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ARTICLE

Palaeoweathering, Provenance and Hydrothermal Alteration Characteristics of Nahuta Clay, Jos-Plateau, Northcentral Nigeria

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ABSTRACT

The geochemical characteristics of Nahuta clay, Jos-Plateau, northcentral Nigeria were obtained to ascertain the provenance, palaeoweathering and hydrothermal alteration characteristics. Clay samples were collected at different horizons. SiO_2 contents along the profile show a decrease from the deepest sample to the topmost sample and were consistent with the predicted reduction in SiO_2 compositions up-profile associated with weathering. The Chemical Index of Alteration (CIA) values (96.68–99.81%) of Nahuta clays suggest weathering in the area. The SiO_2 content and CIA values indicate weathering in Nahuta area. The topmost part of the clay profile increases in Na_2O and K_2O concentrations and this is against the expected gradual decrease in Na_2O and K_2O concentrations up-profile which should reflect destruction of plagioclase (K-feldspar) and removal due to weathering. This probably indicates the addition of Na_2O and K_2O to the clay deposit from other sources, possibly hydrothermal fluids. This is indicative that the process of formation of Nahuta clay is through hydrothermal alteration. Based on the mineralogical compositions (quartz, albite, kaolinite, illite and osumilite), the provenance of Nahuta clay could be associated with hydrothermal alteration and weathering of granitic host rocks.

Keywords: Provenance; Palaeoweathering; Hydrothermal; Alteration and granitic

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1. Introduction

The standard of weather in an environment increases with the presence of rainfall and temperature ^[1]. According to the research by Wilson ^[2], Potassium and sodium can be depleted through the weathering process. The observed chemical composition of paleoweathering profiles is, therefore, the sum of the effects of various stages of weathering, diagenesis and hydrothermal alteration ^[3–5]. High field strength elements (HFSE) are of interest in pedogenic studies due to their resistance to weathering ^[6]. The mobility of HFSE ions is probably confined to strongly acidic solutions ^[7].

Clay minerals are formed when rocks are subjected to different conditions such as water and temperature aside from conditions under which they were initially formed ^[8,9]. The mineralogical compositions of the rocks could be altered to secondary minerals when the weather changes. Hydrothermal alteration can also occur when hydrothermal fluids pass through the rock and can change the mineralogical composition by removing or redistributing the components of the rocks ^[10,11]. Minerals within the rocks can be altered to hydrothermal minerals depending on temperature, pressure, composition of hydrothermal fluids and rock compositions ^[12–15].

Nahuta Clays occur in the Rop Complex, Jos Plateau, northcentral Nigeria (**Figure 1**). The Rop Complex is a roughly triangular area of 360 km² of which 105 km² are underlain by the Younger Granite suites. The Basement Complex rocks are the Oldest rocks and they underlie the Rop Complex ^[16]. Nahuta area is locatedbetweenLatitudes 9°29¹ to 9°32¹ N and Longitudes 8°51¹ to 8°53¹ E on the North East of Topographical Sheet 189 (Kurra). This area is bounded to the North by Gana Rop and to the west by Rarin Sho^[17].

The geochemical compositions of Nahuta Clay were carried out with the aim of ascertaining the provenance, palaeoweathering and hydrothermal alteration characteristics.



Figure 1. Location of the younger granite complexes and Nahuta area in Northern Nigeria.

2. Methodology

The representative clay samples were collected using a chisel from the mining pits in different sections starting from the deepest to the upper section of Nahuta Clay, corresponding to macroscopic features. The variations in grain sizes, chemical properties and mineralogical compositions were observed and adopted in the identification of different horizons. According to the research of Maynard ^[18] to assess a profile with the hope of providing information about atmospheric evolution, the section must be shown to be an in situ product of weathering and not allochthonous. The samples collected along the clay profile were placed in different sample bags and labelled with appropriate sample numbers. The samples were shipped from Nahuta clay deposit to the laboratory for sample preparation and geochemical analysis. X-Ray diffraction analysis was carried out at the University of Pretoria.

The samples were air-dried in the Laboratory to remove moisture and the dried samples were ground to powdered form using agate mortar and pestle. Five (5) grams of the ground samples were measured using analytical balance and packaged into different sample bags that were properly labeled for geochemical analysis. Five (5) samples from the Nahuta area were subjected to ICP-MS analysis at Acme Laboratory Ltd, Vancouver, Canada. The clay samples were analyzed for major oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O_{3(T)}, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, Cr₂O₃, Tot/C and Tot/S) and trace elements (Ba, Cs, Ga, Hf, Nb, Rb, Sr, Ta, Th, U and Zr) using a Lithium metaborate/tetraborate fusion and nitric acid digestion of 0.2 g of each sample. To better characterise the paleaoweathering proxy of Nahuta Clay, the values of major oxides and trace elements were plotted against depth. The Chemical Index of Alteration (CIA) values were computed using whole rock geochemical data of major oxides: CIA= $\{Al_2O_3/(Al_2O_3 + Na_2O + K_2O + CaO)\}^{[19]}$.

3. Results

3.1 Field characteristics of Nahuta Clay

Three groups of rocks have been identified in Nahuta area ^[20] and they include: Older granites (porphyritic granite); Younger granites (granite porphyry, biotite granite and microgranite); and Volcanic rocks (Older basalt) as shown in **Figure 2**. The granite porphyry, microgranite and biotite granite are well exposed occurring as Ring Dyke Complexes which constitute part of the Rop Complex of Younger Granite province of northcentral Nigeria ^[20].



Figure 2. Geology of Nahuta area

Source: Odewumi [20].

Nahuta Clays occur in Nahuta area and overlying the crystalline basement. The thickness of Nahuta clay ranges from 25 m and above. Nahuta clay can be classified into four horizons namely: kaolinized granite horizon with thickness ranging from 2.5 to 4.5m that is overlying the variegated reddish clay horizon and the thickness of the variegated reddish clay horizon varies from 3.0 to 4.0 m (**Figure 3**). The variegated reddish clay horizon is overlying the whitish kaolin horizon (**Figure 4**) with thickness ranging from 5.0 to 6.6 m, which in turn overlies the light grey horizon with thickness ranging from 5.5 m onwards until weathered basement is reached.



Figure 3. Weathering section of Nahuta Clay (Longitude 8° 51¹12¹¹ E; latitude 9° 29¹ 22¹¹ N; Elevation 1,217 m).



Figure 4. Mining face of Whitish Kaolin from Nahuta Clay.

3.2 Mineralogy

Quartz, albite, kaolinite, illite and osumilite were identified in the mineralogical composition of Nahuta Clays (**Figures 5 and 6**). Osumilite was identified in the mineralogical compositions of Nahuta Clay which could be found in hydrothermal settings, suggesting the occurrence of hydrothermal alteration in the area.

3.3 Geochemistry

The result of the major oxide compositions of Nahuta clay is presented in **Table 1** while trace elements compositions are presented in **Table 2**. SiO₂ value ranges from 45.18 to 65.1 weight percent (wt%), Al₂O₃ value ranges from 24.09 to 36.77 (wt%). Fe₂O₃ content varies from 0.48 to 2.75 (wt%), CaO varies from < 0.01 to 0.05 (wt%), MgO varies from < 0.01 to 0.02, Na₂O varies from < 0.01 to 0.05,

 K_2O varies from 0.04 to 0.99 (wt%) and MnO varies from < 0.01 to 0.02 (wt%) respectively.

Sample number NA 1 represents the deepest sample while sample number NA 5 represents the topmost sample as shown in **Figure 3**. The values of CaO, Na₂O, K₂O and TiO₂ (wt%) from Nahuta Clays were plotted against depth from the deepest sample to the topmost sample as shown in **Figure 7** while the values of SiO₂, Al₂O₃, Fe₂O₃ and MgO (wt%) of Nahuta Clays were plotted against depth from the deepest sample to the topmost sample against depth from the deepest sample against depth from the deepest sample to the topmost sample against depth from the deepest sample to the topmost sample are shown in **Figure 8**.

The values of Ba, Sr and Rb (ppm) from Nahuta Clays (**Table 2**) were plotted against depth from the deepest sample to the topmost sample as shown in **Figure 9** while the values of Zr, Th and Nb (ppm) from Nahuta Clays (**Table 2**) were plotted against depth from the deepest sample to the topmost sample as shown in **Figure 10**. The CIA value ranges from 96.68 to 99.81% (**Table 1**).



Figure 5. Mineralogical compositions of sample NA 1.



Figure 6. Mineralogical compositions of sample NA 2.

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Table 1. Major Oxide (wt/0) compositions of Nanda Ciay.					
Major oxides	NA 1	NA 2	NA 3	NA 4	NA 5
SiO ₂	65.1	62.13	45.18	48.35	50.52
Al_2O_3	24.09	26.43	36.77	36.65	31.72
Fe_2O_3	0.79	0.69	2.7	0.48	2.75
CaO	0.02	< 0.01	0.03	0.02	0.05
MgO	< 0.01	< 0.01	0.02	< 0.01	0.1
Na ₂ O	0.02	< 0.01	< 0.01	< 0.01	0.05
K ₂ O	0.06	0.12	0.26	0.04	0.99
MnO	< 0.01	0.01	0.02	< 0.01	< 0.01
TiO_2	0.04	0.02	0.05	0.04	0.28
P_2O_5	< 0.01	< 0.01	< 0.01	0.01	0.02
Cr ₂ O ₃	< 0.001	< 0.001	< 0.001	< 0.001	0.005
LOI	9.2	9.89	13.97	13.68	12.6
SUM	99.36	99.34	99.01	99.36	99.15
TOT/C	0.11	0.05	0.07	0.05	0.27
TOT/S	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
CIA	99.59	99.47	99.19	99.81	96.68
Fe ₂ O ₃ t/TiO ₂	19.75	34.5	54	12	9.82
Na ₂ O/TiO ₂	0.5	0.5	0.2	0.25	0.18
K ₂ O/TiO ₂	1.50	6	5.2	1.0	3.54
SiO_2/TiO_2	1627.5	3106.5	903.60	1208.8	180.43
Al_2O_3/TiO_2	602.25	1321.5	735.4	916.25	113.29
CaO/TiO ₂	0.50	0.5	0.6	0.5	0.18

Table 1. Major oxide (wt%) compositions of Nahuta Clay.

Note: LOI: Loss of Ignition; SUM: Sum total of major oxides; CIA: Chemical Index of Alteration; TOT/C: Total Carbon and TOT/S: Total sulphur.

0.0m

Table 2. Trace	elements	(parts	per	million;	ppm)	compositions
of Nahuta Clay.						

Trace elements	NA 1	NA 2	NA 3	NA 4	NA 5
Ba	5	3	5	5	52
Cs	0.2	0.3	0.9	< 0.1	1.5
Ga	148	159.3	224.3	214.4	174
Hf	79.5	93.1	1.6	213.5	73.7
Nb	225.3	286.4	682.2	206.7	166.1
Rb	17.6	55.3	153.7	13.3	344.3
Sr	1.5	0.7	2.9	6.3	17
Та	318.3	368.9	466.8	257.3	413.2
Th	40	43.3	19	32.6	47.3
U	19.6	25	10.9	15.4	16.2
Zr	163.8	185.4	4.1	350.4	220.5

4. Discussion

Kaolinite and halloysite were identified in the mineralogical compositions of Nahuta Clay (**Figures 5 and 6**) which could be derived through weathering or hydrothermal alteration of rocks ^[21,22]. The osumilite in the mineralogical composition of Nahuta clay suggests hydrothermal alteration because osumilite is restricted to hydrothermal occurrence ^[23–26]. Illite is formed by chemical alteration of K-feldspar ^[10,15,27] and the occurrence indicates K-feldspar as part of the mineralogy of the protoliths which is the characteristics of granitic sources ^[28,29].



Figure 7. Geochemical characteristics of CaO, Na₂O, K₂O and TiO₂ (wt%) for Nahuta Clays.



Figure 8. Geochemical characteristics of SiO₂, Al₂O₃, Fe₂O₃ and MgO (wt%) for Nahuta Clays.



Figure 9. Geochemical characteristics of Ba, Sr and Rb (ppm) for Nahuta Clay.



Figure 10. Geochemical characteristics of Zr, Th and Nb (ppm) for Nahuta Clay.

Quartz and albite constitute part of the mineralogy of granitic sources while kaolinite and illite could be derived from the weathering and hydrothermal alteration of K-feldspar^[30]. Clays from Sabon Gida^[31] and Delimi River^[32] were reported to have been produced through weathering but the mineralogical compositions of Nahuta Clays indicates predominantly hydrothermal alteration and partly through weathering.

The top part of Nahuta clay profile (**Figure 7**) shows increase in the concentration of Na₂O and is against the expected gradual decrease in Na₂O concentration that shows destruction of plagioclase feld-spar and removal due to weathering ^[19]. This indicates addition of Na₂O from other sources. The decrease in Na₂O composition from NA 1 to NA 4 (**Figure 7**) is similar to the work of Nesbitt et al. ^[33] where Na was removed from a modern weathering profile formed on Toorongo granodiorite in Australia and granitic rocks from southwestern Nigeria ^[34,35]. The observed K₂O values (**Figure 7**) show a gradual decrease from NA1 to NA 4 indicating weathering ^[19] while the NA

5 shows an increase in K_2O (**Figure 8**) values and this possibly indicates addition of K from hydrothermal sources ^[36].

The SiO₂ contents show a gradual decrease from NA1 to NA5 (**Figure 8**) and is consistent with the predicted decrease in SiO₂ composition during weathering. This indicates weathering in Nahuta area and is similar to the report of Nesbitt et al. ^[33] on chemical processes of alkalis and alkali earth elements during continental weathering. CaO value shows an upward decrease up-profile from NA1 to NA5 (**Figure 8**) attesting to the weather in the area. The concentrations of SiO₂(45.18–65.1 wt%) and Al₂O₃ (24.09–36.77 wt%) suggest that Nahuta Clays are hydrated siliceous aluminosilicate ^[37].

 Al_2O_3/TiO_2 ratio exhibits a lot of variations (**Table 1**) and is inconsistent with the predicted fairly constant Al_2O_3/TiO_2 ratio, suggesting other alteration processes in addition to weathering ^[38]. There was a slight increase in Al_2O_3 composition from NA 1 to NA 4 (**Figure 8**) followed by a decrease in Al_2O_3 content (NA 5). This increase in Al_2O_3 composition along the profile indicates preferential translocation of Al-rich phases ^[27]. Nahuta Clay shows an increase in MgO composition from NA1 to NA5 (**Figure 8**) suggesting addition of MgO from other sources since MgO is expected to decrease up-profile ^[36]. MgO shows enrichment in Nahuta area and is in contrast to the report of Schau et al. ^[25] on weathering of Toorongo granodiorite where negligible amount of Mg was removed from the system. The relative decrease in TiO₂ composition of Nahuta clay from NA 1 to NA 4 (**Figure 8**) followed by an increase in TiO₂ composition at the topmost sample (NA 5) suggesting a source of TiO₂ probably from hydrothermal fluids ^[39].

The values of Ba, Sr and Rb deviate from the trends of decrease up-profile from NA1 to NA5 (**Figure 9**) that would have suggested weathering. The deviations in Ba, Rb and Sr are associated with hydrothermal alterations. The fractionation of Sr and Ba can result from the selective weathering of plagioclase and K-feldspar^[40]. A depletion of Ba could be due to recrystallization of clays and progressive destruction of feldspars^[41]. Rb with respect to K is preferentially retained in the weathered illite^[42,43].

The little variations in the values of Zr and Hf (**Figure 10**) could be as a result of local heterogeneity of the protoliths. The values of Zr and Hf (**Table 3**) indicate occurrence of zircon in the protoliths ^[44,45]. The value of Nb ranges from 166.1 to 682.2 ppm and Ta value ranges from 257.3 to 466.8 ppm (**Table 3**). The values of Nb and Ta obtained from Nahuta area are indicative of titanite and columbite in the protoliths ^[46,47]. The value of Th ranges from 19.0 to 47.3 ppm and U ranges from 10.9 to 19.6 ppm (**Table 3**). The values of Th and U are relatively constant, indicating that they are immobile during weathering and were not introduced by hydrothermal fluids ^[48].

The CIA values (96.68–99.81) are higher than CIA values of 45 to 55 according to studies ^[49–52] that are indicative of lack of weathering. The CIA values are suggestive of weathering in the area. This signifies the occurrence of weatherin the Nahuta area.

5. Conclusions

The provenance of Nahuta Clay could be associ-

ated with hydrothermal alteration of granitic protoliths as indicated by quartz, albite, kaolinite and illite in the mineralogical compositions of Nahuta Clay. The occurrence of osumilite in Nahuta Clay attests to hydrothermal alteration in the area.

The SiO_2 and CaO contents along the profile show a gradual decrease from the deepest sample to the topmost sample indicating weathering in Nahuta area. The CIA values of Nahuta Clay range from 96.68 to 99.81% and are suggestive of weathering in Nahuta area.

The increase in Na₂O and K₂O concentrations up-profile is against the expected gradual decrease in the values of Na₂O and K₂O up-profile that should reflect destruction of plagioclase and K-feldspar and removal due to weathering. This probably indicates addition of Na₂O and K₂O to the clay deposit from other sources, possibly hydrothermal fluids.

The process of formation of Nahuta Clay was predominantly through hydrothermal alteration and partly through weathering of granitic protoliths based on geochemical and mineralogical compositions.

Author Contributions

S.C. Odewumi: Conceptual framework of the study, geological mapping, gathering of geological data and supervision. M.A. Onimisi: collection of clay samples for geochemical tests. M.O. Adeoye: validation, writing original draft, writing review. A.N. Changde: writing original draft, writing review and editing. B.T. Omoyajowo: interpretation of Geochemical data and manuscript editing.

Conflict of Interest

No conflict of Interest.

Data Availability Statement

The data for the research were obtained from petrographic analysis of rock samples, X-ray Diffraction analysis of the clays and ICP-MS of major and trace elements of the clays.

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