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GEOCHEMISTRY OF MAJOR ELEMENTAL OXIDES ON A LITHOSEQUENCE IN KADUNA STATE NIGERIA

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ABSTRACT

Geochemistry of major elemental oxides of soils developed on basement complex rocks namely: older granite (OG), migmatite gneiss (MG), mica schist (MS) and quartzites (QZ) was studied in Kaduna State. The contents of major elemental oxides were similar in the soils, except for K_2O and TiO_2 that varied significantly between the soils. Relative weathering intensity showed significant variation in all the major elemental oxides' relative retention in the soils. Thus elemental concentrations and retention were attributed to inheritance from parent rocks and differential weathering (pedogenic age). Two main behavioural groups exist for the major elemental oxides in the soils due to relative accumulation and loss of concentration of elemental oxides. Calcium group (Ca, Si, K and Mn) exhibited loss through leaching and desilication, whereas, Fe group (Fe, Al and Ti) accumulated through illuviation and recrystallization. Relative retention of CaO compared to other elemental oxides was found to be an indicator of pedogenic order in comparing soils developed on different basement complex rocks as parent materials. Several features of the soils such as Si/C ratio, mineral constituents, relative weathering intensity (loss/ gain) and CaO relative retention all indicated order of weather intensity (pedogenic age) as MG > QZ ≥ OG > MS. Sequential order of dominantly retained elemental oxides reflected key constituent of dominant minerals in the different soils.

Key word: Geochemistry, pedogenesis, relative weathering intensity, elemental oxides, basement complex rock.

INTRODUCTION

Nature of parent material is said to profoundly influence the development and characteristics of soils. Differentiation in soil characteristics due to variations in parent material is reffered to as lithosequences. In small regions with uniform climate, the nature of the parent material is probably more important than any other single factor in determining the characteristics and productivity of a soil (Olaitan and Lombin, 1984).

Elemental chemistry has been used widely in pedogenetic studies to identify sources of soil parent materials. It has also been used to evaluate parent material uniformity in soil profile, and to measure losses and gains of elements that result from soil development.

(Bussaca and Singer, 1989). During early pedogenesis, the chemical composition of a soil will be highly controlled by the composition of the geological parent material, whereas the chemical composition of mature soils strongly reflects the effects of weathering environment (Bussaca and Singer, 1989). With time, soil composition diverges progressively from that of the parent material under the influence of pedogenic processes determined by vegetation, topography and, in particular, climate. The divergence may be due to redistribution of elements within soil fabric, between profile horizons and between soils within landscape. The process of elements mobilization and redistributions varied as were affected differently by various pedogenic processes including dissolution of primary minerals, formation of secondary minerals, redox processes, transportation of materials and ion exchange (Thanachit *et al*., 2006).

Pedogenic changes have been assessed using silica-sesquioxide ratio Yakubu and Ojanuga, (2009). Barshad, (1965), and Bussaca and Singer (1989) made use of internal indices to measure weathering and pedogenic development more accurately. Oxides of silicon (Si), titanium (Ti) and zirconium (Zr) total elements have been used as index elements as they have been reported to dominate quartz, rutile and zircon minerals (resistant to weathering) respectively and their choice were based on the presence of index element in both soil and parent material, their resistance to weathering processes and relative immobility (Bussaca and Singer, 1989). The use of index elements used for determination of relative accumulation (gain) and depletion (loss) of elements in soils has been useful in determination of extent of weathering and pedogenic development (age) (Muhs *et al.,* 2001). Several studies reported titanium to be slowly mobilized in soil profiles by mineral weathering hence Bussaca and Singer (1989) suggested the use of Zr as stable index element. Muhs *et al.,* (2001) reported similar trends in relationship and a similar degree of explanation whether Ti or Zr was used as stable index element. Choice of stable index element should therefore be guided by assessment of their relative immobility in soils.

Pedogenic studies using geochemistry cut across major elements (Si, Al, Fe, Mn, Ti, Mg, Ca, Na and K), trace elements (Mo, Cu, Zn, Zr, Ba, Co, Ni, Pb, Sr, Y, Th, U, V, etc), heavy rare earth elements (lanthanide elements; La to Sm) and light rare earth elements (lanthanide elements; Eu to Lu) (Thanachit *et al*., 2006). Geochemistry of iron and aluminium under slightly acid and oxidizing conditions indicates relative accumulation, whereas, mobile cations (Si, Ca, Mg, K, Mn and Na) move to lower position in slope or leached out of soils Kendrick and Graham (2004) similarly reported loss of Si, Na and K, as attributed to loss of feldspar in the soils. They reported that Si loss in surface horizons was adequate to account for pedogenic Si accumulation in subsoils and was equivalent to amount of pedogenic Fe oxide; hence serve as indicator of relative soil age in the soils. Bussaca and Singer (1989) reported more enrichment of Si, K, Ti and Zr with less enrichment of Na, Mg, Al, Ca and Fe in silt fraction of chronosequence in Sacramento Valley, California. The more enriched elements may be associated with resistant minerals present in silt fraction, whereas Fe may have accumulated in clay fraction. Study of soil geochemistry is not only important in pedogenesis, but offers a means by which background levels of heavy metals in soils are defined, thus leading to assessment of their behavior in soils and their input as pollutants (Lasheras Adot *et al*., 2006).

Despite the abundant literature on soils developed on basement complex rocks in many parts of Nigeria (Fagbami, 1981; Esu, 1987; Mosugu, 1989; Mustapha and Fagam, 2007; Fasina et al., 2007), there have been no studies of the chemical composition of soils developed on different basement complexes in

Nigeria. These soils extensively occupy about 98% of the land area of Kaduna State, therefore understanding the content, weathering and pedogenesis of the major elements in these soils will be of values to soil scientists and soil resource managers. The paper therefore reports on the geochemistry of major elemental oxides in soils developed on different parent materials on basement complex rocks in Kaduna State, Nigeria.

MATERIALS AND METHODS

Study Location

The locations for the study area were situated within older granite (OG), quartzite (QZ), mica schist (MS) and migmatite gneiss(MG) basement complexes parent material area, within Northern Guinea Savanna Zone of Kaduna State, Nigeria. The sites lie within latitude $10^{o}27'55.7"N$ to $10^{o}43'43.2"N$ and longitude $06^{o}11'14.0"E$ to $07^{o}39'27.3"E$ (Figure 1). The mean amount of rainfall of the study areas ranged between 1,180 and 1,286 mm/annum. Mean annual evaporation record ranged between 2194 to 2822 mm/ annum. Rainfall was in excess of evaporation in the month of July to September as the peak rainfall occurs in these months. The mean annual temperature ranged between 25.0 and 26.4 ^{o}C.

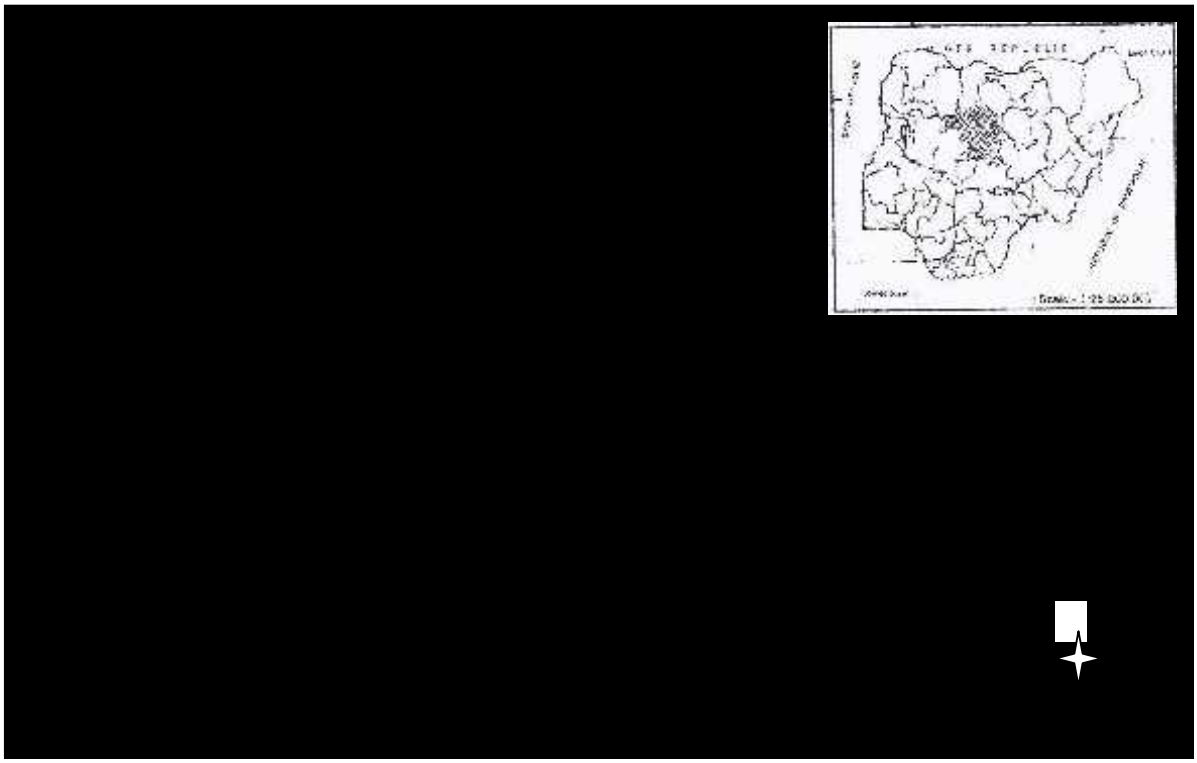


Figure 1 Geological Map of Kaduna State, Nigeria indicating Project Sites (▬) Courtesy: National Bureau of statistics (2009)

Soil Sampling

Profile pits were sited on crestal slope position, dug, described and soils were sampled within pedogenic horizons. The soils were sampled from three profile pits within cultivated fields on each of the four (4) parent material locations.

Laboratory Analysis

The soil samples (< 2 mm) were used to analyze some selected physico-chemical

properties in laboratory. Particle size was determined by hydrometer method. Soil pH was determined in a 1:1 soil/ water. Cation exchange capacity (CEC) was determined by neutral (pH 7.0) NH_4OAc saturation method. Organic carbon (OC) was determined by Walkley-Black dichromate wet oxidation method.

Mineralogical Studies

Determination of minerals was carried out by X-ray diffraction (XRD) analysis at the National Steel and Raw Materials Exploration Agency, Malali, Kaduna. The silt and clay fractions were saturated with magnesium ions after removing organic carbon, sesquioxides and exchangeable bases. Diffraction patterns were obtained using CuKα radiation and a Shimadzu X-ray diffractometer (XRD-6000). The samples were step-scanned between 2 and 45^o 2θ using scanning speed of 4^o min^{-1} at sampling pitch of 0.020^o and a preset time of 0.30 second. Oriented specimens were prepared by air drying on a standard glass slide for the examination.

Total Elemental Oxides Analysis

Modal profile pit of each soil parent material was selected and used for geochemical analysis. The total elemental oxides were determined using energy dispersing X-ray fluorescence (EDXRF) XRF SPEC (Minipal 4) at the National Geoscience Research Laboratories Centre, Barnawa Kaduna. The < 2 mm soil samples were further ground to 150 µm along with their parent rocks and the powdered samples were used for the total elemental oxides analysis. The conditions for analysis set were as followed:

(i) Mo filter at 30 kV for rare earth elements
(ii) Kapton filter at 20kV for Si, Al, P, etc
(iii) Filter (none) at K kV for alkaline and alkaline earth elements.

The contents of major elemental oxides (mostly > 1%) determined were used for the study. The relative intensity of weathering of total elemental oxides was determined after choosing titanium and zirconium, by assessing the more stable and less weatherable element among the two in these soils using total element of least coefficient of variability as the suitable indexing element and titanium was selected (Muhs *et al.*, 2001). The relative gain or loss of element was estimated using relative retained element (Ro) formula Caspari *et al.*, 2006).

$$R_o = \frac{X_h}{X_p} \times \frac{Ti_p}{Ti_h}$$

Where, X_h = element of interest in horizon to estimate
X_p = element of interest in parent material (rock)
Ti_h = index element (Titanium) in horizon to estimate
Ti_p = index element (Titanium) in parent material (rock).
R_o >1 = Relative accumulation of element (Gain)
1 = No relative accumulation or depletion of element
<1 = Relative depletion of element (Loss)
0 = Element absent in soil.

Statistical Analysis

Descriptive statistics were used to assess soil properties. Two factor analysis of variance (ANOVA) was used to analyse the variation between the parent materials and between the surface and subsoil horizons. Correlation analysis was used to determine relationship between the free oxides and soil properties (SPSS Statistics 17.0).

RESULTS AND DISCUSSIONS

Soil Physico-Chemical Properties

The soils were generally deep to very deep (135 – 190cm). The depth of some soils on quartzites (QZ1) and mica schist (MS2 and MS3) were restricted due to parent materials encountered between 14cm and 72cm. Soils on migmatite gneiss all had presence of plinthite within 48 - 172cm depths, and earlier studies by several workers (Raji, 1995; Yaro 2005; Idoga *et al.*, 2007) attributed extent of soil depth to parent material, plinthite, erosion and slope of the area.

Sand dominated the particle size fraction of the fine earth (< 2mm) portion in all the soils formed from the different parent materials (Table 1). This is in harmony with previous

studies in soils formed on basement complex rocks in different regions of Nigeria (Odunze, 2006; Fasina *et al.*, 2007; Obi and Akinbola, 2009; Ande, 2010). The mean clay content in subsurface horizon was three times greater than the mean surface value. The increase in clay with soil depth had been attributed to clay translocation and erosion in surface horizon (Raji, 1995; Obi and Akinbola, 2009). The mean values of silt/ clay ratio of all the soils were higher than the 0.15 critical value considered to be highly or intensively weathered (Yakubu and Ojanuga, 2009), hence soils in this study were considered to be fairly to moderately weathered. Weathering intensity significantly increased in order of soils on MS < OG < QZ < MG

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Table 1: Range and means of selected physical and chemical properties of soils of the studied areas.

Parameters	Unit	Older Granite		Quartzites		Mica-Schist		Mignatite	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
Sand	g kg^{-1}	271-651	482	371-771	547	398-691	515	271-771	511
Silt	g kg^{-1}	147-327	229	107-227	156	187-367	248	107-367	204
Clay	g kg^{-1}	122-442	289	82-462	298	102-329	237	109-449	311
Si/C	-	0.44-2.30	0.97	0.27-2.77	0.82	0.69-3.60	1.25	0.39-2.50	0.79
pH	-	5.49-6.29	5.83	5.78-6.27	6.02	5.84-6.44	6.09	5.30-6.90	6.05
CEC	Cmol(+)g kg^{-1}	5.6-9.9	7.90	4.8-15.3	8.97	5.4-14.3	8.33	5.4-7.9	6.46
OC	g kg^{-1}	1.20-8.78	5.66	0.40-11.57	4.56	0.80-7.98	3.51	0.60-7.78	3.37

The chemical properties of soils indicated strongly acid to neutral pH (H_2O) (5.30 - 6.90) and were within range reported on soils on basement complexes in different parts of Nigeria (Raji and Mohammed, 2000; Fasina *et al.,* 2007). The soils were rated low to high in CEC (NH_4OAc) with moderate base saturation influencing their classification as Alfisols. Parent materials significantly influenced forms of CECs and base saturation, with most of the least significant means found in soils on MG indicating more leaching in soils on MG (Table 1).

The soils were generally low in organic carbon (range 0.40 and 11.57 gkg^{-1}). The low content of OC was attributed to continuous cultivation, bush burning, high rate of mineralization, crop removal for livestock feeding, fuel wood, fencing and building purposes without incorporation (Odunze, 2006).

Major Elemental Oxides and Relative Weathering Intensity

The content of major elements from X - ray fluorescence in the soils was dominated by SiO_2 (ranged between 46.1 and 78.7%) followed by Fe_2O_3 and Al_2O_3 (5.20 to 22.85% and 7.60 to 22.00% respectively). Calcium oxide, K_2O, MnO and TiO_2 were all less than 5.20% (Table 2). Most of the major elemental oxides of the soils formed in the different basement complex parent material did not significantly vary, except for K_2O and TiO_2 (Table 3). Mean values of K_2O in soils on MS and QZ were statistically at par and significantly higher than soils on OG and MG which were at par. The mean content of TiO_2 of soils developed on MG, OG and QZ were at par, but MG was significantly higher in TiO_2 than MS. However, soils on MS were at par with OG and QZ in mean content of TiO_2. The trend of variation of K_2O and TiO_2 in the soils indicated that with advancement in pedogenesis K_2O tend to be lost in soil probably via leaching and TiO_2 through accumulation as it is resistant to weathering, and similar trend was reported by Caspari *et al.,* (2006) and Thanachit *et al.,* (2006).

Hence, these soils exposure to pedogenic processes ranked in order of MS < OG ~ QZ < MG and similar to the trend of Si/C ratio in these soils. Silicon oxide, CaO, MnO and K_2O had similar distribution pattern (Table 2) showing irregular decrease with soil depth and might be attributed to desillication of SiO_2 in the subsoil horizons, and biocycling and leaching of CaO, MnO and K_2O in these soils.

Table 2: Percentage (%) Major elemental oxides of soils studied

Pedon	Depth (cm)	SiO_2	Al_2O_3	CaO	K_2O	TiO_2	Fe_2O_3	MnO	ZrO_2
Soils on Older Granites:			**Pedon OG 1**						
Ap	0-26	72.2	8.90	0.47	1.14	2.02	5.60	0.06	0.89
Bt1	26-75	54.4	20.0	0.37	1.01	2.25	20.40	0.07	0.72
Bt2	75-119	49.4	18.0	0.31	0.70	2.04	21.99	0.10	0.76
BC	119-183	48.6	20.0	0.31	0.58	2.08	21.17	0.03	1.10
P. Rock		54.4	10.0	4.49	7.73	2.38	14.70	0.13	0.10
Soils on Quartzites:			**Pedon QZ 2**						
Ap	0-19	75.2	9.40	0.55	2.72	1.57	9.57	0.16	0.63
Bt1	19-51	53.7	19.0	0.37	2.26	2.12	17.33	0.09	0.39
Bt2	51-84	45.3	22.0	0.33	2.07	2.39	22.22	0.07	0.46
Bt3	84-139	46.1	22.0	0.33	2.10	2.25	21.44	0.06	1.00
Btc	139-187	46.1	22.0	0.33	2.20	2.35	22.85	0.09	0.20
P. Rock		91.8	2.40	0.19	0.13	0.01	4.120	0.01	Trace
Soils on Mica Schists:			**Pedon MS 3**						
Ap	0-19	78.7	8.92	0.57	2.01	1.70	5.20	0.09	0.30
Bt1	19.42	58.6	17.0	0.40	3.43	1.78	14.30	1.00	0.47
Bt2	42-96	49.6	16.0	trace	5.10	1.99	18.70	0.05	0.41
BC	96-168	55.2	18.0	trace	2.37	1.89	17.65	0.04	3.00
P. Rock		43.3	19.1	0.001	12.7	2.25	14.69	0.11	0.37
Soils on Migmatite Gneisses:			Pedon MG2						
Ap	0-18	72.3	7.60	1.97	0.77	2.24	7.04	0.10	1.00
AB	18-44	54.1	18.0	0.44	0.52	2.21	16.00	0.03	0.73
Bt1	44-78	51.0	18.0	0.39	0.55	2.48	17.70	0.01	0.82
Bt2	78-123	54.3	18.0	0.35	0.55	2.46	16.00	0.01	0.79
BCcv	123-167	48.9	19.0	0.28	0.42	2.07	22.28	0.03	0.73
P. Rock		65.0	16.1	4.29	2.68	0.43	5.35	0.07	0.02

Table 3: Ranking of mean percent (%) of Major elemental oxides of soils studied

Element Oxide	Older Granites	Quartzite	Mica Schist	Migmatite Gneiss	SE±	LOS
SiO_2	56.23	53.28	60.53	56.12	2.38	NS
Al_2O_3	16.73	18.48	14.98	16.12	0.74	NS
CaO	0.37	0.38	0.24	0.69	0.75	NS
K_2O	0.86b	2.27a	3.23a	0.56b	0.42	**
TiO_2	2.10ab	2.14ab	1.84b	2.29a	0.10	*
Fe_2O_3	17.29	18.68	13.96	15.80	1.60	NS
MnO	0.066	0.095	0.069	0.035	0.16	NS

LOS (P): NS > 0.05, * ≤ 0.05, ** ≤ 0.01

Note: Means followed by the same letters in the rows are not significantly different at 5% LOS.

Silicon oxide significantly correlated with CaO and MnO (Table 4), thus affirming similarity in their distribution pattern. A related group was reported by Thanachit et al. (2006) as they were mobile and tend to loss, and was referred to as Ca group (Ca, Si, K and Mn).

Table 4: Correlation matrix for major elemental oxides of soils studied

	SiO_2	Al_2O_3	CaO	K_2O	TiO_2	Fe_2O_3	MnO
SiO_2	-						
Al_2O_3	-0.946***	-					
CaO	0.541*	-0.596**	-				
K_2O	0.023	-0.058	-0.062	-			
TiO_2	-0.593**	0.528*	-0.080	-0.473*	-		
Fe_2O_3	-0.961***	0.937***	-0.771***	-0.134	0.474*	-	
MnO	0.474*	-0.424	0.338	0.562*	-0.566*	-0.324	-

Titanium oxide content was fairly constant with increase in depth of soils and might be attributed to its resistant to weathering and immobility, thus characterizing TiO_2 as a more favorable indexing element in these soils (Muhs *et al.*, 2001). Aluminum oxide and Fe_2O_3 contents were similar in distribution pattern and were significantly and positively correlated (r = 0.937***). Their contents increased irregularly with increase in soil depth and sharp increase was noted between surface and subsoils. The significant accumulation of Al_2O_3 and Fe_2O_3 in the subsoil horizons might be attributed to their illuviation, along with clay and recrystallization with advancement in pedogenesis as buttressed by the significant correlation between clay and Al_2O_3, Fe_2O_3 and TiO_2 (r = 0.868***, 0.753*** and 0.774 respectively). The geochemical accumulation and distribution trend exhibited by these elements warrant being grouped as Fe group (Fe, Al and Ti).

Silicon oxide had significant negative correlation with aluminum oxide, titanium oxide and iron oxide, indicating that SiO_2 decreased relative to increase of these elements in the soils. Caspari *et al.,* (2006) reported on metamorphic soils that were largely illitic, that decrease in SiO_2 resulted in increase in Al_2O_3 and Fe_2O_3 in the soils. Aluminum oxide was noted to significantly correlate positively with iron and titanium oxides (r = 0.937***and 0.528* respectively) and may be associated with similarity in their distribution pattern. As soils advance in their development, Al_2O_3 and Fe_2O_3 have been reported to be transported and accumulated within the subsoil horizons (allitization and ferritization respectively) Buol *et al.*, 1997). Allitization (Al_2O_3 enrichment) ferritization (Fe_2O_3 enrichment) and desillication (SiO_2 depletion) processes occur in soils simultaneously (Mohr *et al.,* 1972; Buol *et al.,* 1997), thus reflects the significant negative correlation between Al_2O_3, Fe_2O_3 with SiO_2 (Table 4).

Examination of relative weathering intensity showed that relative depletion of major elemental oxides was more pronounced in soils on MG and QZ compared to OG and MS soils (Table 5) and may be attributed to inherent nature of the parent materials and their exposure to pedogenic processes. Potassium oxide and MnO were relatively depleted in all the soils, whereas, SiO_2, Al_2O_3, CaO and Fe_2O_3 were relatively depleted but with accumulation in MS (SiO_2, CaO and Fe_2O_3) and OG (SiO_2, Al_2O_3, and Fe_2O_3) (Table 6). The trend of relative retention of major element tends to indicate soils on MS had least weathering intensity followed by soils on OG and QZ, and soils on MG considered to be the most weathered.

Relative intensity of weathering of SiO_2, Al_2O_3 and Fe_2O_3 shows that soils on OG and MS were relatively enriched, whereas QZ and MG soils were relatively depleted (Table 5). Kendrick and Graham (2004) attributed SiO_2, enrichment (accumulation) in soil to increase in silication. The present study found that SiO_2, Al_2O_3 and Fe_2O_3 relative enrichment (OG and MS soils) in soils depended more on

initial weathering of parent material and with advancement in pedogenesis relative depletion dominated the soils (QZ and MG). Similarly, Thanachit *et al*. (2006) attributed early geochemical differentiation to parent material composition and chemical composition of matured soils to weathering environment.

Table 5: Relative retention (Gain/Loss) of major elemental oxides of soils studied

Pedon	Depth (cm)	SiO_2	Al_2O_3	CaO	K_2O	Fe_2O_3	MnO
Soils on Older Granites:			**Pedon OG 1**				
Ap	0-26	1.564	1.049	0.123	0.174	0.449	0.562
Bt1	26-75	1.058	2.116	0.087	0.138	1.468	0.570
Bt2	75-119	1.066	2.100	0.081	0.106	1.745	0.897
BC	119-183	1.022	2.288	0.079	0.086	1.648	0.264
Soils on Quartzites:			**Pedon QZ 2**				
Ap	0-19	0.005	0.025	0.018	0.133	0.015	0.255
Bt1	19-51	0.003	0.037	0.009	0.082	0.020	0.103
Bt2	51-84	0.002	0.038	0.007	0.067	0.023	0.074
Bt3	84-139	0.002	0.041	0.008	0.072	0.023	0.070
Btc	139-187	0.002	0.036	0.007	0.072	0.024	0.100
Soils on Mica Schists:			**Pedon MS 3**				
Ap	0-19	2.406	0.618	754.4	0.209	0.469	1.023
Bt1	19.42	1.711	1.125	505.6	0.341	1.230	1.149
Bt2	42-96	1.295	0.947	0.113	0.454	1.440	0.493
BC	96-168	1.518	1.122	0.119	0.222	1.430	0.476
Soils on Migmatite Gneisses:			Pedon MG 2				
Ap	0-18	0.214	0.091	0.088	0.055	0.253	0.266
AB	18-44	0.162	0.218	0.020	0.038	0.582	0.083
Bt1	44-78	0.136	0.194	0.016	0.036	0.574	0.025
Bt2	78-123	0.146	0.195	0.014	0.036	0.523	0.025
BCcv	123-167	0.156	0.245	0.014	0.033	0.865	0.089

Table 6: Ranking of mean of relative retention (Gain/Loss) of major elemental oxides of soils studied

Element Oxide	**Older Granites**	**Quartzite**	**Mica Schist**	**Migmatite Gneiss**	**SE±**	**LOS**
SiO_2	1.455a	0.003d	1.312b	0.162c	0.06	***
Al_2O_3	1.888a	0.035d	0.813b	0.188c	0.04	***
CaO	0.915b	0.010b	315.11a	0.030b	87.56	**
K_2O	0.126b	0.085bc	0.307a	0.040c	0.04	**
Fe_2O_3	1.327a	0.021c	1.142a	0.559b	0.08	***
MnO	0.573a	0.120b	0.785a	0.098b	0.15	**

LOS (P): NS > 0.05, * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001

Note: Means followed by the same letters in the rows are not significantly different at 5% LOS.

On Comparing the relative intensity of weathering statistically, older granite soil was significantly more pronounced in relative accumulation of SiO_2 compared to all other soils (MS, MG and QZ). All the soils differed significantly from each other in the intensity of their relative weathering of SiO_2, Al_2O_3 and Fe_2O_3 in the sequence of OG > MS > MG > QZ (Table 6). Difference in horizons were found to significantly influence relative retention of major elements (SiO_2, Al_2O_3 and Fe_2O_3) indicating significant desilication, allitization and fertilization in subsoils than surface horizons (Table 7).

Table 7: Ranking of mean of relative retention (Gain/Loss) of major elemental oxides

Parameter of soils Studied	Surface Horizon	Subsurface Horizon	SE±	LOS
SiO_2	1.047a	0.591b	0.38	***
Al_2O_3	0.446b	0.764a	0.24	***
CaO	188.56	36.16	112.34	NS
K_2O	0.143	0.127	0.03	NS
Fe_2O_3	0.297b	0.828a	0.14	***
MnO	0.527	0.316	0.13	NS

LOS (P): NS > 0.05, * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001,

Note: Means followed by the same letters in the rows are not significantly different at 5% LOS.

The whole trend of relative weathering intensity indicated by mean relative retention of major element oxides in the soils were ranked in the following sequence:

Soils on Older granite	$Al_2O_3 > SiO_2 > Fe_2O_3 > CaO > MnO > K_2O$
Soils on Quartzite	$MnO > K_2O > Al_2O_3 > Fe_2O_3 > CaO > SiO_2$
Soils on Mica schist	$CaO > SiO_2 > Fe_2O_3 > Al_2O_3 > MnO > K_2O$
Soils on Migmatite gneiss	$Fe_2O_3 > Al_2O_3 > SiO_2 > MnO > K_2O > CaO$

The trend of major element oxides showed that relative retention of elements was similar between soils on OG and MS, except that there was an interchange of position in the sequence between Al_2O_3 and CaO. Calcium oxide was the most relatively retained element in MS and imply that less weathering and leaching occurred in this soil, as calcium have been reported to be most sensitive to weathering and leaching and was used as indicator for pedogenic age (Jones and Beavers, 1966), this indicates that soil on MS was the youngest in pedogenic development. The relative retention of CaO more than other elements in the soils on MS indicate its less exposure to weathering, hence the wide range and types of mineral dominating its clay fraction (muscovite, kaolinite and diaspore). Aluminum and Si were the most relatively retained oxides in soils on OG and correlated kaolinite and halloysite as dominant minerals found in the clay fraction. Manganese and Fe oxides were the most relatively retained elements in soils on QZ and MG respectively, and correlated diaspore and kaolinite minerals dominating the soils as were the most weathered soils. Following position of CaO in relative retention sequence of each soil in the various parent materials, order of pedogenic development of the soils is considered to be in order of MS < OG < QZ < MG. The relative retention sequence of major elemental oxides for soils on MG indicated dominance of Fe_2O_3, Al_2O_3 and SiO_2, also indicated soils on MG to be the most weathered among all the soils. This affirmed previous reports that as weathering advances, relative retention of sesquioxides and their minerals dominate soils (Yakubu and

Ojanuga, 2009). The sequences showed that dominantly retained elemental oxides were reflection or key constituent of dominant minerals.

CONCLUSION

The study showed that contents of major elemental oxides were similar in the soils, except for K_2O and TiO_2 that were significantly varied between the soils. Relative weathering intensity was used as index of soil development and there was significant variation in the relative retention (relative accumulation or depletion) of all the major elemental oxides in the soils. Thus parent materials significantly influenced relative weathering intensity of these elements in the soils studied. The trends of relative retention of the major total elemental oxides correlated with the dominant minerals constituting the different soils.

Two main behaviour groups exist for the major elemental oxides in the soils due to relative accumulation and loss of concentration of elemental oxides. Calcium group (Ca, Si, K and Mn) exhibiting loss through leaching and desilication, whereas, Fe group (Fe, Al and Ti) accumulated through illuviation and recrystallization). Relative retention of CaO compared to other elemental oxides was found to be an indicator of pedogenic order in comparing soils developed on different basement complex rocks as parent materials.

Several features of the soils such as Si/C ratio, mineral constituents, relative weathering intensity (loss/ gain) and CaO relative retention all indicated order of weathering intensity (pedogenic age) as MG > QZ ≥ OG > MS.

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