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MAJOR AND TRACE ELEMENTS GEOCHEMICAL CHARACTERISTICS OF NAHUTA CLAY, JOS PLATEAU, NORTHCENTRAL NIGERIA: IMPLICATIONS FOR PALEOWEATHERING PROXY

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ABSTRACT

Nahuta clay occurs between latitudes 9º 29ˡ 05ˡˡ to 9º 30ˡ 42ˡˡ N and longitudes 8º 50ˡ 45ˡˡ to 8º 51ˡ 33ˡˡ E within the Ropp Complex. Representative clay samples were collected at different horizons and subjected to Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis. The present study focuses on the geochemical characteristics of major and trace elements along clay profile and their implications for paleoweathering proxy. SiO_2 contents along clay profile show gradual decrease from the deepest sample to the topmost sample in this order NA1 (65.1wt%), NA2 (62.13wt%), NA3 (45.18wt%), NA4 (48.35wt%) and NA5 (50.52wt%), and were consistent with the predicted decrease in SiO_2 compositions up-profile associated with weathering. This indicates weathering in Nahuta area. The topmost part of clay profile shows increase 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 addition of Na_2O and K_2O to the clay deposit from other sources possibly hydrothermal fluids. Ba, Sr and Rb are expected to decrease in composition up-profile but Ba, Sr and Rb from Nahuta clay deviate from these trends. This suggests that Ba and Rb were introduced to clay profile from hydrothermal fluids. The Chemical Index of Alteration (CIA) values (96.68 - 99.81%) are suggestive of weathering in Nahuta area. This attests that Nahuta clays were derived from weathering of the granitic protoliths and/or influence of hydrothermal fluids.
Keywords: *paleoweathering, alteration, weathering, profile and deposit*

INTRODUCTION

Nahuta clay is located in the Ropp Complex of Younger Granite Province in northcentral Nigeria (Figure 1). Weathering of crystalline rocks depends on the amount of rainfall and heat which supports the depletion of alkali and alkaline earth elements (Sheldon *et al*., 2002). According to Wilson (1994) potassium can be removed during weathering but to a lesser extent than sodium. Representative samples derived from geochemical composition of soils are useful tools for palaeoclimatic interpretation (Hamer *et al*., 2007).

The observed geochemical characteristic of paleoweathering profiles is the sum of the impacts of weathering processes, diagenesis and hydrothermal alteration (Schau and Henderson, 1983; Rye and Holland, 1998; Ohmoto, 1996). High field strength elements (HFSE) are resistant to weathering and are of importance in provenance studies (Middelburg *et al*., 1988). The ions of HFSE are relatively mobile in strongly acidic solutions (Baes and Mesmer, 1976). Geochemical features observed throughout paleoweathering sections are products of weathering, diagenesis and metamorphism (Nesbitt and Young, 1982).

According to Maynard (1992), in order to provide information about a weathered profile, the section must occur as an in situ product of weathering not allochthonous. The effects of weathering in Nahuta area have not been reported but clay minerals such as illite, smectite and kaolinite were identified in the area and these clay minerals could as well be produced by chemical weathering (Odewumi, 2016). There are limited reports on major and trace elements geochemical characteristics of Nahuta clays. The present study focuses on the application of geochemical characteristics of major and trace elements along clay profile and their implications for paleoweathering proxy.

MATERIALS AND METHOD

The representative clay samples were collected using chisel from the mining pits at different horizons from the deepest to the topmost part of Nahuta clay deposit, corresponding to macroscopic features. The variations in grain sizes, chemical properties and mineralogical compositions were observed and adopted in the identification of different horizons. The samples collected along the clay profile were placed in different sample bags and labelled with appropriate sample number. The thickness of each horizon was measured using a measuring tape. The samples were shipped from Nahuta clay deposit to the Laboratory for sample preparation and geochemical analysis.

The samples were air-dried at room temperature in the Laboratory to remove moisture and the dried samples were ground to powdered form using agate mortar and pestle. Two 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 Nahuta area were subjected to ICP-MS analysis at Acme Laboratory Ltd, Vancouver, Canada. The clay samples were analyzed for major oxides (SiO_2, TiO_2, Al_2O_3, $Fe_2O_{3(T)}$, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Cr_2O_3, 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= $[Al_2O_3/(Al_2O_3 + Na_2O + K_2O + CaO)]$ (Nesbitt and Young (1982)**.**

RESULTS AND DISCUSSION

Field Characteristics of Nahuta Clay

Nahuta clay extensively overlies the Basement and is underlain by porphyritic granite and microgranite while older basalt is the youngest rock unit overlying the

Younger granites and Nahuta clay deposit. Three groups of rocks have been identified in Nahuta area by Odewumi et al. (2015) 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 Ropp Complex of Younger Granite province of northcentral Nigeria.

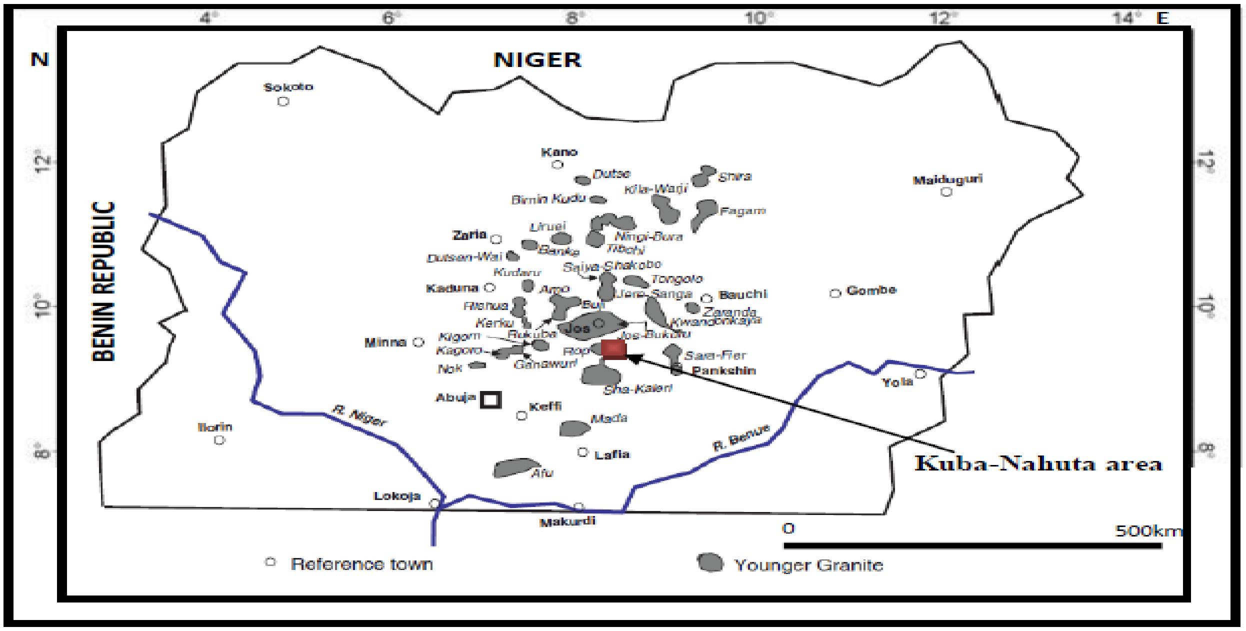

Figure 1: Location of the Younger Granites Complexes in northern Nigeria showing Kuba-Nahuta area (Odewumi *et al.*, 2015)

Sampling was carried out at main pit of Nahuta Clay and the pit has a depth of about 20 to 22 m, which, in places extends to 25 m. The deposit can be divided into four horizons (Fig. 3): 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. The variegated reddish clay horizon is overlying the whitish kaolin horizon (Fig. 4) with thickness ranging from 5.0 to 6.6 m which in turn is overlying the light grey horizon with thickness ranging from 5.5 m onwards until weathered Basement is reached. The overburden encountered was lateralized ironstone with an average thickness of 1.5 m.

Geochemistry

The result of the major oxide compositions of Nahuta clay is presented in Table 1 while trace elements compositions is Presented in Table 2. SiO_2 values ranges from 45.18 to 65.1 weight percent (wt.%), Al_2O_3 value ranges from 24.09 to 36.77 (wt.%). Fe_2O_3 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 (wt.%), Na_2O varies from < 0.01 to 0.05 (wt.%), K_2O varies from 0.04 to 0.99 (wt.%) and MnO varies from < 0.01 to 0.02 (wt.%) respectively. The concentrations of SiO_2 (45.18 - 65.1 wt.%) and Al_2O_3 (24.09 - 36.77 wt%) suggest that Nahuta clays are hydrated siliceous aluminosilicate (Emofurieta *et al*., 1992).

Sample number NA 1 represents the deepest sample while sample number NA 5 represents the topmost sample as presented in Figure 3. The values of CaO, Na_2O, K_2O and TiO_2 (wt%) from Nahuta clays were plotted against depth from the deepest sample to the topmost sample as shown in Figure 5 while the values of SiO_2, Al_2O_3, Fe_2O_3 and MgO (wt%) of Nahuta Clay were plotted against depth from the deepest sample to the topmost sample are shown in Figure 6.

The values of Ba, Sr and Rb in Nahuta Clay (ppm) from Nahuta clays (Table 2) were plotted against depth from the deepest sample to the topmost sample as shown in Figure 7 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 8.

The CIA values ranges from 96.68 to 99.81% (Table 1). The CIA values (96.68-99.81) are higher than the CIA values of 45 to 55 according to Depetris and Probst (1998) that are indicative of lack of weathering. The CIA values are suggestive of weathering in the area. This signifies occurrence of weathering in Nahuta area.

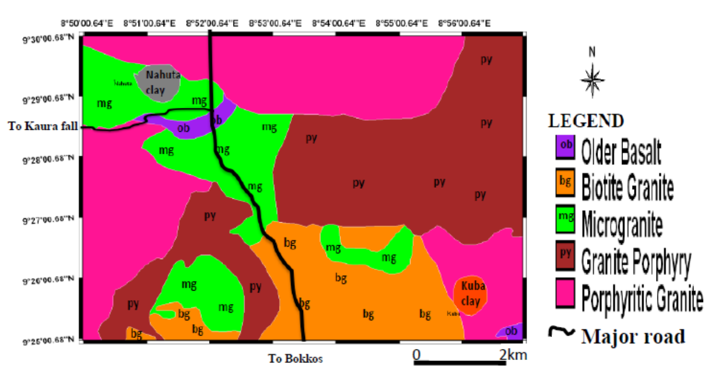

Figure 2: Geological map of Kuba-Nahuta area, Jos Plateau (Odewumi *et al*., 2015).

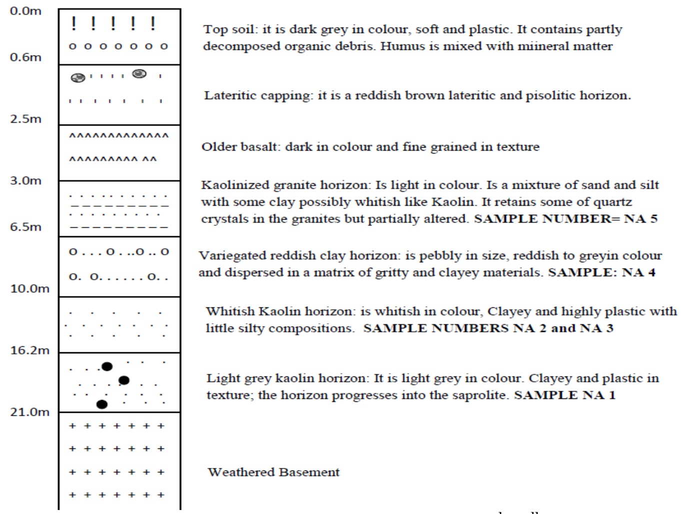

Figure 3: Weathering Profile of Nahuta Clay (Longitude 8° 51' 12'' E; latitude 9° 29' 22'' N; Elevation 1,217 m).

Figure 4: Mining face of Whitish kaolin from Nahuta clay

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

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_2O	0.02	<0.01	<0.01	<0.01	0.05
K_2O	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_2O_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_2O_3t/TiO_2	19.75	34.5	54	12	9.82
Na_2O/TiO_2	0.5	0.5	0.2	0.25	0.18
K_2O/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

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

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
Ta	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

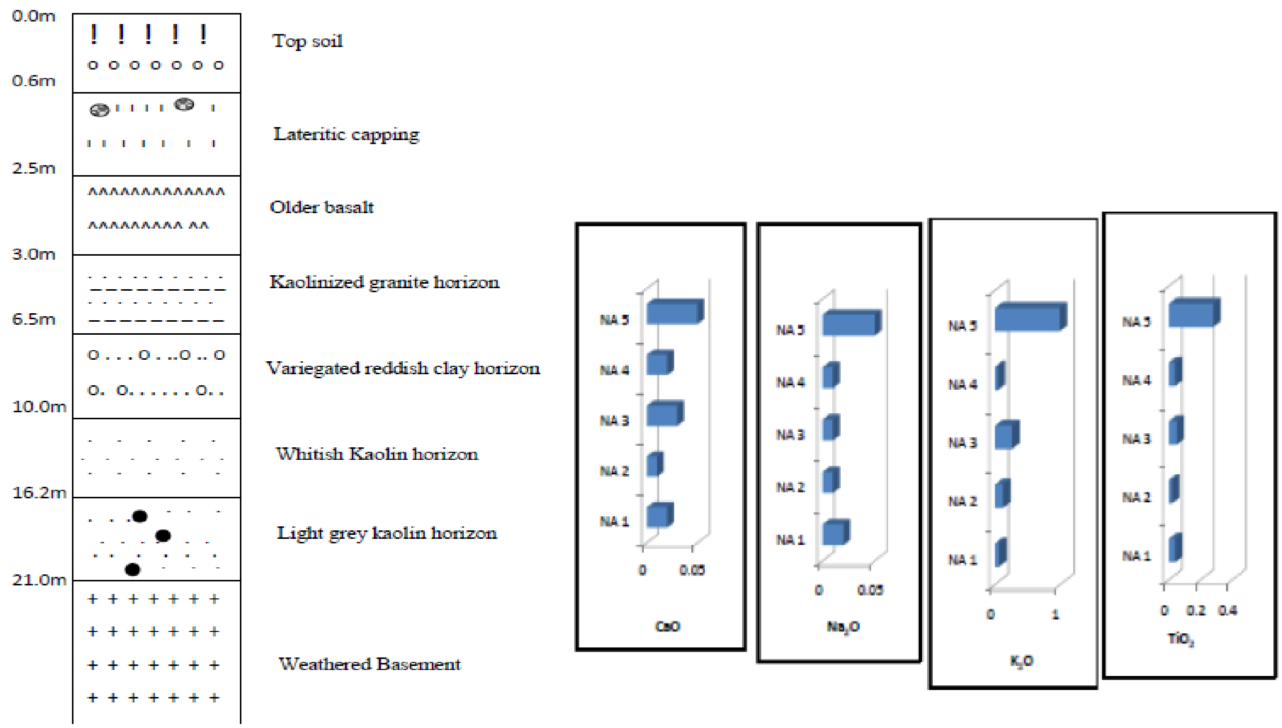

Figure 5: Geochemical characteristics of CaO, Na_2O, K_2O and TiO_2 (wt%) for Nahuta clays

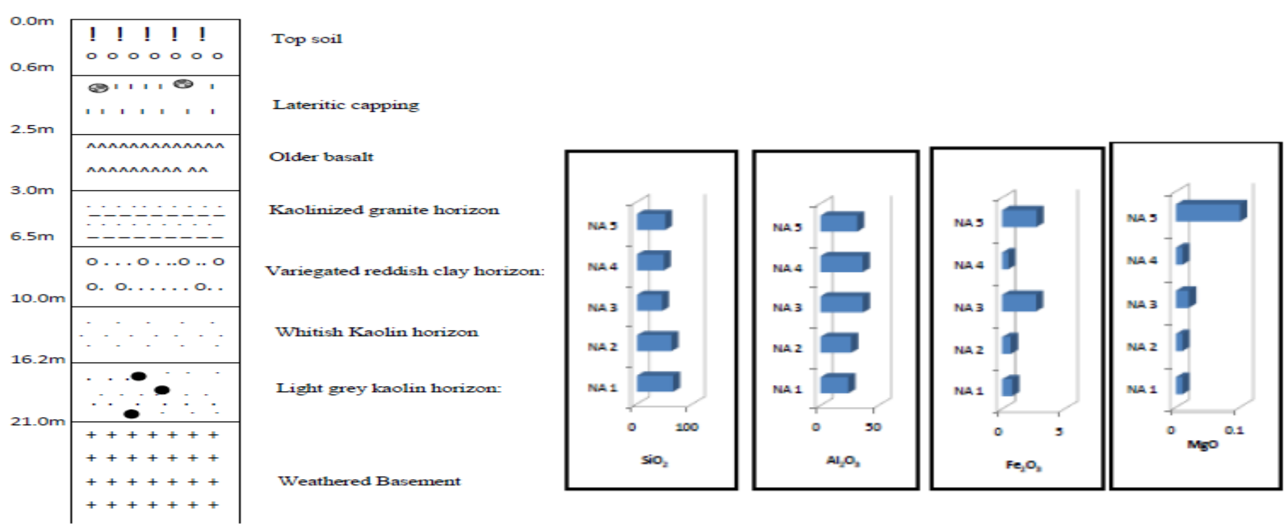

Figure 6: Geochemical characteristics of SiO_2, Al_2O_3, Fe_2O_3 and MgO (wt%) for Nahuta Clays

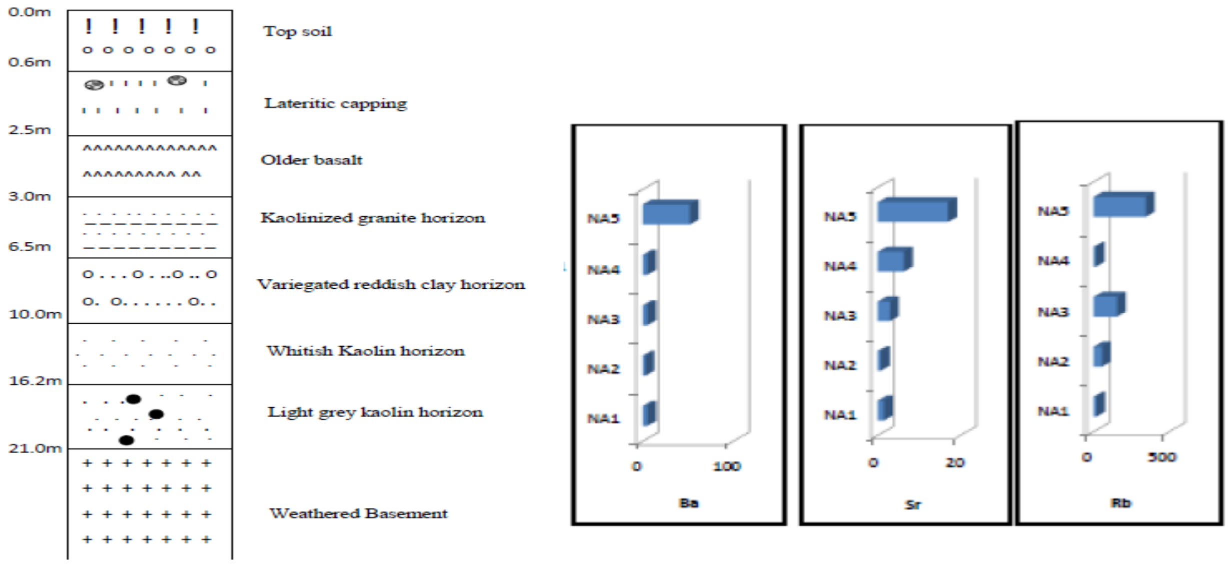

Figure 7: Geochemical characteristics of Ba, Sr and Rb (ppm) for Nahuta Clay

Figure 8: Geochemical characteristics of Zr, Th and Nb (ppm) for Nahuta Clay

DISCUSSION

The topmost part of Nahuta clay profile (Fig. 5) shows increase in the concentration of Na_2O and is against the expected gradual decrease in Na_2O concentration that shows destruction of plagioclase feldspar and removal due to weathering (Nesbitt and Young, 1982). This indicates addition of Na_2O from other sources. The decrease in Na_2O composition from NA 1 to NA 4 (Fig. 5) is similar to the work of Nesbitt et al. (1980) where sodium was removed from a modern weathering profile formed on Toorongo granodiorite in Australia. The observed K_2O values (Fig. 5) show gradual decrease from NA1 to NA 4 indicating weathering (Nesbitt and Young, 1982) while the NA 5 shows increase in K_2O (Fig. 5) values and this possibly indicates addition of K from other sources (Rainbird *et al.*, 1990).

The SiO_2 contents show gradual decrease from NA1 to NA5 (Fig. 6) and consistent with the predicted decrease in SiO_2 composition during weathering. This indicates weathering in Nahuta area and is similar with the report of Nesbitt et al. (1980) on chemical processes of alkalis and alkali earth elements during continental weathering. CaO value shows an upward decrease up-profile from NA1 to NA5 (Fig. 6) attesting to weathering in the area.

Al_2O_3/TiO_2 ratio exhibits a lot of variations (Table 1) and inconsistent with the predicted fairly constant Al_2O_3/TiO_2 ratio suggesting other alteration processes in addition to weathering (Young and Nesbitt, 1998). There was a slight increase in Al_2O_3 composition from NA 1 to NA 4 (Fig. 6) followed by a decrease in Al_2O_3 content (NA 5). This increase in Al_2O_3 composition along the section indicates preferential translocation of Al-rich phases (Panahi *et al.*, 2000).

Nahuta clay shows an increase in MgO composition from NA1 to NA5 (Fig. 6) suggesting addition of MgO from other sources since MgO is expected to decrease up-profile (Rainbird et al. 1990). MgO shows enrichment in Nahuta area and is in contrast to the report of Nesbitt et al. (1980) on weathering of Toorongo granodiorite where magnesium was removed from the system. The relative decrease in TiO_2 composition of Nahuta clay from NA 1 to NA 4 (Fig. 6) followed by increase in TiO_2 composition at the topmost sample (NA 5) suggesting a source of TiO_2 probably from hydrothermal fluids (Sugitani et al., 1996).

The values of Ba, Sr and Rb deviate from the trends of decrease up-profile from NA1 to NA5 (Fig. 7) 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 (Puchet, 1972). The reduction in Ba values could be as a result of recrystallization of clays and progressive destruction of feldspars (Heier and Billings, 1970). Rb with respect to K is preferentially retained in the weathered illite (Garrels and Christ, 1965; Middleburg et al., 1988).

The little variations in the values of Zr and Hf (Fig. 8) could be as a result of local heterogeneity of the protoliths. The values of Zr and Hf (Table 2) indicate occurrence of zircon in the protoliths (Levinson 1980; Baes and Mesmer, 1976). The value of Nb ranges from 166.1 to 682.2 ppm and Ta value ranges from 257.3 to 466.8 ppm (Table 2). The values of Nb and Ta obtained from Nahuta area are indicative of titanite or rutile in the protoliths (Deer et al., 1966; Goldschmidt, 1954). The value of Th ranges from 19.0 to 47.3 ppm and U ranges from 10.9 to 19.6 ppm (Table 2). The values of Th and U are relatively constant indicating that they are immobile during weathering and were not introduced by hydrothermal fluids (Deer *et al*., 1966; Braun *et al*., 1990).

CONCLUSION

The SiO_2 and CaO contents along the profile show gradual decrease from the deepest sample to the topmost sample indicating weathering in Nahuta area.

The increase in Na_2O and K_2O concentrations up-profile is against the expected gradual decrease in the values of Na_2O and K_2O up-profile that should reflect destruction of plagioclase feldspar and removal due to weathering. This probably indicates addition of Na_2O and K_2O to the clay deposit from other sources possibly hydrothermal fluids.

The CIA values of Nahuta clay ranges from 96.68 to 99.81%. The CIA values suggest occurrence of weathering in Nahuta area.

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