identification and a semi-quantitative estimation of the proportions of the different minerals present in the clay deposits. The XRD patterns of the unonoriented whole clay samples have kaolinite and quartz (Figures 6 – 15). The modal abundances of minerals calculated by using the RIR method affirms the presence of kaolinite in all the samples analysed (Table 2, Note that the RIR method is not always very accurate and percentages may have an error of ± 5 %). The quantitative results of the clay fraction indicate the percentages following minerals; kaolinite, quartz, mica, feldspar, gibbsite, goethite and smectite (Table 3).

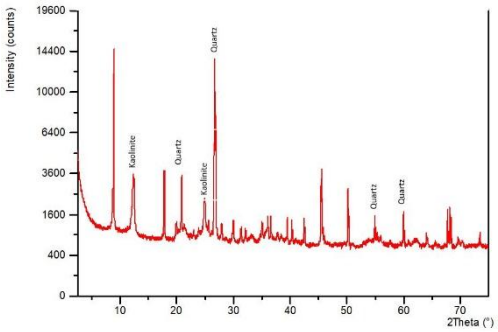

Figure 6: X-ray diffractogram of Clay Sample 4 From Origo.

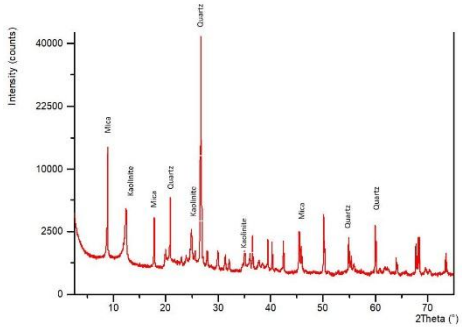

Figure 7: X-ray diffractogram of clay famples 8 from Origo.

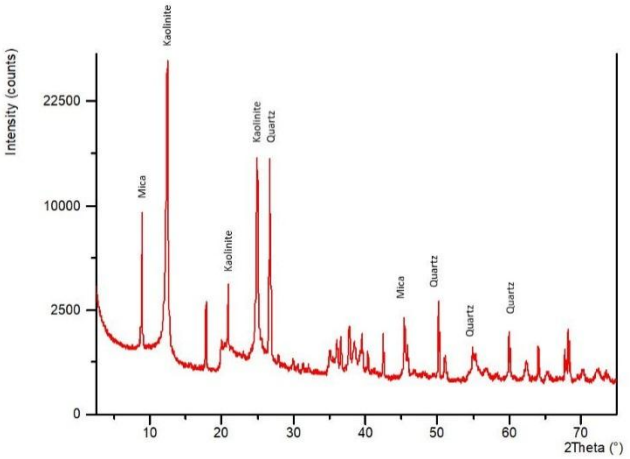

Figure 8: X-ray diffractogram of clay sample 9 from Origo

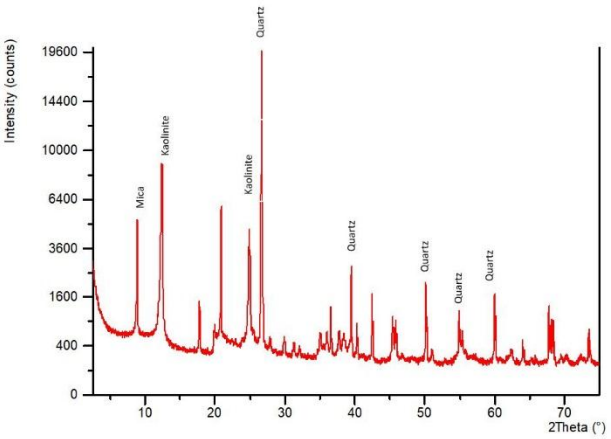

Figure 9: X-ray diffractogram of clay sample 10 from Origo.

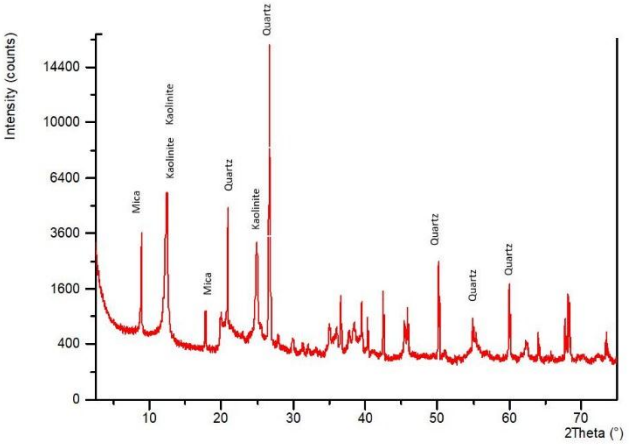

Figure 10: X-ray diffractogram of clay sample 11 from Origo.

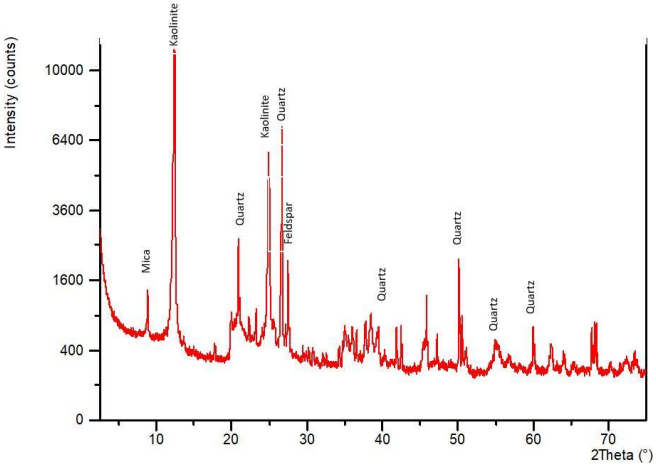

Figure 11: X-ray diffractogram of clay sample 14 from Origo

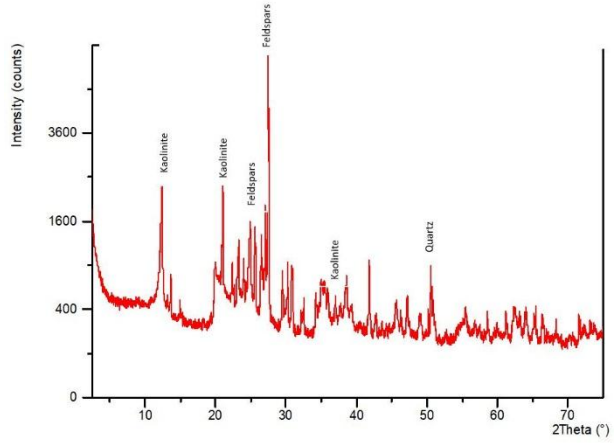

Figure 12: X-ray diffractogram of clay sample 16 from Awo

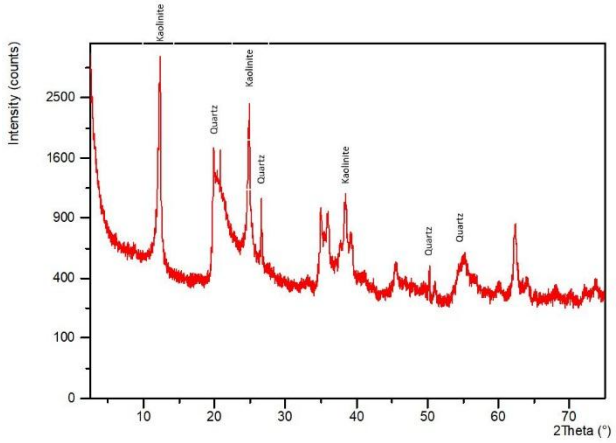

Figure 13: X-ray diffractogram of clay sample 17 from Awo.

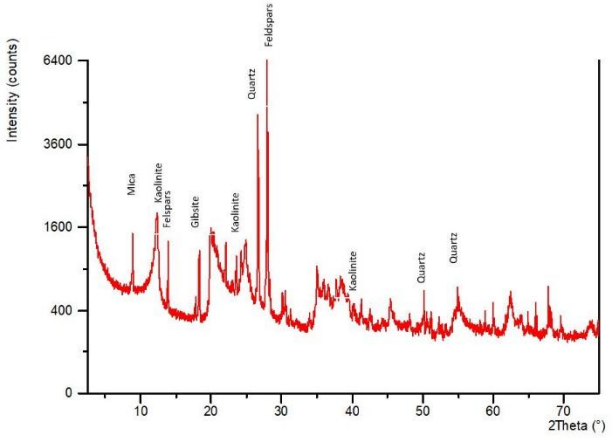

Figure 14: X-ray diffractogram of clay sample 18 from Awo

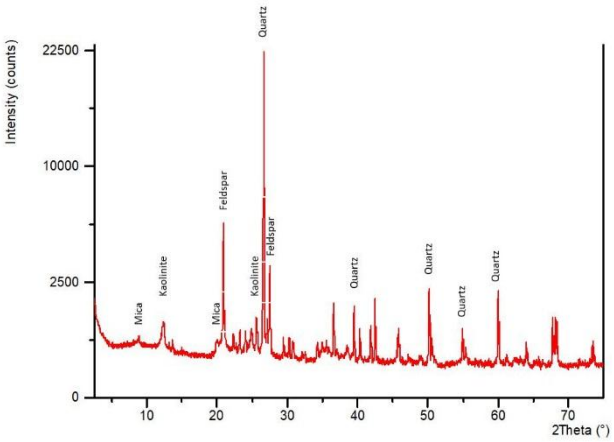

Figure 15: X-ray diffractogram of clay sample 19 from Origo

Table 2: Calculated modal abundance of minerals

Sample No	4	8	9	10	11	14	16	17	18	19
Albite $NaAlSi_3O_8$				1					24	
Beryl $Be_3Al_2(Si_6O_{18})$					1	2				
Biotite $K_2Fe_3Mg_2(AlSi_3O_{10})[OH,F]_2$	12	4		11	5	4		12	2	8
Columbite $FeNb_2O_6$	12				1	1				5
Diopside $CaMgSi_2O_6$			6	5		12	8	15	7	
Dolomite Ca Mg $(CO_3)_2$	2		3		3	4	8	6		
Dravite $NaMg_3Al_6B_3Si_6[O,OH]_{30}[OH,F]$	13	2	4		6	13				
Elbaite $Na[Li,Al]_3Al_6B_3Si_6[O,OH]_{30}[OH,F]$		3	4		2	4	13			3
Gibbsite $Al(OH)_3$	11	4	7	3	3	3	12	13	4	16
Goethite FeO.OH			1	1	1	1	2	3		
Halloysite $Al_2Si_2O_3(OH)_8$	11	4		3	10	6				
Hedenbergite $CaFeSi_2O_6$			3				4	12	12	
Ilmenite $FeTiO_3$								2		
Kaolinite $Al_4(Si_4O_{10})(OH)_8$	6	6	47	11	14	24	16	29	2	2
Lepidolite $K[Li, Al]_3[Si, Al]_4O_{10}$		6		13						29
Microcline $KAlSi_3O_8$				14			16			9
Muscovite $K_2Al_4(Si_6Al_2O_{20})$ [OH,F]4	10	31	18	19	18	10	14			
Nontronite Na Fe4$(Si_7Al)O_{20}(OH)4.n\ H_2O$									11	
Orthoclase $KAlSi_3O_8$		2				5				
Quartz SiO_2	14	28	19	17	26	10		5	12	20
Rutile TiO_2										1
Sanidine $KAlSi_3O_8$	6	7		3			18			
Spodumene $LiAl(Si_2O_6$	3	3			5	2	3	2	7	1

Table 3: Minerology of Clay Analysis

SAMPLE	QTZ	Kt	Mi	Go	Fs	St	Dt	Gb
	1	2	3	4	5	6	7	8
4	3	76	17	4	0	0	0	0
8	16	74	10	0	0	0	0	0
9	1	93	3	0	0	3	0	0
10	9	82	4	0	0	5	0	0
11	14	77	9	0	0	0	0	0
14	1	94	3	0	0	2	0	0
16	10	68	0	10	8	0	4	0
17	10	76	7	0	0	0	0	7
18	0	74	0	0	0	0	0	26
19	20	51	10	0	19	0	0	0

KEY NOTES:

1	Qz	Quartz	6	St	Smectite
2	Kt	Kaolinite	7	Dt	Dolomite
3	Mi	Mica	8	Gb	Gibbsite
4	Go	Goethite			
5	Fs	Feldspa			

Table 4: Major element analysis by raw clay samples XRF, Rh Tube

Sample name	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3T	K_2O	MgO	MnO	Na_2O	P2O5	SiO_2	TiO_2	LOI	H_2O^-	Sum
Unit							**(wt%)**							
2	24.59	0.04	0.021	12.43	2.59	0.13	0.03	0.27	0.08	43.39	1.35	12.25	4.51	101.68
4	21.38	0.02	0.016	9.98	2.95	0.14	0.03	0.32	0.06	51.70	1.04	10.06	3.85	101.55
6	20.17	0.01	0.007	5.13	2.19	0.10	0.02	0.18	0.04	59.65	0.51	9.86	3.84	101.70
8	18.60	0.01	BD	1.11	2.08	0.08	0.02	0.13	0.02	68.92	0.12	7.10	1.81	100.00
9	26.33	0.02	0.004	0.42	0.75	BD	0.01	BD	0.07	53.80	0.02	14.07	4.91	100.40
10	19.57	0.01	0.001	0.78	1.09	0.03	0.01	BD	0.02	67.43	0.04	9.69	3.28	101.93
11	21.42	0.01	0.004	1.78	0.98	0.14	0.01	BD	0.02	65.07	0.23	8.87	1.38	99.91
12	16.06	0.01	BD	0.71	4.03	0.06	0.01	0.10	0.01	71.56	0.04	5.97	1.69	100.25
13	14.71	0.03	0.003	0.69	2.99	0.03	0.10	0.17	0.02	68.00	0.02	9.17	4.76	100.69
14	24.35	0.01	0.002	0.99	2.57	BD	0.34	0.06	0.04	60.32	0.03	10.11	2.26	101.07
15	33.35	0.04	BD	0.18	4.05	BD	0.00	0.11	0.15	47.89	0.01	13.12	2.26	101.15
16	28.86	0.03	BD	0.25	7.24	BD	0.01	0.22	0.14	52.32	0.02	9.09	1.21	99.39
17	36.73	0.14	0.009	3.22	0.45	0.03	0.01	BD	0.05	42.45	0.33	15.96	2.36	101.73
18	29.54	0.01	BD	0.36	0.23	BD	0.01	1.56	0.07	46.82	0.01	16.80	6.50	101.91
19	14.00	0.02	BD	2.08	4.02	0.13	0.00	0.09	0.07	69.97	0.25	7.24	3.51	101.38

Table 5: Trace element in raw samples of clay

Sample name	Unit	2	4	6	8	9	10	11	12	13	14	15	16	17	18	19
V	**(ppm)**	257	187	77	17	1	3	23	4	3	1	2	4	34	1	31
Cr	**(ppm)**	182	114	65	21	7	22	23	8	70	9	10	9	41	9	50
Co	**(ppm)**	113	108	106	79	141	80	61	82	100	66	19	16	19	83	123
Ni	**(ppm)**	36	21	28	30	33	16	13	11	20	15	10	14	22	13	12
Cu	**(ppm)**	39	31	16	6	2	1	2	10	8	4	2	11	3	BD	13
Zn	**(ppm)**	28	21	19	19	14	19	8	16	12	10	8	10	37	24	25
Ga	**(ppm)**	42	36	25	17	41	36	20	22	23	38	52	45	61	81	21
Rb	**(ppm)**	86	95	64	44	89	95	52	210	155	138	1225	3467	153	106	162
Sr	**(ppm)**	69	66	58	74	13	7	19	17	15	10	45	27	28	11	206
Y	**(ppm)**	39	42	20	9	4	18	8	84	85	21	28	64	10	6	44
Zr	**(ppm)**	312	267	154	80	22	27	133	21	42	42	16	17	80	16	274
Nb	**(ppm)**	27	28	18	5	157	38	6	17	12	19	BD	BD	23	12	7
Ba	**(ppm)**	887	732	698	1145	16	6	205	24	99	259	54	25	33	82	651

La	**(ppm)**	51	81	43	51	249	26	51	39	108	28	128	48	29	10	312
Ce	**(ppm)**	173	260	112	136	421	94	228	15	28	86	170	40	31	14	310
Nd	**(ppm)**	68	98	44	50	159	35	84	12	19	33	69	18	13	7	130
Pb	**(ppm)**	42	41	32	62	253	33	29	62	219	188	68	47	40	34	59
Th	**(ppm)**	27	27	11	BD	1	9	4	7	5	11	BD	BD	9	0	79
U	**(ppm)**	11	18	8	5	4	6	8	5	7	6	4	4	8	9	7

3.2 Geochemistry

Results of the major element analysis indicate high amount of SiO_2, Al_2O_3, Fe_2O_3, K_2O and H_2O^-, a relatively low value of Na_2O, CaO, MgO, MnO, Cr_2O_3 and P_2O_5 (Table 4). Trace analysis show values of zircon to range from 16 -312 ppm (Table 5).

4. DISCUSSION

Kaolinite is the dominant mineral for all the samples followed by quartz. In some samples, the percentage of quartz is as low as 2 % (Table 3). The results of both the raw samples and the clay fraction indicate that all the samples contain Kaolinite. The quartz content of the clay fraction is lower than that of the raw samples. For the raw samples, it ranges from 5 to 28 % and from 0 to 20 % for the clay fraction.

The Kaolinite content of the clay fraction is higher than that of raw samples. For the raw samples it ranges from 2 to 47 % (Table 2) and from 74 to 94 % for the clay fraction (Table 3). The decrease in the amount of quartz and increase in the amount of Kaolinite in the clay fraction is as result of the beneficiation process which has reduced the non-clay fractions. The beneficiation process has also succeeded in removing some of the minerals totally, most of which are in small amount in the raw samples. The presence of smectite in the oriented samples indicates the presence of swelling clay mineral (montmorillonite). The three samples where smectite was confirmed are all from Origo deposit. The high concentrations of SiO_2 ranges from 42.45 % to 71.56 %, Al_2O_3 ranges from 14.00 % to 36.73 %, Fe_2O_3 from 0.18 % to 12.43 %, K_2O from 0.23 % to 7.24 % and H_2O from 1.21 % to 6.5 %, which is a direct reflection of high abundance of Kaolinite, while the lower concentrations of K_2O (0.23 % to 7.24%), CaO (0.1 % to 0.14 %), MgO (0.3 % to 0.14 %) is in consonance with the relative chemical mobility of the elements during the process of chemical weathering which in turn account for the high percentage of Kaolinite.

Samples 2,4,6, and 8 which were taken from the same pit at intervals of 1 m show an increase in the amount of SiO_2 and a decrease in the amount of Al_2O_3, Fe_2O_3T, TiO_2, H_2O, CaO as well as the LOI from the top to the bottom of the pit. The decrease in the amount of Fe_2O_3T from top to bottom can be related to the variation in colour from red to white, which is attributable to the effect of direct precipitation of Fe-Oxides. The whitest of the clays which was taken from Awo has the least amount of SiO_2 (42.45%) and has the highest values for Al_2O_3, with Na_2O below detection limit. The total K and Na contents of the clays can be attributed largely to the mica and feldspar component of the residual clay which are visible in the unweathered pegmatite (Figures 1, 2, 3 and 4). The samples from Origo have high Zr compared to those from Awo and there is a relatively high Ba content in most of the clay samples (Table 5)

5. CONCLUSION

The results of mineralogical analyses of whole rock samples and clay fractions show that Kaolinite is the dominant clay mineral while smectite occurs in trace amounts. Non-clay mineral identified in the clay fraction include quartz, mica, feldspar, goethite, gibbsite, dolomite. The Kaolinite content of the clay fraction was greatly enhanced by the beneficiation process; thus, this process can be recommended to upgrade the mineralogical quality thereby increasing its application for different industrial purposes. Comparison with standards show that Origo and Awo clays if properly beneficiated can be utilized by several clay-based industries. The presence of significant proportion of Kaolinite in clays of Origo and Awo reflects a warm, wet terrestrial climate. The residual clay of Origo can be used as Fire clay. The fire clay with its high percentage of alumina and silica is used as refractory clay. There is a match between the X-ray diffraction patterns, calculated modal abundance and the quantitative result of the pure clay fractions.

RECOMMENDATION

The clay samples can further be characterized by means of transmission electron microscopy (TEM) in order to determine the morphology, crystal habit, and element distribution of the different minerals present in the clay.

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