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FORMS OF IRON IN SOILS ON BASEMENT COMPLEX ROCKS OF KADUNA STATE IN NORTHERN GUINEA SAVANNA OF NIGERIA

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ABSTRACT
The forms of iron extracted by different methods were studied in soils developed on four basement complex rocks within Northern Guinea Savanna of Nigeria namely: migmatite gneisses, older granite, quartzites and mica schists. The study shows that forms of iron generally decreased in the order of total elemental iron (Fe_T) determined by XRF > double acid extractable total iron (Fe_a) > dithionite extractable iron oxide (Fe_d) > oxalate extractable iron oxide (Fe_x) > pyrophosphate extractable iron oxide (Fe_p) > 0.1M HCl extractable micronutrient available iron (Fe_h). Variation in content of total irons (Fe_T and Fe_a) were not significant in the soils, but content of Fe_h, Fe_d, Fe_x and $Fe_{x/d}$ significantly varied in the soils on the various parent materials. Therefore processes and extent of pedogenesis were considered to influence the variations resulting in recrystallization and increase in content of Fe_h and Fe_d in these soils. The significant correlation between various forms of Fe (Fe_a, Fe_d, and Fe_x) with active iron ratio further affirmed that as soils on basement complexes increase in their pedogenetic age, Fe content generally increases irrespective of total forms of iron. The strong correlation between Fe_T, Fe_a and Fe_d indicate that these forms of iron were extracted from similar sources.
Keywords: Iron, basement complex rock, pedogenesis, Northern Guinea Savanna, Nigeria.

INTRODUCTION

Iron is a major constituent of the lithosphere and occurs in several mineralogical forms as discrete particles or associated with surfaces of other minerals. The earth crust is made up largely of iron which is the most abundant element on earth. It is regarded as a micronutrient in crops and plays a special role in the behavior of several trace elements in soil, and considerably affects the availability of both macro and micro nutrients (Sillanpaa, 1972; Brady and Weils, 2005; Havlin *et al*., 2005). Iron is very essential for most animal species, being the central unit in haemoglobin molecules and plays a key role in many physiological reactions along with oxygen exchange (Havlin *et al*., 2005).

Iron oxides and hydroxides may occur evenly dispersed throughout the soil, concentrated in particular horizons or in certain morphological features such as mottles, nodules and concretions (Dolui and Chattopadhyay, 1997; Schwertmann and Taylor, 1989). They serve as indicators of the stage and degree of soil development and environmental conditions (Juo *et al*., 1974; Udo, 1980; Mahaney and Fahey, 1988; Schwertmann and Taylor, 1989). Several factors such as pH, organic matter, clay content, carbonates and cationic oxides can be effective on iron distribution by influencing the soil adsorption characteristics, participating in specific and nonspecific adsorption, co-precipitation processes and isomorphic substitutions. Sub-surface pH-Eh regime is a critical factor controlling the concentration and distribution of iron in soils. In poorly drained more acid condition, iron reduction to a divalent state usually occur inducing high solubility and the resultant loss of the element by leaching (Udo, 1980; Kabata-Pendias and Pendias, 1984; Agbede, 2009). Under good drainage and slightly acid or alkaline conditions, iron persists in a relatively immobile trivalent state, with resultant accumulation of hydrous oxides such as haematite, goethite and limonite in soil profiles (Sillanpaa, 1972; Kabata-Pendias and Pendias, 1984). Organic matter with high cation exchange capacity (CEC) are able to adsorb large amount of heavy metals to form metal – organic matter complexes, leading to the less mobility of such elements (Adriano, 2001; Samndi *et al*., 2006).

Soils on basement complex rock are considered to have adequate available iron, as the values have been reported by several researchers (Mustapha and Singh, 2003; Yaro, 2005; Fasina *et al*., 2005; Olatunji *et al*. 2007) to be above the critical levels (>5 mg kg^{-1}) in soil developed on granite, biotite gneiss, banded gneisse and quartzite schist across Nigeria. The content of iron is rated high in soils on basement complex rocks in Bauchi State, Nigeria (Mustapha and Singh, 2003). Total iron mean value in soils formed from different parent material decreased in the order; basalts > basement complex > coastal sand > shale (Udo, 1980). In Nigeria, the amount of amorphous iron oxides is relatively small in most Alfisols and Ultisols derived from acidic parent rocks (Juo *et al*., 1974; Juo, 1981).

The content ranged from 0.05 to 0.2%, which comprised less than 10% of the total free iron oxides. The amount of total free iron oxides present in the soil is influenced by the type of parent rock from which the soils developed. Alfisols, Ultisols and Oxisols derived from basic parent materials are considerably higher in amount of dithionite form of Fe than in soils derived from acidic parent rocks, although the active iron ratio may not be significantly different (Juo, 1981).

Most previous studies treated soils developed on basement complex rocks as one unit due to the intricate nature of their complexity (Fagbami, 1981; Esu, 1987; Mosugu, 1989; Mustapha and Singh, 2003; Fasina *et al.*, 2005; Fasina *et al.*, 2007; Olatunji *et al.* 2007). However rocks of the basement complex are variable both in mineral assemblage and response to soil forming factors, resulting in soils with variable iron forms. Therefore, comprehensive information on the distribution of various forms of iron and factors influencing their behavior are essential for maintaining soil fertility and environmental quality. The study therefore is aimed at assessing the distribution of different forms of iron in soils developed on different basement complex rocks within Kaduna State in Northern Guinea Savanna of Nigeria.

MATERIALS AND METHODS

Study Location

The study area is generally underlain by basement complex rocks. These rocks extensively cover Kaduna State Nigeria occupying about 98% of the land area. The study was carried out arround Kujama in Chikun Local Government Area for older granite (OG). Birnin Gwari Local Government Area (along Kaduna-Lagos route) was explored for the mica schist (MS) and quartzite (QZ) sites, and migmatite gneiss (MG) was studied at the northern out-sketch of Kaduna within Igabi Local Government Area, within Northern Guinea Savanna zone of Kaduna State, Nigeria. The sites lie within latitude 10°27′55.7″N to 10°43′43.2″N and longitude 06°11′14.0″E to 07°39′27.3″E (Figure 1). The mean amount of rainfall of the study areas ranged from 1,180 to 1,286 mm/annum. Mean annual evaporation record ranged from 2194 to 2822 mm/annum, with rainfall in excess of evaporation in the months of July to September. The mean annual atmospheric temperature ranged from 25.0 to 26.4 °C.

Field Studies

The sites for the study were identified through exploratory survey using geological map of Kaduna State (Figure 1), ecoclimatological zones map and Topo map sheets (1:50,000). Three soil profile pits were sited and dug on crest slope position on cultivated fields within each of the four (4) parent material locations. Soils were sampled within pedogenic horizons and the morphological properties observed in field were described based on procedures in the USDA Soil Survey Manual (Soil Survey Division Staff, 1993).

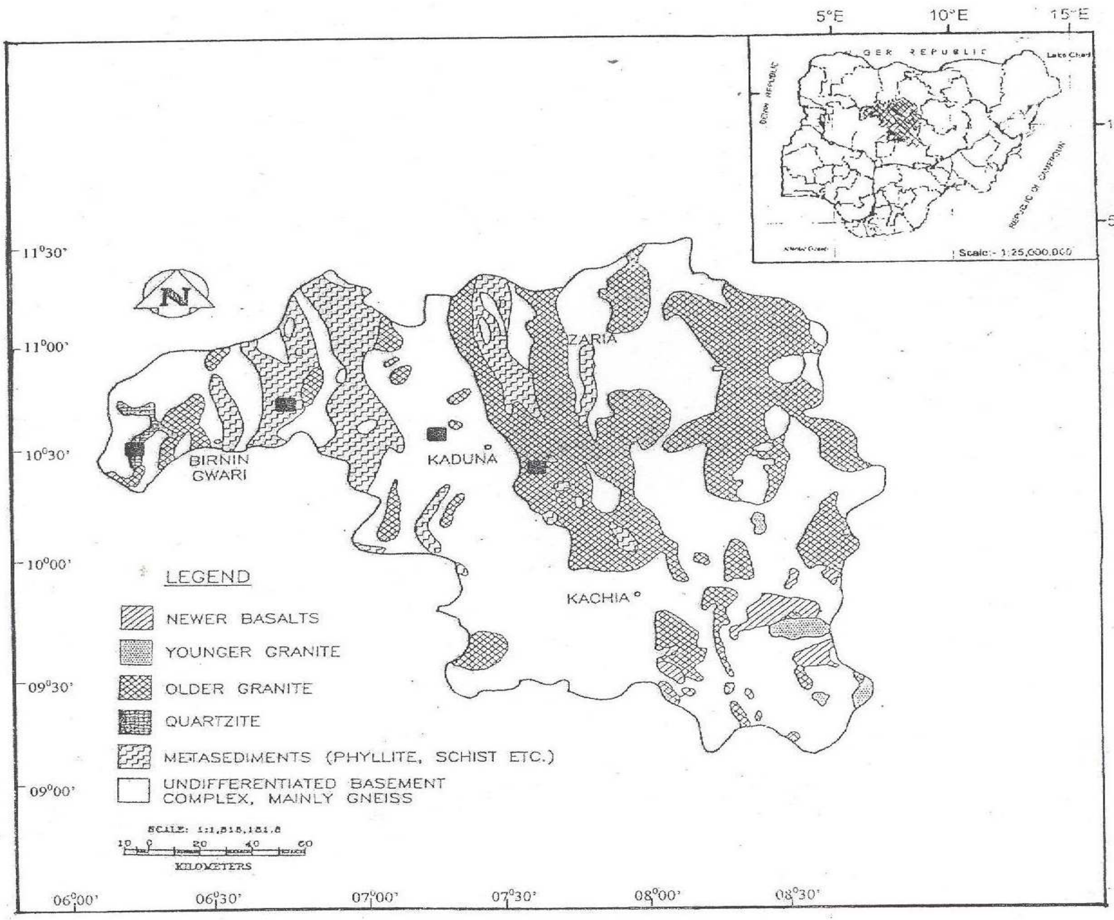

Figure 1: Geological Map of Kaduna State, Nigeria indicating Project Sites ( )
Courtesy: Wadrop Engineering Incorporated and Mai & Associates. (1994).

Laboratory Analysis

Soil properties of the fine earth (< 2mm) samples were analysed using standard laboratory methods. Particle size distribution was determined by hydrometer method (Gee and Bauder, 1986). Soil pH was determined in a 1:1 soil/ water ratio. Cation exchange capacity (CEC) was determined by neutral (pH 7.0) ammonium acetate (NH_4OAc) saturation method (Rhoades, 1982). Organic carbon was determined by Walkley-Black dichromate wet oxidation method (Nelson and Sommer, 1982) and available phosphorus (AP) by methods described in soil laboratory manual (IITA, 1979).

Available iron (Fe_h) was extracted with 0.1M HCl solution by shaking soil paste for 4 hours and then centrifuged at 10,000rpm. Double acid extractable total iron (Fe_a) was analysed through digestion using a mixture of 3 parts of HCl to 1 part of HNO_3 (USDA NRCS, 2004). Total free iron oxide (Fe_d) was extracted following the method of Mehra and Jackson (1960) as described by IITA (1979) using citrate-bicarbonate-dithionite mixtures. Amorphous inorganic form of Fe oxide (Fe_x) was extracted using ammonium oxalate (pH 3) in the dark (Mckeague and Day, 1966) using the modified Tamm's method (IITA, 1979). Amorphous organo-complexed Fe oxide (Fe_p) was extracted using pyrophosphate solution (Mckeague, 1967). The contents of Fe in the respective extracts were determined with atomic absorption spectrophotometer (AA500 spectrophotometer PG Instrument model).

The soil samples were further grinded to 150 µm and the powdered samples used to determine total elemental iron oxide (Fe_T) using energy dispersing X-ray fluorescence (EDXRF) XRF SPEC (Minipal 4 model) machine.

Statistical Analysis

Descriptive statistics were used to assess soil properties. Mean differences in the various forms of iron between soils developed on older granite, quartzite, mica schist and migmatite gneiss parent materials were analysed using two way analysis of variance (ANOVA). Correlation analysis was used to determine relationship between the various forms of iron and some selected soil properties (SPSS Statistics 17.0).

RESULTS AND DISCUSSIONS

Physical and Chemical Properties

The soil depths of the respective parent materials varied between 135 and 190cm and were rated as deep to very deep. Soils developed on quartzites and mica schist encountered depth restriction between 14 and 72cm in quartzite pedon 1, mica schist pedons 2 and 3, while plinthite was encountered within 48 - 172cm in all pedons formed on migmatite gneiss. Earlier studies by several workers (Raji, 1995; Yaro 2005; Idoga *et al.*, 2007) have attributed extent of soil depth to parent material, plinthite, erosion and slope in Savanna regions of Nigeria.

The particle size fraction was dominated by sand in all the soils (Table 1), similar to findings made by Odunze (2006), Obi and Akinbola (2009) and Ande (2010) on soils formed on basement complex rocks in different regions of Nigeria. Clay content in subsurface horizon was three times greater than the mean surface value (128.8 gkg^{-1}), this was attributed to clay translocation, eluviation and erosion in surface horizon (Raji, 1995; Obi and Akinbola, 2009). The soils were considered to be moderately weathered as 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 (Van Wambeke, 1962; Yakubu and Ojanuga, 2009). From Si/C ratio, weathering intensity significantly increased in order of soils on mica schist (MS) < older granite (OG) < quartzite (QZ) < migmatite gneiss (MG).

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

Parameters		Older Granite		Quartzites		Mica- Schist		Migmatite Gneiss	
	Unit	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	$cmol(+)kg^{-1}$	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
AP	$mg\ kg^{-1}$	1.75–21.0	12.89	1.75–15.75	6.44	1.40 – 8.75	4.07	3.50 – 35.00	9.90

Soil reaction varied from strongly acid to neutral pH (5.30 - 6.90; H_2O) and values were within ranges reported on soils on basement complexes in different parts of Nigeria (Raji and Mohammed, 2000; Fasina *et al.*, 2007). The values of cation exchange capacity ranged between 4.8 and 15.3 cmol (+) kg^{-1} (Table 1) and are rated low to high. Low values of CEC in soils on basement complexes were also reported by Esu *et al.* (1987) and Fasina *et al.* (2005). Parent materials significantly influenced CEC, with the significantly lowest mean values in soils on migmatite gneiss and might be attributed to leaching of more exchangeable bases in the soils on migmatite gneiss. Organic carbon (OC) values ranged between 0.40 and 11.57 gkg^{-1} of the soils and was generally considered as been low.

The low contents of OC might be attributed to continuous cultivation, bush burning, high rate of mineralization, and removal of crop for livestock feeding, fuel wood, fencing and building purposes without incorporation in savanna region of Nigeria (Odunze, 2006). The content of available phosphorus varied between 1.40 and 35.00 mgkg^{-1}, and was rated low to high (Table 1). Esu and Ojanuga (1985), Ezenwa and Esu (1999) and Hassan and Raji (2007) found low content of available phosphorus in soils formed on basement complex rocks in Savanna regions of Nigeria and attributed the low values to low organic matter in the soils, crop uptake without replacement and fixation by aluminum oxides.

Forms of Iron (Fe) in the Soils

The results on forms and distribution of iron are presented in. The content of available iron extracted with 0.1M HCl acid was the least form of Fe compared to other forms of Fe in the soils and varied between 7.14 and 71.43mgkg^{-1} (Table 2). The mean values are 22.86, 23.67, 30.41 and 33.88 mgkg^{-1} in soils on older granite, quartzite, mica schists and migmatite gneiss respectively. The content of available Fe significantly varied (P: <0.01) with parent material. Mean values of Fe_h in soils on MG, QZ and MS were statistically at par, while values of Fe_h on soils of MG had significantly higher available Fe than those of the OG soils. Soils on MS were statistically similar to OG and QZ (Table 3). Available Fe values were well above the critical available level of 4.5 mg kg^{-1} reported for savanna soils by Kparmwang *et al.* (2000). The values were rated medium to high for OG and QZ, and high for soils on MS and MG (Soil Survey Division Staff, 1993; Kparmwang *et al.*, 2000). It is therefore, unlikely for iron deficiency to occur in crops grown on these soils. The high available Fe fertility status is apparently due to the nature of the parent materials and high amount of ferromagnesian minerals in these soils (MS and MG). The values were generally within the range reported in basement complexes in Bauchi (Mustapha and Singh, 2003) and plinthitic landscape of Zaria (Yaro, 2005). Available Fe was irregularly distributed in the soil profiles developed on the different parent materials and may be associated with the various pedogenic processes in the soils.

Table 2: Soil profiles distribution of forms of iron of the study areas

Pedon	Depth (cm)	Fe_a* %	Fe_h mgkg^{-1}	Fe_d	Fe_x <------- gkg^{-1} ------->	Fe_p	Fe_T %	$Fe_{x/d}$ -	Clay/Fe_d -
				Soils on Older Granites					
Pedon OG 1									
Ap	0 - 26	2.90	32.86	7.14	1.43	3.43	5.60	0.20	17.09
Bt1	26 - 75	5.98	17.14	14.29	2.14	3.43	20.40	0.15	29.53
Bt2	75 - 119	9.96	22.86	11.40	4.29	1.72	21.99	0.25	16.45
BC	119 - 183	3.98	71.43	17.14	3.57	1.72	21.17	0.21	14.12
Pedon OG 2									
Ap	0 - 17	2.98	25.71	8.00	2.86	2.57	-	0.36	20.25
Bt	17 - 70	3.98	18.57	17.14	2.86	2.57	-	0.17	23.45
Btc	70 - 190	7.97	7.29	28.57	3.57	3.43	-	0.13	8.47
Pedon OG 3									
Ap	0 - 23	7.97	17.14	8.57	2.86	2.57	-	0.33	16.57
Bt	23 - 57	9.96	18.57	22.86	5.00	2.57	-	0.22	14.96
Btc1	57 – 121	11.95	18.57	28.57	5.71	3.43	-	0.20	13.37
Btc2	121 - 160	9.96	14.29	22.86	4.29	1.72	-	0.19	19.34
				Soils on Quartzites					
Pedon QZ 1									
Ap	0 - 14	1.99	17.14	5.71	2.14	3.43	-	0.38	14.36
AC	14 - 40	3.98	7.14	7.14	2.86	4.28	-	0.40	19.89
C1	40 - 98	2.90	45.71	14.29	4.29	4.28	-	0.30	29.53
C2	98 - 135	1.99	28.57	22.86	5.00	1.72	-	0.22	14.09
Pedon QZ 2									
Ap	0 - 19	5.98	17.14	5.86	2.14	1.72	9.57	0.37	13.99
Bt1	19 - 51	3.98	28.57	25.71	3.57	0.86	17.33	0.14	14.08
Bt2	51 - 84	7.97	35.71	20.00	4.29	3.43	22.22	0.22	23.10
Bt3	84 - 139	9.96	30.00	17.14	3.57	2.57	21.44	0.21	22.29
Btc	139 - 187	5.98	37.14	28.57	4.29	2.57	22.85	0.15	11.97
Pedon QZ 3									
Ap	0 - 19	1.99	18.57	5.71	2.14	4.28	-	0.38	17.86
AB	19 - 40	3.98	8.57	22.86	3.57	2.57	-	0.16	8.84
Bt1	40 - 63	7.97	12.86	25.71	2.86	2.57	-	0.11	16.41
Bt2	63 - 97	5.98	17.14	20.00	5.71	3.43	-	0.29	23.10
BC	97 - 167	3.98	27.14	25.71	2.86	2.57	-	0.17	14.86

* Fe_a: Double acid extractable Fe, Fe_h: available Fe, Fe_d: dithionite extractable free Fe oxide, Fe_x: Oxalate extracted Fe, Fe_p: Pyrophosphate extractable Fe, Fe_T: Total Fe by XRF, - : Not determine Fe_T.

Table 2 *continued*: Soil profiles distribution of forms of iron of the study areas

Pedon	Depth (cm)	Fe_a* %	Fe_h $mgkg^{-1}$	Fe_d <-------	Fe_x gkg^{-1}	Fe_p ------->	Fe_T %	$Fe_{x/d}$ -	Clay/Fe_d -
Soils on Mica Schists									
Pedon MS 1									
Ap	0 - 18	1.99	38.86	12.86	6.43	2.57	-	0.50	12.60
Bt	18 – 54	7.97	37.14	28.57	5.71	5.14	-	0.20	10.57
Btc	54 - 177	5.98	25.71	22.86	4.29	3.43	-	0.19	13.21
Pedon MS 2									
Ap	0 - 16	3.98	41.43	17.14	5.71	3.43	-	0.33	7.12
Bt	16 - 37	3.98	28.57	22.86	4.29	1.72	-	0.19	12.34
BC	37 - 72	5.98	27.14	25.71	5.71	3.43	-	0.22	12.52
C	72 - 143	3.98	25.71	28.57	3.57	3.43	-	0.13	11.52
Pedon MS 3									
Ap	0 – 19	2.90	34.29	12.86	6.43	0.86	5.20	0.50	7.93
Bt1	19 - 42	5.98	20.00	17.14	5.71	1.72	14.30	0.33	14.12
Bt2	42 - 96	7.97	25.71	25.71	6.43	4.28	18.70	0.25	8.63
BC	96 - 168	5.98	30.00	20.00	4.29	3.43	17.65	0.21	11.10
Soils on Migmatite Gneisses									
Pedon MG 1									
Ap	0 - 15	5.98	31.43	12.86	3.57	4.28	-	0.28	11.59
Bt	15 - 47	3.98	44.29	25.71	4.29	4.28	-	0.17	12.80
Btcv1	47 - 103	3.98	42.86	31.00	2.86	5.14	-	0.09	11.90
Btcv2	103 - 147	3.98	41.43	27.24	2.86	1.72	-	0.11	10.61
Pedon MG 2									
Ap	0 - 18	3.98	30.00	20.00	2.86	2.57	7.04	0.14	5.45
AB	18 - 44	5.98	27.14	22.86	2.14	1.72	16.00	0.09	15.27
Bt1	44 - 78	5.98	38.57	14.29	2.14	1.72	17.70	0.15	30.02
Bt2	78 - 123	7.97	37.14	31.43	2.14	5.14	16.00	0.07	12.38
BCcv	123 - 167	3.98	15.71	17.14	4.29	1.72	22.28	0.25	16.86
Pedon MG 3									
Ap	0 - 25	2.90	28.57	13.86	2.14	2.57	-	0.15	15.08
Bt1	25 - 47	3.98	24.14	20.00	2.14	4.28	-	0.11	17.45
Bt2	47 - 89	5.98	38.86	34.86	2.86	2.57	-	0.08	12.88
BCcv	89 - 162	7.97	37.29	27.14	1.43	3.43	-	0.05	12.12

* Fe_a: Double acid extractable Fe, Fe_h: available Fe, Fe_d: dithionite extractable free Fe oxide, Fe_x: Oxalate extracted Fe, Fe_p: Pyrophosphate extractable Fe, Fe_T: Total Fe by XRF, - : Not determine Fe_T.

Table 3: Ranking of means of iron and manganese oxides of parent materials

Parameter	Unit	Older Granites	Quartzite	Mica Schist	Migmatite Gneiss	SE±	LOS
Fe_T	%	17.29	18.68	13.96	15.80	1.60	NS
Fe_a	%	7.05	4.90	5.15	5.13	0.77	NS
Fe_h	$mgkg^{-1}$	22.86b	23.67b	30.41ab	33.88a	0.47	**
Fe_d	gkg^{-1}	17.48b	17.66b	21.30ab	22.95a	0.15	*
Fe_x	gkg^{-1}	3.51b	3.62b	5.32a	2.75c	0.03	***
Fe_p	gkg^{-1}	2.65	2.87	3.04	3.16	0.46	NS
$Fe_{x/d}$	-	0.22b	0.25ab	0.28a	0.13c	0.01	**
Clay/Fe_d	-	17.60a	17.46a	11.06b	14.19b	0.55	*

LOS (P): NS (Not Significant) > 0.05, * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001

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

Total iron extracted with double acid was the second largest form of iron after Fe_T and ranged between 1.99 and 11.95 with means of 7.05, 4.90, 5.15 and 5.13 % in the soils on granites, quartzites, mica schists and migmatite gneisses respectively. All the soils were rated high in Fe_a content (Soil Survey Division Staff, 1993; Kparmwang *et al.*, 2000). The Fe_a content of these soils were slightly lower than the values reported in basaltic soils (Kparmwang, 1993) and in plinthitic landscape soils (Yaro, 2005) and might be attributed to accumulation of Fe due to advancement in pedogenic age and difference in parent material of those soils compared to soils of the study areas. The content of double acid extractable total Fe increased regularly with increased in depth of soils formed on OG, MS and MG, except for soils on QZ which had irregular distribution within the profiles.

The irregular distribution of Fe might be attributed to pedological development of the soils (Hassan *et al.* 2004) and influence of different parent materials (Udo, 1980).
Double acid extractable iron correlated with clay and was attributed to Fe occurrence in tropical soils as coatings of clay surfaces (Agbenin and Tiessen, 1995; Raji *et al*., 2000). Soil organic carbon significantly correlated negatively with Fe_a (Table 4). Iron (Fe_d and $Fe_{x/d}$) significantly influenced double acid extractable iron content (r = 0.373**, -0.283* respectively) (Table 5). This indicates that increase in soil age increase Fe_d and crystalline iron ($Fe_{x/d}$) resulting in increase in double acid extractable form of Fe. The significant correlation with Fe_d also indicated that double acid extraction method extracted more iron inclusive of those extracted by citrate–bicarbonate-dithionite extractant.

Table 4: Correlation matrix between physical and chemical properties and forms of iron

Parameter	Fe_T	Fe_a	Fe_h	Fe_d	Fe_x	Fe_p	$Fe_{x/d}$	Clay/Fe_d
Physical properties								
Sand	-0.477*	-0.466***	-0.087	-0.563**	-0.176	-0.053	0.411**	-0.310*
Silt	-0.611**	0.087	-0.018	-0.144	0.267	0.037	0.214	-0.184
Clay	0.753**	0.411**	0.111	0.617***	0.041	0.034	-0.533***	0.406*
Si/C	-0.867**	-0.309*	-0.160	-0.592***	0.026	-0.074	0.544***	-0.342*
Chemical properties								
pH(H_2O)	-0.114	0.089	0.049	0.054	0.176	-0.035	0.042	-0.080
CEC	0.489*	-0.042	-0.097	-0.090	0.055	0.073	0.237	0.136
OC	0.613**	-0.307*	-0.128	-0.719***	-0.252	-0.072	0.529***	0.028
AP	0.182	0.019	-0.122	-0.231	-0.311*	-0.041	0.015	0.073

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

Table 5: Correlation matrix of forms of iron

Parameter	Fe_T	Fe_a	Fe_h	Fe_d	Fe_x	Fe_p	$Fe_{ox/d}$
Fe_a	0.559*						
Fe_h	0.102	-0.248					
Fe_d	0.447	0.373* *	0.193				
Fe_x	0.138	0.160	0.049	0.223			
Fe_p	0.118	0.060	0.123	0.131	-0.069		
$Fe_{ox/d}$	-0.374	-0.283*	-0.212	-0.724***	0.408**	-0105	
Clay/ Fe_d	0.429	-0.044	-0.272	-0 280*	0.175	0.179	0.176

LOS (P): * ≤ 0.05, ** ≤ 0.01, *** ≤ 0.001.

Total iron oxide (Fe_T) constituted the largest form of iron in the soils with values ranging between 5.60 and 22.85 % with mean values of 17.29, 18.68, 13.96 and 15.80 % in the respective soils on older granites, quartzites, mica schists and migmatite gneisses. Iron oxide content increased with increase in soil depth; however values were irregularly distributed in the lower part of the subsoils. The mean values of Fe_2O_3 did not significantly varied, but were in the order of QZ > OG > MG > MS. Total iron oxide distribution and accumulation in subsoil horizons was strongly influenced by clay (lessivation) (Buol *et al*., 1980; Sharma *et al*., 2008). Clay and cation exchange capacity (NH_4OAc) were observed to correlate with Fe_2O_3 (r = 0.753** and 0.489*) indicating that clay and CEC influenced distribution and increase in content of Fe_T in these soils. Sharma *et al.* (2007) similarly observed total Fe increase with increase in CEC and clay in Arid and Semi-Arid soils of India. The negative correlation between total Fe with organic matter (r = -0.618**) indicate that total elemental iron oxide was inhibited by organic matter, hence the variation in their distribution pattern. Total iron oxide correlated more with Fe_a and Fe_d (Table 5), thus indicating that both forms of iron were from similar sources, and double acid only extracted less Fe compared to X ray fractionation method.

The content of total free iron oxide (Fe_d) extracted with citrate- bicarbonate- dithionite varied between 5.71 gkg^{-1} and 34.86 gkg^{-1} (Table 2), while mean values of 17.48 gkg^{-1}, 17.66 gkg^{-1}, 21.30 gkg^{-1} and 22.95 gkg^{-1} (Table 3) were obtained in soils on older granites, quartzites, mica schists and migmatite gneisses respectively. Parent materials significantly influenced the distribution of Fe_d, mean values of Fe_d in soils on MG and MS were statistically at par, however significantly higher Fe_d content was obtained in soils on MG parent material compared to those on QZ and OG as shown in Table 3. This high value of Fe_d might be attributed to higher amount of ferromagnesian minerals in these soils (MG and MS). Udo (1980) also observed that parent material influenced relative distribution of free iron oxides. Total free iron oxide values were significantly higher in subsoil than the surface horizons, and was attributed to co-translocation of Fe with clay through eluviation - illuviation processes (Blume and Schwertmann, 1969; Juo *et al*., 1974). This is further buttressed by the significant correlation between Fe_d and clay (r = 0.617***).

All the pedons on the respective parent materials showed an increase in Fe_d content with increased soil depth. The highest values of 31.00 – 34.86 gkg^{-1} was recorded within plinthite horizons (Btcv) of soils on migmatite gneiss parent material.

The values of Fe_d obtained were lower than values reported by Kparmwang (1993) in lateritic basaltic soils, but higher than those reported on the floodplain of southeastern Nigeria (Ibia, 2002; Essoka *et al.*, 2007). Oxalate extractable iron values varied from 1.43 to 6.43 gkg^{-1} in all the soils, while the mean values were in the order 3.51 gkg^{-1}, 3.62 gkg^{-1}, 5.32 gkg^{-1} and 2.75 gkg^{-1} (Tables 2 and 3) for soils on older granites, quartzites, mica schists and migmatite gneisses respectively. The amorphous inorganic iron oxide varied significantly between the soils (Table 3). Mean values for soils on MS was significantly greater than those on the QZ, OG and MG, while values on soils on MG parent material was significantly lower. The values of Fe_x were generally within range for soils on the older granite and basalts in the Northern Guinea Savanna (Mosugu *et al.*, 1999). The values obtained were higher than those obtained on the aeolian materials by Raji *et al.* (2000) and Owonubi *et al.* (2003). Amorphous Fe content increased with depth in soils on OG and QZ, but was irregularly distributed within soils on MS and MG.

Pyrophosphate extractable iron values ranged between 0.86 and 5.14 gkg^{-1} in all the soils on the various parent materials, however values were not significantly different. The values obtained were higher than those values reported by Raji *et al.* (2000), but lower than the values reported in wetland soils of Nigeria (Olaleye *et al.,* 2000). The variation Fe_p values might be due to difference in the amount of organic matter generated by vegetations in the different ecological zones of the various studies. The values obtained were within range reported in established forest in Southern Guinea Savanna of Nigeria (Samndi *et al.*, 2006). The soils generally had irregular distribution of Fe_p in their profiles and were similar to those reported by Abdourahamane and Yaro (2007).

Active Fe ratio values generally ranged between 0.05 and 0.50, while the mean values are in the order 0.22, 0.25, 0.28 and 0.13 in soils on older granites, quartzites, mica schists and migmatite gneisses (Tables 2 and 3). Mean values of $Fe_{x/d}$ significantly varied between the soils, thus indicating pedogenic development (recrystallization) of the soils in order of soils on MS < QZ $\simeq$ OG < MG (Table 3). The values of $Fe_{x/d}$ were generally greater than 0.1 and less than 0.5, implying the soils were of moderate pedogenetic development. Active Fe ratio decreased with increase in soil depth, thus implying that recrystallization of iron oxide occurred more in subsoil compared to surface soil, as buttressed by significant correlation value (r = 0.529***) between organic carbon and $Fe_{x/d}$ ratio. This confirms that crystallization is inhibited by organic matter in the soils. The inhibitory effect of soil organic matter on Fe crystallization in surface soils was also reported by Blume and Schwertmann (1969), Yaro (2005) and Samndi *et al.* (2006).

Clay/ dithionite iron ratio in the soils ranged between 5.45 and 29.53. Clay/ dithionite ratio values for soils on QZ and MS were irregularly distributed in their profiles, whereas, clay/ dithionite ratio for soils on OG and MG decreased regularly with depth in some portion of their profiles except for Pedon MG 2 which had an irregular distribution. This indicates that with advancement in pedogenic development in these soils, independent migration of clay and Fe_d (QZ and MS) shift towards partial co-migration (OG and MG) (Juo et.al., 1974). The mean values of clay/ dithionite Fe ratios of surface and subsoil were not significantly different. This indicates that there was partial co-migration between clay and iron in these soils and more clay seems to be illuviated into the subsoil than Fe oxide. Active iron correlated significantly with total sand (r = 0.411**), Si/C (r = 0.544***) and clay (r = -0.533***), thus increase in sand and silt weathering to clay increased active Fe co-migration and coating of clay surface, and increased in Fe crystallization increased clay content.

CONCLUSION

The study showed forms of iron generally decreased in the order of $Fe_T > Fe_a > Fe_d > Fe_x > Fe_p > Fe_h$ in the soils developed on basement complex parent materials. Variation in content of total Fe obtained with XRF and double acid extraction were not significantly influenced by the parent materials, but content of available iron, dithionite extractable Fe oxide, amorphous inorganic complex iron and crystalline form of iron were significantly different in the soils formed on the various parent materials. Therefore processes and age of pedogenesis were considered to influence the variations resulting in recrystallization and increase in content of some forms of Fe in these soils. The significant correlation between various forms of Fe with active iron ratio further affirmed that as soils on basement complexes increase in pedogenetic age, Fe content generally increase irrespective of total forms of iron.

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