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Geochemical and Geological Characterization of Clay in the Eastern Part of Hawal Massif Around Mubi and Environs, Northeastern Nigeria

Abdulaziz Mohammed [a], Jude Sunu B.[b], Abdu Sajo [b], Ismaila Vela Haruna [c]

[a]Department of Geology and Mining Technology,
Federal Polytechnic Mubi

[b]Department of Civil Engineering,
Federal Polytechnic Mubi

[c]Department of Geology,
Modibbo Adama University Yola

Email: finthanboniface@gmail.com

Abstract

The geochemical and geological characterization of clay is an important approach to determining the quality and productivity of clay for industrial use. This paper is aimed at providing detailed geochemistry, distribution, and utilization of clay from the eastern part of Hawal massif. The field study revealed that clay occurs in Bagira, Vimtim, Didif, Bulamary, Ngavahi, Dou-Gada, Madanya, Tudun-Wada, Moda, and Kwabapale. The clays are residual deposits formed by weathering of feldspars from the granitic rocks, the clay deposits are restricted to the basal parts of highly weathered granite. The depth to which the samples were collected ranged from 0.6-1 meter. The clay was analyzed using the X-ray Fluorescence (XRF) machine. The average concentration of the major oxides shows that SiO_2 is 38.7%, Al_2O_3 is 9.62%, Fe_2O_3 is 5.48%, TiO_2 is 0.69% and CaO is 0.598% while MnO, ZrO_2, ZnO, V_2O_5, CdO, Cr_2O_3, SnO_2 and Sb_2O_5 all have lower than 0.07%. This result shows that the clay in the study area can serve as a good raw material for the manufacture of traditional ceramics, refractories, and structural clay products especially burnt bricks.

Keywords: Clay, Geotechnical, Hawal Massif, burnt bricks, basement.

INTRODUCTION

Clay is one of the most abundant and important sediments widely distributed. It has a huge economic advantage and can be used as raw material for different purposes (Ampian, 1985; Murray, 2007; Reeves & Sims, 2006). The word clay refers to any sediment particles less than 2μm in diameter, and clay mineral refers to sheet-structured alumino-silicate minerals that primarily occur in the clay-sized fraction of soils, sediments, sedimentary rocks, and weathered or altered rocks (Velde, 1995a,1995b; Velde and Meunier, 2008). Clay minerals forms as a result of the weathering of silicate rocks under low-temperature condition, they are part of the phyllosilicate or layered silicate group, which is an abundant mineral group on the

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**Author for Correspondence*

surface of the earth due to weathering of felsic crustal rocks. Clay deposits are mostly composed of phyllosilicate minerals containing variable amounts of water trapped in the mineral structure (Velde, 1995a,1995b; Velde and Meunier, 2008). Clays are plastic due to their particle size and geometry as well as water content and become hard, brittle, and non-plastic upon drying or firing (Kamseu et al., 2007; U C Melo, 2003). Clay can appear in various colors from white to dull grey or brown to deep orange-red (Velde and Meunier, 2008). Clay minerals are the most important industrial minerals (Velde, 1995a). Millions of tons are utilized yearly in various applications, including geology, processing industries, agriculture, environmental remediation, medicine, and construction (Velde, 1995a,1995b; Velde and Meunier, 2008). The reason for using certain clay minerals in a specific application is the physical and chemical properties of a particular clay mineral which depend on its structure and composition (Ali & Dikko, 2015; Valdon et al., 2021). Primary clay, also known as kaolin is always found or located at the site of their formation, while the secondary clays are transported by weathering action of wind and water from their original site of formation. The weathering process tends to mix the clay with non-clay minerals (notably iron) (Ali & Dikko, 2015). Deposits of clay raw materials are widely distributed in Nigeria. To determine the profitability of utilizing clay from a particular deposit for any application, it is of paramount importance to analyze the chemical and geological properties of such clay deposits.

This paper is aimed at providing detailed geochemistry, distribution, and utilization of clay from the eastern part of Hawal massif, since the clay deposits of this locality were not assessed scientifically before now.

GEOLOGIC SETTING

The study area (Fig. 1) lies within the eastern part of Hawal Massif in the northeastern sector of Nigeria's eastern Basement Complex. Ferré et al., (1996) reported that the rocks within the Hawal Basement are characterized by high-grade metamorphic rocks, pervasive migmatization, and extensive granite plutonism. Most of the migmatization has been dated at 580±10 Ma. It is bounded by the Tertiary-Quaternary Chad Basin northward, the Yola arm of the Cretaceous Benue Basin southward, and the Gongola Basin westwards. The area experienced Tertiary magmatism between 7 to 1 Ma (Grant et al., 1972), during which volcanic and sub-volcanic rocks were emplaced. These volcanic and sub-volcanic rocks are extensions of the Cameroun volcanic line into Nigeria (Fitton, 1980, 1983). Earlier during the Mesozoic, transitional alkali basalts were emplaced in the Shani area 146 Ma± 7.3<age<127 Ma ± (Baudin, 1986; Popoff et al., 1982).

Hawal Massif consists of gneiss, granite gneiss, granites, and some minor rocks such as dolerite, aplite, and pegmatite (Adekeye and Ntekim, 2004; Ajibade and Fitches, 1988; Bassey and Valdon, 2011; Eriksson et al., 2005; McCurry, 1976; Oye, 1972; Rahaman, 1988; Reyment and Tait, 1983). In the same vein, Bassey et al., (1999) and Kwacha, (1992) stated that the basement complex rocks in Hawal and Adamawa Massifs are part of the extension of Cameroun uplifts into Northeastern Nigeria. Oluyide et al., (1988) reported that the basement complex rocks in this area are believed to be polycyclic having been affected by various tectonic events with different intensities resulting in different episodes of folding, faulting, and granitic emplacement along the linear shear zones from Archean to late Proterozoic (Pan African). Bassey, (2006) reported that the character of the magmatic residual field over Hawal basement supports results from satellite imagery and structural geology of the area. The N-S lineaments which are the majority are expressions of the basement rocks and river course. Benkhelil, (1986) reported that the N-S trending fault system predominates the in lower

Gongola Basin. The volcanic vents of the Biu basalt plateau are observed on satellite imagery to be aligned N-S. He also reported that in Mubi, the shearing of the granites is intense and is in the NW direction. Also, Adebayo and Dayya, (2004) reported that NW shearing and faulting are commonly observed in Chibok, Michika, and Uba. Some of the faults are lateral slip faults, others are normal faults, and NW fold axes are common in the migmatite- gneiss of Hong and Mubi area.

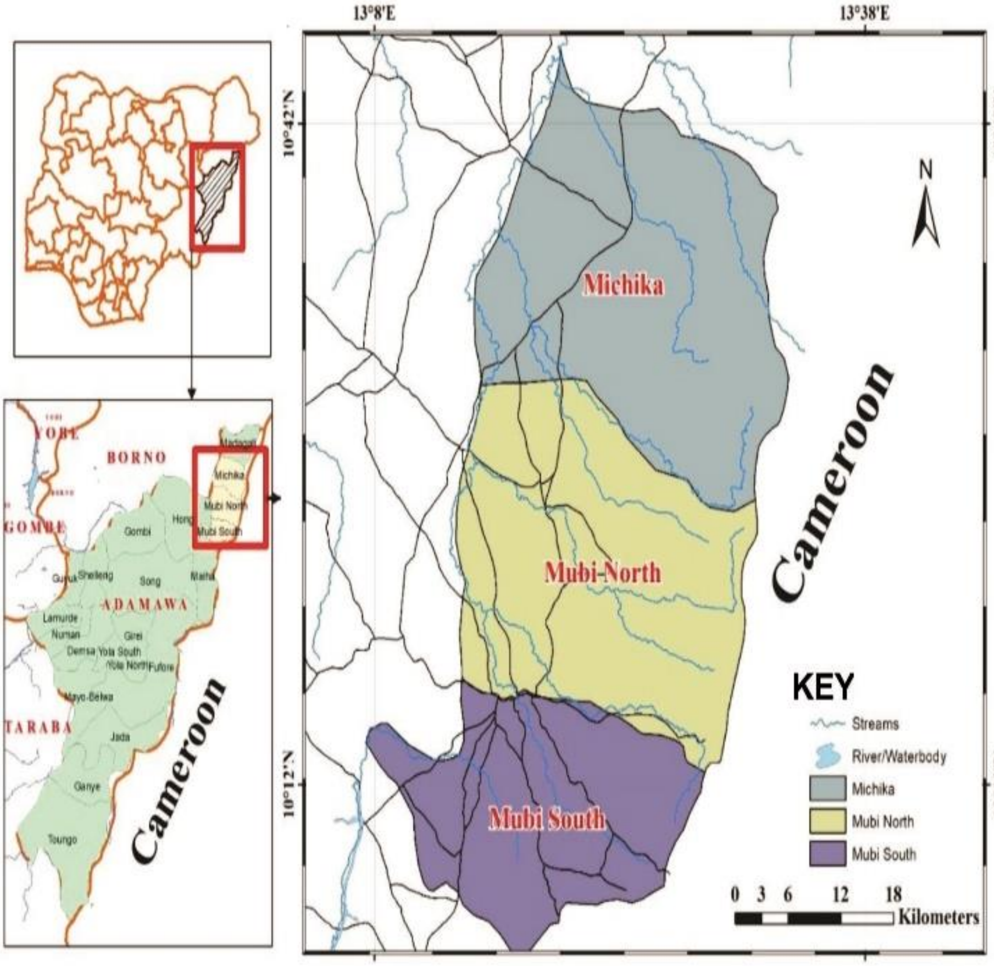


Figure 1: Geologic and Location map of the Study Area (Modified after NGSA (2010))

METHODOLOGY

Laboratory: X-ray Fluorescence (XRF)

The geochemical analysis was carried out in the department of Geology, Bayero University Kano, Nigeria. The major oxides of 10 clay samples were analyzed using the X-ray Fluorescence (XRF) machine. All the samples locations fall within latitude10° 5′00″N, 10° 43′ 00″N and longitude 13° 8′ 00″E, 13° 36′ 00″E. Fresh chips of the clay samples were handpicked and a standard volume of chips of about 28 g was ground in a swing mill with tungsten carbide surfaces for 2 minutes. Three and a half grams of 3.5 g of the sample powder was weighed into a plastic mixing jar with 7.0 g of spec pure dilithium tetra borate ($Li_2B_4O_7$) and, assisted by an enclosed plastic ball, mixed for ten minutes. The mixed powders were emptied into graphite crucibles with internal measurements of 34.9 mm in diameter by 31.8 mm deep. Twenty-four (24) filled crucibles were placed on a silica tray and loaded into a muffle furnace only large enough to contain the tray. Fusion took 5 minutes from the time the preheated furnace returns to its normal 1000°C after loading. The silica plate and graphite crucibles were then removed from the oven and allowed to cool. Each bead was reground in the swing mill for 35 seconds, and the glass powder was then replaced in the graphite crucibles and refused for 5 minutes. Following the second fusion, the cooled beads were labeled with an engraver, their lower flat surfaces were grounded on 600 silicon carbide grit, finished briefly on a glass plate which removed any metal from the grinding wheel and washed in an ultrasonic cleaner, rinsed in alcohol and wiped dry. The glass beads were then ready to be loaded into the XRF spectrometer. The preparation of a single bead took an average of 45 minutes. The concentrations of 27 elements in the unknown samples were measured by comparing the X-ray intensity for each element with the intensity of each of nine USGS standard samples (PCC-1, BCR-1, BIR-1, DNC-1, W-2, AGV-1, GSP-1, G-2, and STM -1. The values recommended by Imai et al., (1995)and two beads of pure vein quartz were used as blanks for all elements except Si. The 20 standard beads were run and used for recalibration after the analysis of about 300 unknowns. The intensities for all elements were corrected automatically for line interference and absorption effects due to all the other elements using the fundamental parameter method.

RESULTS AND DISCUSSION

The bulk elemental oxides' chemical composition of the major elements analyses for the clay samples from the study area is presented in (Table 1). The summary of the result of chemical analyses indicates that SiO_2 content in the samples varies from 25.29 to 52.36% with an average of 38.7%, Al_2O_3 content varies from 5.72 to 16.93% with an average of 9.62%, Fe_2O_3 content varies from 2.51 to 14.98% with an average of 5.48, TiO_2 content ranges from 0.073 to 0.98% with an average of 0.69% and CaO content varies from 0.111 to 2.568% with an average of 0.598% while MnO, ZrO_2, ZnO, V_2O_5, CdO, Cr_2O_3, SnO_2, K_2O and Sb_2O_5 all have lower concentrations less than 0.07%.

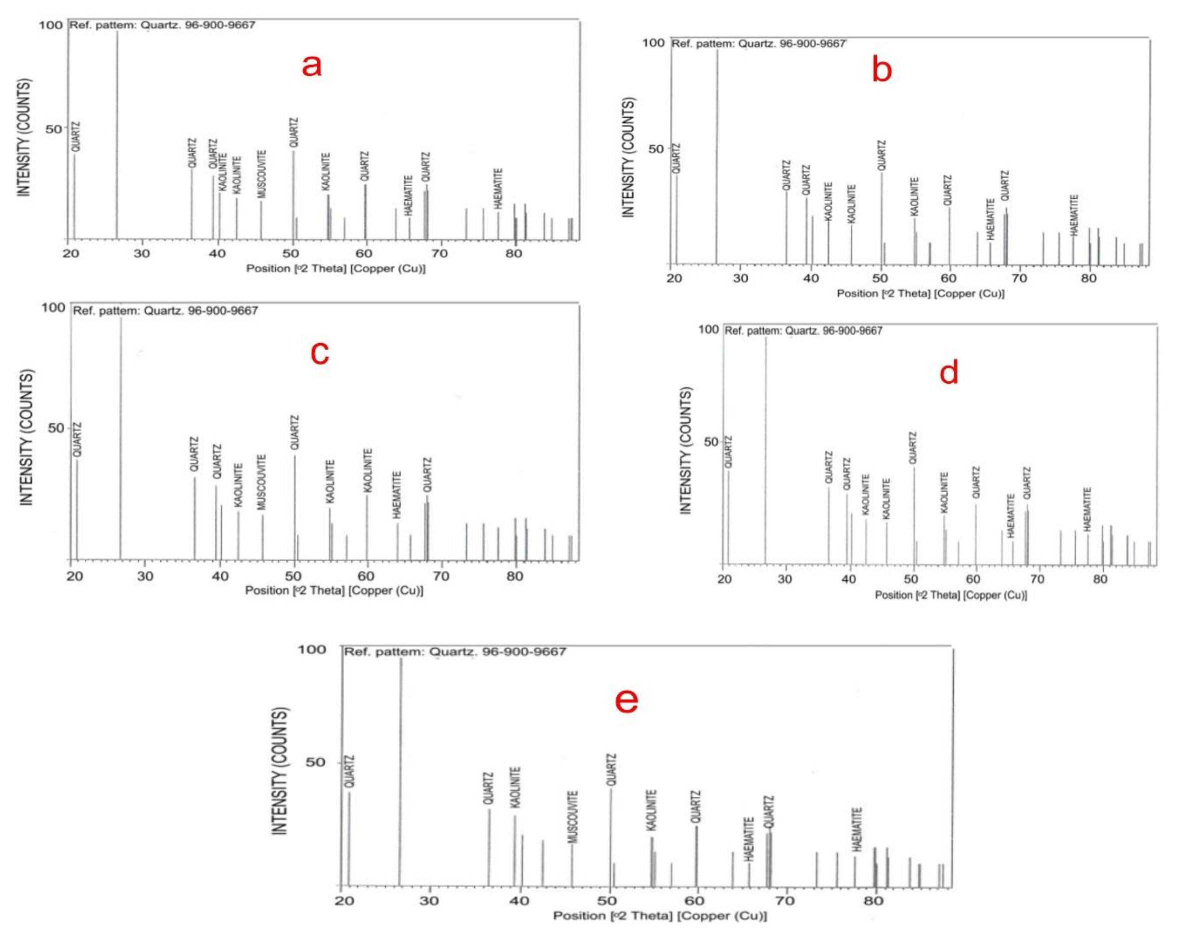


Figure 2a. Signatures of the geochemical compositions of the clays from the study area. X-ray diffraction analysis of (A) Bagira clay (B) Vimtim clay (C) Bulamari clay (D) Ngavahi clay (E) Dou-Gada clay (F) Madanya clay.

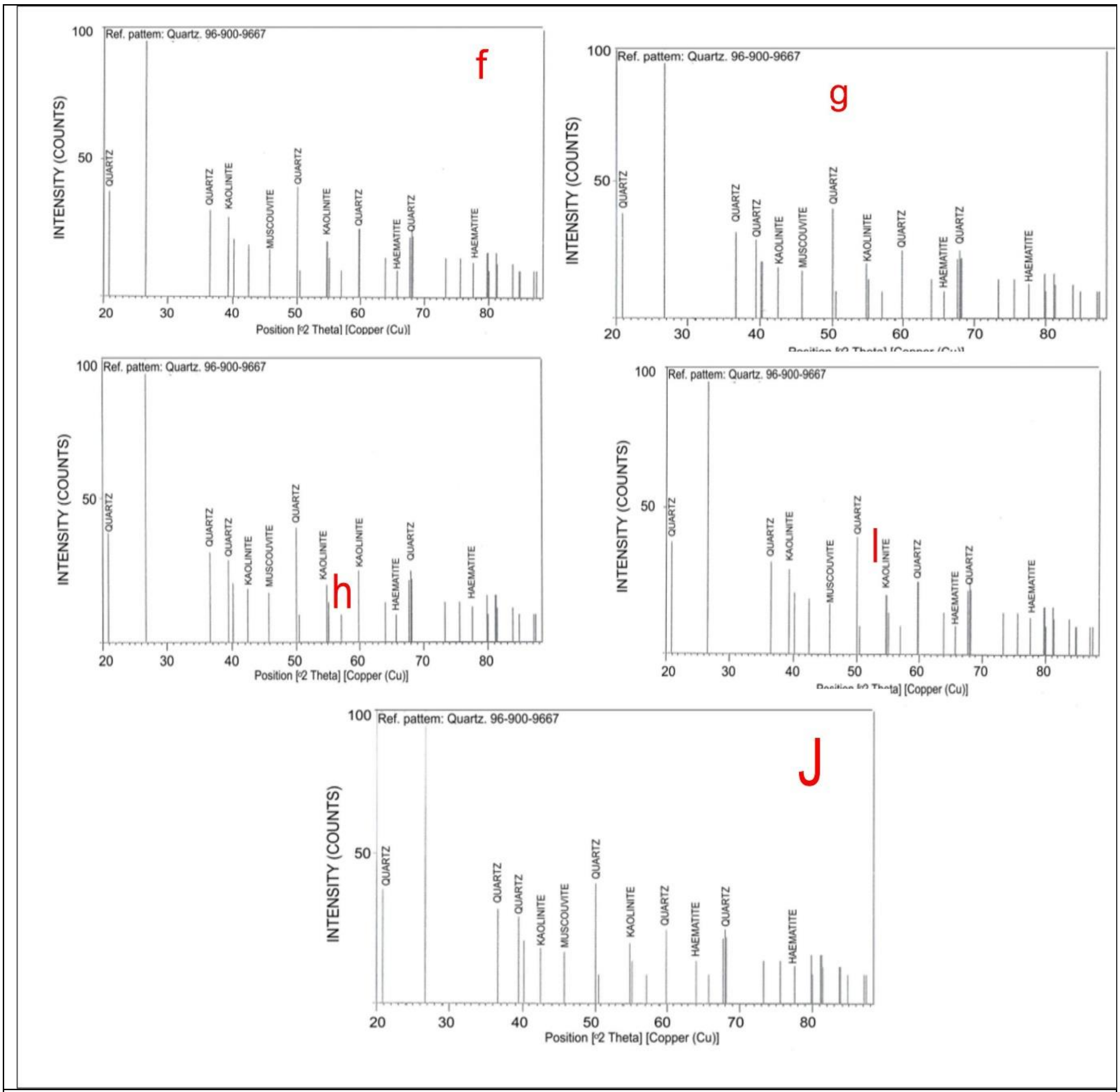


Figure 2b. Signatures of the geochemical compositions of the clays from the study area. X-ray diffraction analysis of (A) Bagira clay (B) Vimtim clay (C) Bulamari clay (D) Ngavahi clay (E) Dou-Gada clay (F) Madanya clay (G) Tudun-Wada clay (H) Moda clay (I) Kwabapale clay

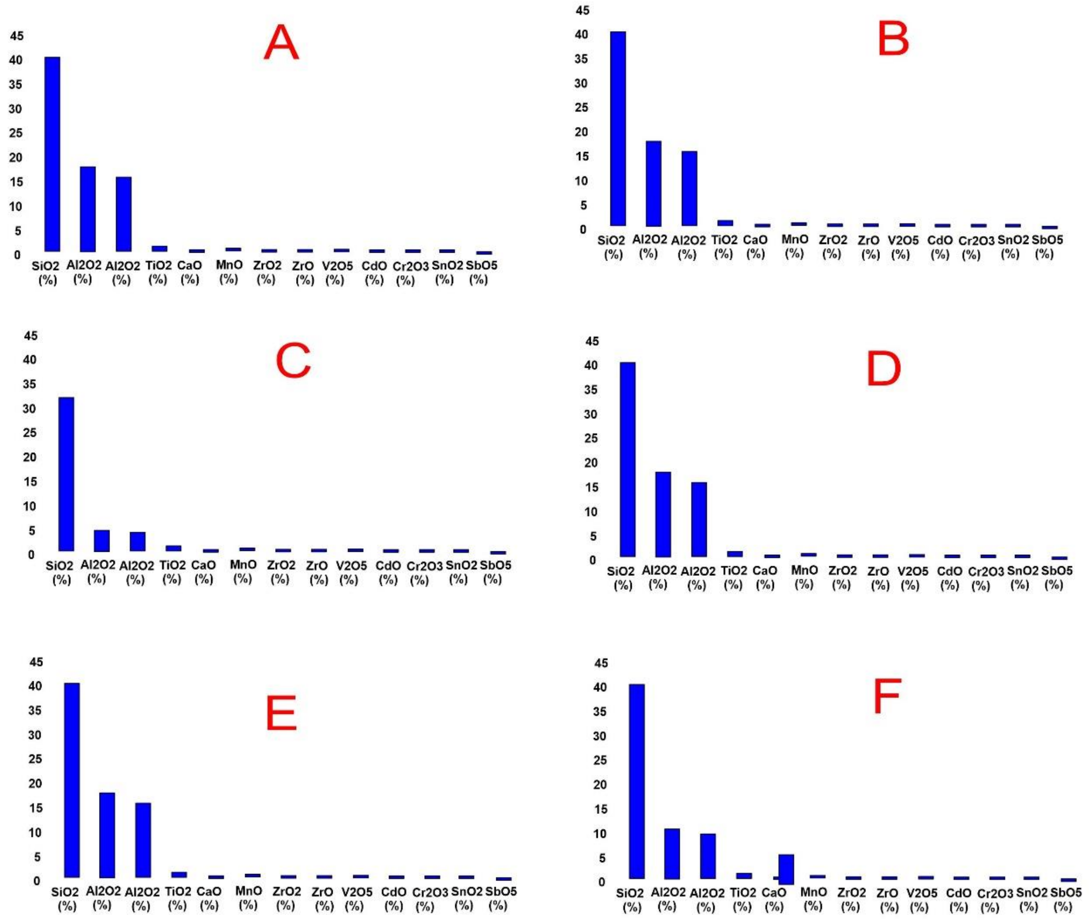
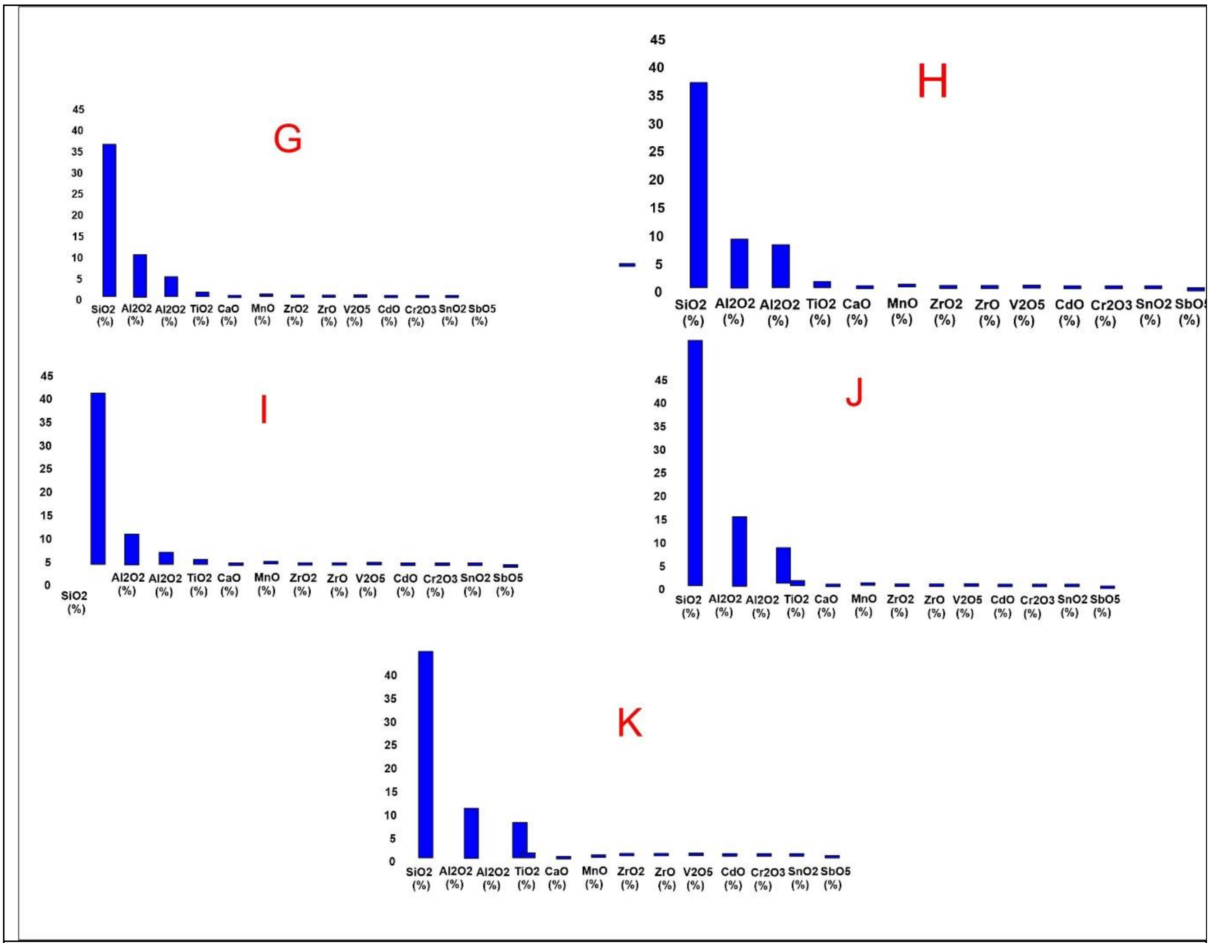


Figure 3a. Histogram of the geochemical compositions of the clays from the study area. Major oxides composition of (A) Bagira clay (MN/02) (B) Vimtim clay (MN/015) (C) Didif clay (MN/022) (D) Bulamari clay (MN/023) (E) Ngavahi clay (MS/06) (F) Dou-Gada clay (MN/07)



(G) Madanya clay (MS/08) (H) Tudun-Wada Bazza clay (MC/011) (I) Moda clay (MC/013) (J) Kwabapale clay (MC/018) (K) The average major oxides composition of the clay in the study area.

Clay occurrence

The result of the field study revealed the clay deposits in the study area are residual clays formed by weathering of feldspars from the granitic rocks. The deposits mostly occurred at the basal parts of highly weathered granite or on the low land covered by the alluvial deposit. In some of the areas the depth to which samples were collected ranges from 0.6-1 meter. The color of the clay deposits ranges from reddish, brownish to grayish which is due to the presence of a high concentration of iron oxides as indicated by the chemical analysis (Fig. 3a&b). The texture of the deposits also ranges from very fine-grained to gritty which is also attributed to the high content of SiO2 (Fig. 3 a&b). People in these communities utilize the clays for the production of traditional ceramics, Kitchen wares, and musical instruments and also used them for building purposes e.g., the production of local bricks.

Geochemical Results for Clay deposit in Bagira

The geochemical analysis revealed a high concentration of silica (40.13%) and iron oxide (14.93%) with a low concentration of alumina (16.93%) (Fig. 2a&b); though flux materials such as CaO, MgO, V_2O_5, ZnO, CdO, TiO_2, Cr_2O_3, K_2O, and ZrO_2 were also found in low concentration in the clay (Table 1). Generally, clays contain low amounts of alkalis and magnesia, Bagira clay has the highest concentration of alumina (Fig. 3a. a) and iron oxide is Kwabapale (Fig. 3b. j) in the study area. The gritty texture of the clay may be attributed to the high content of silica. The high iron oxide and low alumina of Bagira clay did not meet the standard for high-grade ceramic products. For clays to be utilized in high-grade ceramic products it requires more than 30% alumina and less than 1% iron oxide. Clays with a composition of 5% or more iron oxide are used as red-firing clays Murray, (2007).

Geochemical Results for Clay deposit in Vimtim

The XRF analysis revealed high silica content (39.87%) (Fig. 2b and 3 b), low alumina (10.09%), and relatively high iron oxide (6.36%). Flux materials such as CaO, MgO, V_2O_5, ZnO, CdO, Cr_2O_3, TiO_2, K_2O, and ZrO_2 were also found in low concentrations in the clay (Table 1). Vimtim clay has low iron oxide, low alumina, and low silica contents compared to Bagira clay but still did not meet the criteria for utilization in the production of high-grade ceramic materials (Fig. 3a. b). Since the clay has an iron oxide concentration above 5%, it can be used as red firing clays Murray, (2007).

Geochemical Results for Clay deposit in Didif

Geochemical investigation of the clay revealed that the silica content is high (51.022%) (Fig. 3a. c and 2a. c), low alumina content (8.287%), and relatively low iron oxide (2.509%) compared to other locations in the study area (Fig. 3a. c). Flux materials such as CaO, MgO, V_2O_5, CdO, TiO_2, Cr_2O_3 K_2O, and ZrO_2 were also found in low concentrations in the clay while ZnO was not detected (Table 1). Didif clay despite its low iron oxide and low alumina content did not meet the standard for the production of high-grade ceramic products but a magnetic sieve can be used to reduce the iron content and mix it with high alumina clay to meet the standard Murray, (2007).

Geochemical Results for Clay deposit in Bumamari

The geochemical analysis revealed that the clay in Bulamari has the highest silica content (52.36%) (2 d and 3 d), high iron oxide content (4.17%), and low alumina content (11.14%). Flux materials such as MgO, V_2O_5, CdO, TiO_2, and ZrO_2 were also found in low concentrations in the clay while CaO, ZnO_2, K_2O, and Cr_2O_3 were not detected (Table 1). The absence of lime (CaO) suggests that the clay is inorganic. Bulamari clay also did not meet the criteria for producing high-grade ceramic products as the alumina content is less than 30% and iron oxide is more than 1% (Murray,

Geochemical Results for Clay deposit in Vgavahi

The XRF analysis of Ngavahi clay revealed high silica (40.07%) (Fig. 2a. e and 3a. e), low alumina content (11.14%), and high iron oxide (3.081%). Flux materials such as CaO, MgO, CdO, TiO_2, Cr_2O_3, K_2O, and ZrO_2 were also found in low concentrations, V_2O_5 is relatively high (0.124%) compared to other locations while ZnO was not detected (Table 1). Ngavahi clay despite its low iron oxide and low alumina content still did not meet the standard for the production of high-grade ceramic products but a magnetic sieve can be used to reduce the iron content and mix it with high alumina clay to meet the standard Murray, (2007).

Table 1: Major oxides composition of clay of the study area

Compounds	MN/ 02	MN/015	MN/022	MN/023	MS/ 06	MS/ 07	MS/ 08	MC/011	MC/013	MC/018	Range	Average
SiO_2 (%)	40.13	39.87	51.022	52.36	40.07	25.29	35.3	26.18	36.52	39.87	25.29-52.36	38.7
Al_2O_3 (%)	16.93	10.09	8.287	11.65	11.14	6.617	8.5	5.717	7.129	10.09	5.717-16.93	9.62
Fe_2O_3 (%)	14.98	6.36	2.509	4.17	3.081	5.166	4.704	4.477	2.987	6.36	2.509-14.98	5.48
TiO_2 (%)	0.557	0.98	0.759	0.81	0.706	0.697	0.073	0.833	0.559	0.98	0.073-0.98	0.69
CaO (%)	0.139	0.45	0.111	0	0.379	2.568	0.462	0.482	0.945	0.45	0.111-2.568	0.598
MnO (%)	0.146	0.081	0.051	0.059	0.09	0.068	0.018	0.082	0.055	0.081	0.018-0.146	0.073
ZrO_2 (%)	0.071	0.063	0.076	0.11	0.048	0.058	0.095	0.054	0.048	0.064	0.048-0.11	0.069
ZnO (%)	0.017	0.009	Nd	nd	nd	0.009	0.006	0.005	Nd	0.009	0.005-0.017	0.006
V_2O_5 (%)	0.044	0.062	0.046	0.06	0.124	0.074	0.078	0.061	0.036	0.062	0.036-0.124	0.065
CdO (%)	0.027	0.022	0.02	0.024	0.062	0.022	0.024	0.024	0.027	0.022	0.02-0.062	0.03
K_2O	0.16	1.12	0.17	0.18	1.12	1.17	0.46	0.57	0.26	0.16	0.26-1.17	0.537
Cr_2O_3 (%)	0.02	0.016	0.016	nd	0.045	0.146	0.032	0.017	0.0175	0.016	0.16-0.146	0.033
SnO_2 (%)	0.028	0.024	0.022	0.022	0.067	0.03	0.025	0.021	0.029	0.024	0.016-0.067	0.03
Sb_2O_5 (%)	0.035	0.035	0.034	0.035	0.102	0.037	0.036	0.021	0.037	0.035	0.021-0.102	0.041

Nd=not detected, MN=Mubi North, MS=Mubi South, MC=Michika

Geochemical Results for Clay deposit in Dou-Gada

Geochemical analysis revealed that the clay in this area has the lowest silica content of 25.29% in the study area (Fig. 2a. e and 3b. f), the low alumina content of 0f 6.617%, and high iron oxide of 5.166% (Fig. 2a. e and 3b. f). Flux materials such as MgO, V_2O_5, CdO, TiO_2, Cr_2O_3, K_2O, and ZrO_2 were also found in low concentrations, CaO is relatively high (2.568%) compared to other locations (Table 1). The relatively high content of lime (CaO) suggests that the clay is organic. Dou-Gada clay, despite its low iron oxide and alumina content still did not meet the standard for the production of high-grade ceramic products. Clays with iron oxide concentration above 5% can be used as red firing clays Murray, (2007).

Geochemical Results for Clay deposit in Madanya

Geochemical analysis of the clay shows high silica content (35.3%) (Fig. 2b. g and 3b. g), low alumina (08.5%), and relatively low iron oxide (4.704%) (Fig. 2b. g and 3b. g). Flux materials such as CaO, MgO, V_2O_5, ZnO, CdO, Cr_2O_3, TiO_2, K_2O, and ZrO_2 were also found in low concentrations in the clay (Table 1). Madanya clay has low iron oxide, alumina, and silica contents compared to Bagira clay but still did not meet the criteria for utilization in the production of high-grade ceramic materials Murray, (2007).

Geochemical Results for Clay deposit in Tudun-Wada

XRF analysis revealed the clay in this area has relatively low silica (26.18%) (2b. h and 3b. h), low alumina content (5.717%), and relatively low iron oxide (4.477%). Flux materials such as CaO, MgO, V_2O_5, CdO, TiO_2, Cr_2O_3, K_2O, and ZrO_2 were also found in low concentrations (Table 1). Despite its low iron oxide and alumina content, it still did not meet the standard for producing high-grade ceramic products Murray, (2007).

Geochemical Results for Clay deposit in Moda

Geochemical analysis of the clay shows high silica content (36.52%) (Fig. 2b. i and 3b. i), low alumina (07.129%), and relatively low iron oxide (2.987%) (Fig. 2 i and 3 i). Flux materials such as CaO, MgO, V_2O_5, CdO, Cr_2O_3, TiO_2, K_2O, and ZrO_2 were also found in low concentrations in the clay, and ZnO was not detected (Table 1). The clay has low iron oxide, alumina, and silica contents compared to Bagira clay but still did not meet the criteria for utilization in the production of high-grade ceramic materials Murray, (2007).

Geochemical Results for Clay deposit in Kwabapale

The XRF analysis of the clay shows high silica content (39.87%) (Fig. 2b. j and 3b. j), low alumina (10.09%), and relatively high iron oxide (6.36%) (Fig. 2b. j and 3b. j). Flux materials such as CaO, MgO, V_2O_5, ZnO, CdO, Cr_2O_3, TiO_2, K_2O, and ZrO_2 were also found in low concentrations in the clay (Table 1). Vimtim clay based on its chemical analysis has low iron oxide, low alumina, and low silica contents compared to Bagira clay but still did not meet the criteria for utilization in the production of high-grade ceramic materials. Since the clay has an iron oxide concentration above 5%, it can be used as red firing clays Murray, (2007).

Utilization of the Clay

The utilization of clay materials depends largely on their chemical, physical and mineralogical compositions. Clays have several industrial processes with each industrial process requiring certain properties and specifications that must be met by the raw or refined clay. The chemical analysis shows that the average percentage of alumina and iron oxide are (9.62%) and (5.48%) respectively, this revealed that the content of alumina is less than 30% while that of iron oxide is more than 1% in all the samples studied. Thus, these clays do not meet the conditions necessary for refractory fired clays or the manufacture of high-grade ceramic products such as white porcelain, glossy papers, and other products. This requires clay with less than 1% iron oxide content and at least 30% Al_2O_3. Clays with a composition of 5% or more iron oxide are used as red firing clays (Murray, 2007). The high concentrations of iron oxides give rise to brownish and reddish colors which are objectionable in paper and some ceramic industries. In terms of physical properties, plasticity is one of the most important properties of clay in ceramic production hence it transmits to the workability of the clay. The result indicates that clays from Kwabapale and Moda have the highest plasticity index of 16.0 and 16.90% respectively, while clays from Bagira and Bulamari have the lowest plasticity index of 9.5 and 9.0% respectively. This low plasticity index is attributed to the high content of silica in the clays. For industrial applications, plasticity index values lower than 10% are not suitable for ceramic production, due to the risk of cracking during the extrusion process (Ozkan, 2016) Linear shrinkage results showed that almost 90% of the clays in the study area have 10.4% linear shrinkage values except clays from Didif and Madanya which have lower linear shrinkage values of 9.65 and 9.28% respectively. Apart from clays in Didif and Madanya, all the clays have a linear shrinkage that fell slightly above the internationally accepted value of 7 to 10% values for alumino-silicates, kaolin, and fire clays Zubeiru, (1997). Although clays from Didif, Ngavahi, and Moda with low iron oxides (2.509, 3.03, and 2.987 respectively) can be refined to reduce the iron and titanium oxides and also increase the alumina content by mixing it with the clay of high alumina to the desired levels for ceramic production, the process may be too expensive for industrial purposes. Given the results obtained, it appeared that the clays in the study area can serve as a good raw material for the manufacture of refractories and structural clay products especially burnt bricks (Attah, 2008; Attah and Oden, 2010; Okeke and Okogbue, 2012; Serry et al., 2015; Kagonbé et al., 2021).

CONCLUSION

On the bases of geochemical and geological studies; the clays from the Eastern part of Hawal Massif are suitable for use as a raw material for the production of traditional ceramics, refractories, and structural clay products especially burnt bricks. However, these clay deposits are not suitable raw materials for manufacturing high-grade ceramic products such as white porcelain, glossy papers, and other products.

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