[Shettima et. al., Vol.6 (Iss.4): April 2018]
(Received: Mar 29, 2018 - Accepted: Apr 19, 2018)
ISSN- 2350-0530(O), ISSN- 2394-3629(P)
DOI: 10.29121/granthaalayah.v6.i4.2018.1637

INTERNATIONAL JOURNAL OF RESEARCH – GRANTHAALAYAH
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GEOCHEMICAL FACIES OF THE TURONIAN GONGILA FORMATION, BORNU (CHAD) BASIN, NIGERIA: IMPLICATION FOR PROVENANCE, PALEOCLIMATE AND PALEOWEATHERING CONDITIONS

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Abstract

Geochemical evaluation of the Gongila Formation of Bornu (Chad) Basin indicated mineralogical compositions of quartz, feldspar, anatase, gypsum, smectite and kaolinite from XRD analysis. Corresponding major oxides from XRF analysis indicated the dominance of SiO2 with an average of 54.91 wt % followed by Al2O3 with 15.92 wt %. CaO, NaO, K2O, MgO, MnO, Fe2O3 TiO2 and P2O5 occurred with average compositions of 1.87%, 1.02%, 2.15%, 1.17%, 0.06%, 3.04%, 0.03% and 1.52 % respectively. Alteration indexes derivations from these oxides consisting of Chemical Index of Alteration (CIA), Plagioclase Index of Alteration (PIA) and Chemical Index of Weathering (CIW) accounted for a dominantly moderate weathering condition for the formation. Discriminant plots of Fe2O3+MgO versus TiO2 indicated a tectonically passive source area composed of generally intermediate igneous rocks, affirmed by Al2O3 versus TiO2 bivariate model with skewed plot along the granite line. The dominance of smectite suggests prevalence of arid to semi-arid paleoclimatic conditions during the deposition of shales of the Gongila Formation. Intermittent phases of superposed tropical climate are also depicted by the subordinate kaolinite mineralization.

Keywords: Chad Basin; Geochemistry; Mineralogy; Gongila Formation.

Cite This Article: B. Shettima, F. D. Adams, A. I. Haruna, A. I. Goro, and M. Bukar. (2018). "GEOCHEMICAL FACIES OF THE TURONIAN GONGILA FORMATION, BORNU (CHAD) BASIN, NIGERIA: IMPLICATION FOR PROVENANCE, PALEOCLIMATE AND PALEOWEATHERING CONDITIONS." *International Journal of Research - Granthaalayah*, 6(4), 144-156. https://doi.org/10.5281/zenodo.1242621.

1. Introduction

Physical and chemical alteration of pre-existing rocks, precursory to sedimentary evolution preserves relicts of these conditions within the emerging geochemical species, thus hosting vital signatures on weathering conditions, provenance, sediment recycling and regional tectonics [1-2]. Shales constitute over 65% of the entire global sedimentary sequences and because of its relative

ISSN- 2350-0530(O), ISSN- 2394-3629(P)
DOI: 10.5281/zenodo.1242621

preferential enrichment of trace elements, it is considered to represent average composition of the upper continental crust [3]. Therefore, they present an indispensable tool in retracing and reconstruction of not only provenance, but also source rock composition, because of their restricted redistribution during sedimentation, lithogenesis and metamorphism [4-5]. Mineralogical assemblage and abundance in these shales are as well a function of the paleoenvironmental conditions, hence, their associations and suites are reliable indexes to paleoclimate, weathering and tectonics operating within a sedimentary basin [6-7]. The Gongila Formation in the Bornu (Chad) Basin composes of thick sequences of shales and limestones deposits of a shallow marine setting [8-9]. This Turonian shale sequences account for the full marine inundation of the basin and represent the global mid – Cretaceous transgressive event. Its outcrops are generally restricted to the southeastern part of the basin, where it is found well exposed at Mutai village (Fig.1). This research was carried out at this locality with the aim of determining the provenance of these shales, as well as paleoweathering and paleoclimatic conditions characterizing the Turonian of the Bornu (Chad) Basin.

2. Geological and Statigraphic Setting

The Bornu Basin is part of the West African intracratonic basin located in northeastern part Nigeria and originated as a consequence of an active phase of sea floor spreading in the Atlantic during the mid-Cretaceous that led to the separation of the African and South American plates [10-11]. The accompanying subsidence in these basins lead to widespread marine transgression and regression regimes building out sequences of marine and continental deposits [8]. The Albian sediments composing of a continental, sparsely-fossiliferous medium to coarse grained feldspathic sandstone with shale intercalations of the Bima Sandstone records the inception of sedimentation in the Bornu Basin (Fig. 2). This formation rests directly on the Precambrian Basement Complex [8, 12, 13]. The Gongila Formation conformably follows this continental unit and it is typically composed of calcareous shale and limestone deposited in shallow marine environment [14]. (Fig. 3). The deposition of this formation marks the beginning of marine incursion into the Bornu Basin [8]. The marine transgression which started in the Cenomanian reveals its peak in the Turonian during which the bluish-black, ammonites-rich open marine Fika Shale was deposited, and this

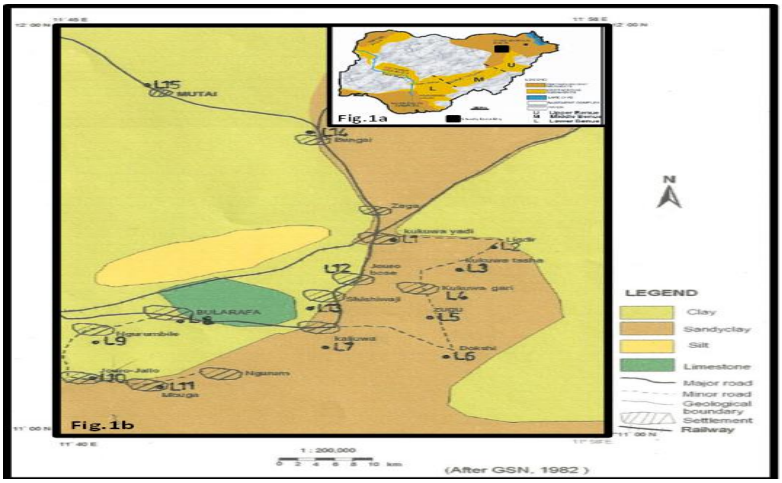

Figure 1(a): Geological map of Nigeris showing study location (b) geological map of the Mutai area showing sample locations

ISSN- 2350-0530(O), ISSN- 2394-3629(P)
DOI: 10.5281/zenodo.1242621

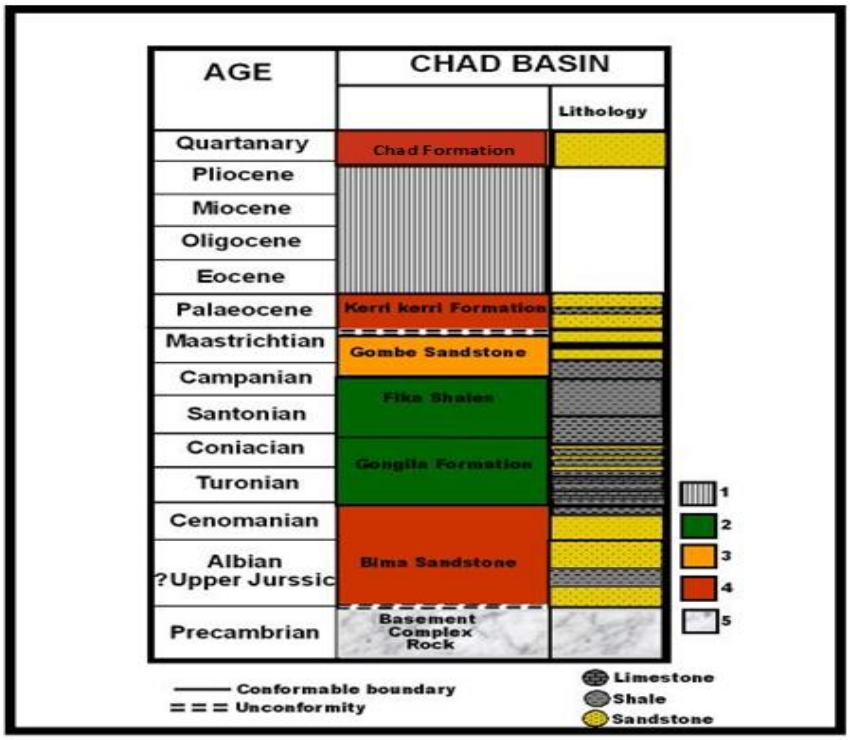

Figure 2: Stratigraphic succession of the Bornu Basin [8] 1-Hiatus, 2-marine sediments, 3-Transitional sediments, 4-continental sediments, 5-basement complex

Deposition continued into the Santonian [8]. The Gombe Sandstone which contains intercalation of siltstone, shale, ironstone and sandstone was deposited in the Maastrichtian unconformably overlying the Fika Shale.

In the Late Maastrichtian times and up to the end of the Cretaceous a phase of extensional deformation occurred in the Bornu Basin. This resulted in reconstructing an elongate NE-SW graben system in the basin. The deformation formed a new depo-center where Paleoene deposits of the Kerri-Kerri Formation accumulated unconformably on the Cretaceous sediments [8, 15]. In the Pleistocene and presumably during the Pliocene, the continental deposits of the Chad Formation were unconformably deposited above the Kerri-Kerri Formation [8, 16]. Toward the end of the Tertiary to recent times, widespread volcanic activities occurred in the south and central part of the basin.

3. Methodology

The study was conducted around Mutai village and environs, falling into sheet 110 of the Federal Survey Map of Nigeria (Fig.1b). A total of fifteen (15) samples claystones were collected for geochemical analyses, out of which ten (10) were further subjected to mineralogical studies. Major element analyses were carried out for clay samples using Inductively Couple Plasma- Optical Emission Spectrometry (ICP-OES) and X-Ray Fluorescence (XRF). ICP-OES (Optimal 2000DV) was used to analyze for K, Al, Ca Mg, Fe, Mn, Ti, and P. For the ICP-OES analysis, the samples were at first ashed and 0.2g of each was digested using concentrated nitric acid (HNO3) and concentrated Hydrochloric acid (HCl). The samples were then introduced into the ICP-OES as

ISSN- 2350-0530(O), ISSN- 2394-3629(P)
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liquid medium and nebulized as aerosol. The aerosol is dissolved, vaporized and atomized, then excited and ionized in order to obtain characteristic atomic radiation from where the elements and their concentration were recorded. In the XRF analysis, SiO2 and AlO3 were determined. Five gramme (5g) of the pulverized samples were introduced into the X-Ray chamber of the minimate (PanAnalytical) XRF machine. The machine was calibrated and run having the results presented in the "result window" of the attached computer in weight percentage oxide (wt% oxide). The lost on ignition (LOI) was determined using Carbolite furnace. One gramme (1g) of the sieved samples of claystones were transferred to crucibles and placed into a furnace that was set to 10000C for about one and a half hours. The samples were left in the furnace to cool, after which they were reweighed to determine the LOI. Clay mineralogical analysis was carried out on 2μm clay – size fraction of 5 mudstone samples based on unoreinted X-ray powder diffractiometry (XRD) technique. X-ray identification of the clay fractionation was performed at University of Liverpool using Panalytical X pert pro MPD X-ray Diffractometer (2008) with reference patterns from international centre for diffraction data, powder Diffraction file 2 release in 2008. Equipment is set with CuKα radiation of 40kv and 40mA, Co Filters and scan range of 5 – 60o 2Θ.

4. Results

Mineralogy

The mineralogical analysis of the claystone samples of the Gongila Formation at Bularafa, Zugu, Ligdir, Gurumbile, Jouro-Jallo, Shishiwaji, Jouro-Bose, Kukuwa-Tasha, Kukuwa-Yadi and Kukuwa Gari villages indicated the occurrence of smectite and kaolinite clay mineral species. Smectite ranges from 6 to 28 wt % with average of 15.70 wt %, whereas kaolinite ranges from 6 to 13 wt % with an average of 8.20 wt % (Table 1). Gypsum is present in samples from Kukuwa-Tasha and Kukuwa-Yadi and range between 1 wt % to 11 wt % with an average of 2.10 wt%. Anatase were recorded only at Zugu and Bularafa village, with concentration of about only 1 wt%. Other non-clay minerals identified are quartz which ranges from 30 wt% at Zugu to 72 wt % at Ligdir with an average of 50.30 wt %. Plagioclase feldspar varies from 6 wt % at Kukuwa Tasha and Kukuwa Gari to 9 wt% at Shishiwaji and Zugu, with an average of 4.5 wt % (Table 1). The minerals are identified in the diffractographs (Fig.3).

Geochemistry

Chemical analyses carried out on clay samples of the Gongila Formation shows that SiO2 and Al2O3 are the major oxides with highest concentrations in the samples analysed. The SiO2 content ranges from 51.80 wt % to 61.22 wt % averaging 54.91 wt % while Al2O3 varies from 12.30 wt % to 20.61 wt % with an average of 15.92 wt % (Table 2). The CaO varies between 1.11 wt% to 2.9 wt % and averages 1.87 wt %. Na2O concentration ranged from 0.42 wt % to 1.45 wt% with an average of 1.02 wt % while K2O (K2O) ranges from 0.34 wt % to 4.51 wt %, averaging 2.15 wt %. MgO and MnO range from 1.06 wt % to 1.3 wt % and 0.01 wt % to 0.13 wt % respectively with averages of 1.17 wt % and 0.06 wt % respectively. Ferric oxide (Fe2O3) content ranged from 0.69 wt % to 5.25 wt % averaging 3.04 wt %. TiO2 ranges from 0.001 wt% to 0.09 wt % with an average of 0.03 wt %. Phosporous pentaoxide (P2O5) content ranges from 0.14 wt % to 3.86 wt % with an average of 1.52 wt %. The Loss On Ignition (LOI) ranges from 6.0 % to 16.0 % with an average of 11.46% (Table 2). Major oxide correlation coefficient analysis indicated a strong negative correlation between SiO2 and Al2O3 (r=-0.53), pointing to a dominance of clays and

ISSN- 2350-0530(O), ISSN- 2394-3629(P)
DOI: 10.5281/zenodo.1242621

micas in the mudstones of the Gongila Formation and corresponding dilution and depletion of SiO2 (e.g. Kanpunzu et al., 2005). This dominance is

Table 1: Average composition of the minerals (wt. %) in Mutai area

Location	Kukawa Yadi (L1)	Ligdir (L2)	Kukawa Tasha (L3)	Kukawa Gari (L4)	Zugu (L5)	Bulara (L8)	Ngurumbile (L9)	Jauro Jallo (L10)	Jauro Bose (L12)	Shishiwaji (L13)	Average Weight (%)
Quartz	40	72	54	53	30	41	36	70	55	49	50.3
Anatase	ND	ND	ND	ND	1	1	ND	trace	trace	ND	0.2
Plagioclas	ND	ND	6	6	9	7	8	trace	ND	9	4.5
K-feldspa	13	16	22	24	21	22	27	10	11	24	19
Kaolinite	6	6	6	6	12	11	13	8	8	6	8.2
Smectite	18	6	11	11	21	18	16	12	23	11	15.7
Gypsum	11	ND	1	ND	6	ND	ND	ND	3	ND	2.1

Further buttressed by the positive correlation of Al2O3 with K2O (r=0.27), indicating a source from k-bearing minerals (k-feldpars, muscovite and biotite). This inference is also supported by the relatively high ratio of K2O / Na2O that ranges from 0.31 – 4.50 indicative of the presences of k – bearing minerals. SiO2 also showed a weak negative correlation with Fe2O3 and P2O5 (r=-0.1 and

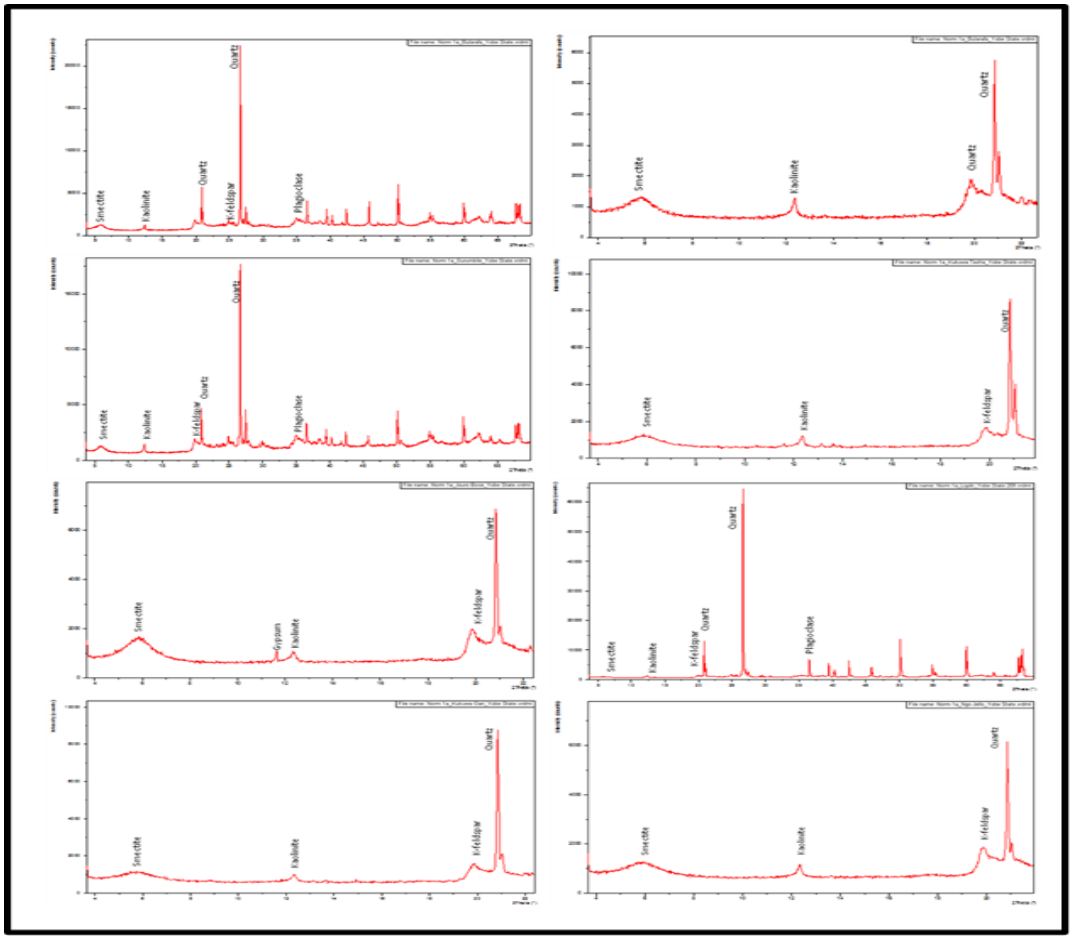

Figure 3: XRD Difractographs of shales of the Gongola Formation

ISSN- 2350-0530(O), ISSN- 2394-3629(P)
DOI: 10.5281/zenodo.1242621

-0.06 respectively) and weak positive correlation with K2O, Na2O, CaO, MgO, MnO and TiO2 (r= 0.2, 0.12, 0.01, 0.16, 0.17 and 0.25 respectively) (Fig.4). This accounts for contributions

Table 2: Showing weight percentage of major oxides

Major Oxides	Ligdir Kukawa Gari Ngurumb		Ngo-jallo Mutai Mbuga	Shishiwaji	Jauro Bose Kaljiwa		Kukawa Tasha Kuykawa	Bularafa Yadi		Bungai Zugu	Dokshi
SiO2	53.21	51.8	54.42	52.46	57.41	45.42	56.73	56.44	54.6	61.22	53.79	56.1
	53.42	58.1	58.47									
Al2O3	17.21	17.4	13.33	20.61	19	18.4	11.3	16.7	18	14.21	15.3	12.3
	18.21	13.42	13.42									
CaO	1.11	1.93	1.76	2.01	2.08	1.6	1.43	1.27	1.49	1.43	2.5	1.95
	1.83	2.7	2.9									
Na2O	0.96	0.99	0.84	1.2	1.35	0.8	1.45	0.42	0.95	0.86	1.25	1.09
	1.09	0.96	1.15									
K2O	1.11	3.17	1.54	2.66	3.97	2.11	1.82	0.87	1.49	1.34	2	0.34
	3.63	4.51	2.74									
MgO	1.06	1.15	1.15	1.17	1.27	1.11	1.18	1.18	1.07	1.08	1.3	1.17
	1.17	1.3	1.11									
Fe2O3	0.69	3.82	3.88	2.99	5.25	3.14	3.71	1.7	1.9	1.16	3.07	3.4
	4.4	3.95	2.46									
MnO	0.01	0.09	0.06	0.08	0.13	0.03	0.02	0.02	0	0.03	0.08	0.07
	0.07	0.2	0.04									
TiO2	0.02	0.001	0.02	0.01	0.004	0.001	0.003	0.086	0.009	0.001	0.071	0.003
	0.01	0.24	0.02									
P2O5	0.88	1.93	2.04	2.23	2.45	1.54	1	1.06	1.2	0.7	1.37	1.71
	0.75	3.86	0.14									
LOI	13.17	12.44	10.21	7.91	11.46	16	15.42	12	13.9	11	10	11.42
	10	6	10									
K2O/Al2O3	0.06	0.18	0.12	0.13	0.21	0.11	0.16	0.05	0.08	0.09	0.13	
	0.03	0.20	0.34	0.20								
CIA	84.4	74.1	76.3	77.8	71.9	80.3	70.6	86.7	82.1	79.7	72.7	78.4
	73.6	62.2	66.4									
PIA	88.6	82.9	81.9	84.8	81.4	87.2	76.7	90.4	87.1	84.9	78	70.7
	83.3	70.9	72.5									
CIW	89.3	85.6	83.7	86.5	87.2	88.5	79.7	90.8	88.1	86.1	80.3	80.2
	86.2	78.6	76.8									

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ISSN- 2350-0530(O), ISSN- 2394-3629(P)
DOI: 10.5281/zenodo.1242621

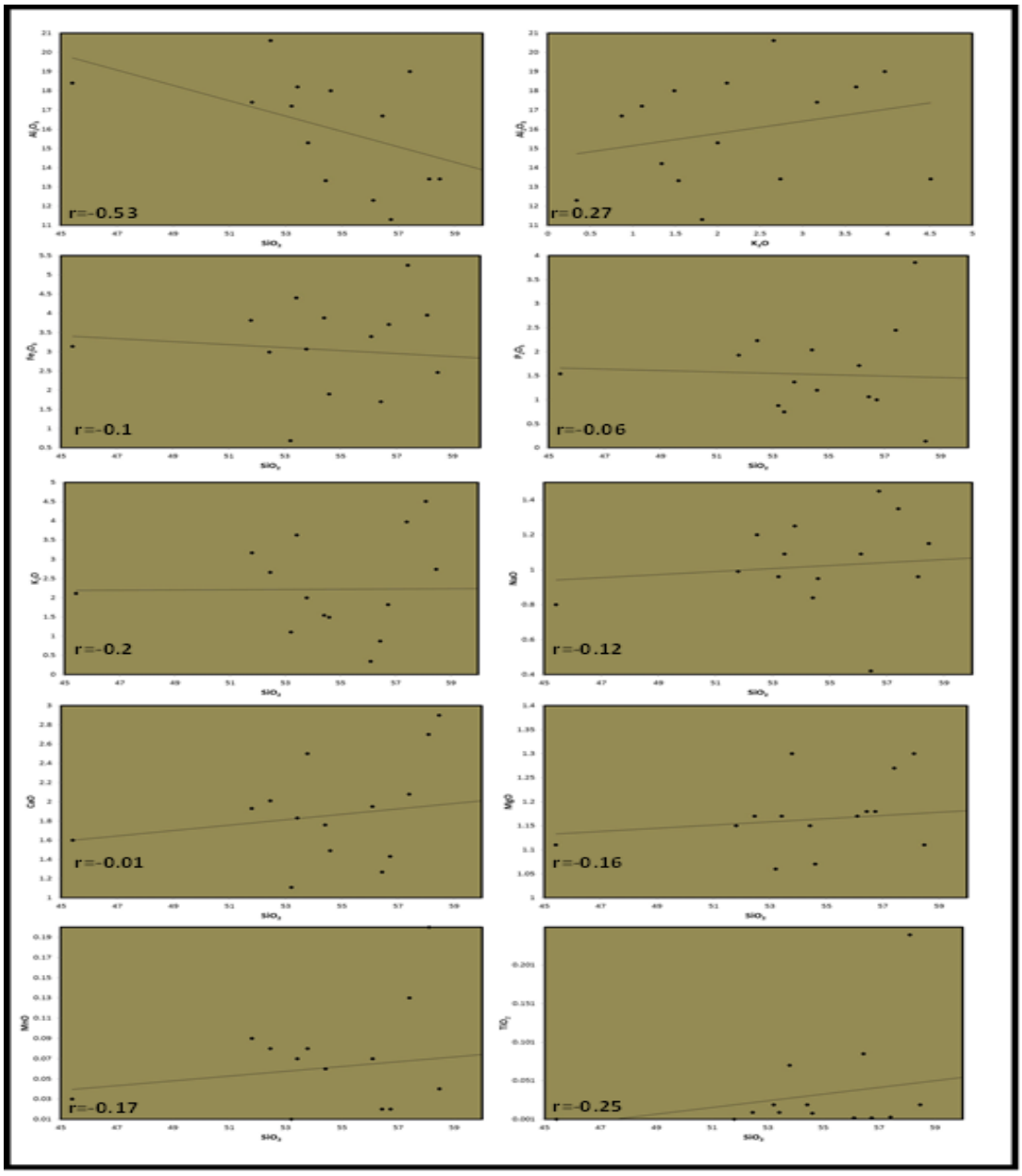

Figure 4: Correlation coefficient plots for SiO2 against major oxides

From clay minerals. However, the negative correlation of TiO2 with Al2O3 (r= -0.53) and its positive correlation with MgO, K2O, Fe2O3 and CaO (0.59, 0.38, 0.073 and 0.43) may also account for derivative from mafic minerals (Fig.5a-e). More so, its low concentration (av. 0.01) points to presence of phyllosilicate, but in relatively small concentrations [17]. The TiO2 is generally immobile during sedimentary dynamic process making it a powerful tool in provenance analysis. Its dominantly low values in the mudstones of the Gongila Formation commonly below the PAAS suggest abundances of felsic materials in the provenances area (Table 2). P2O5 values are commonly higher than the PAAS, this may account for high contribution from accessory minerals as apatite and monzonite. K2O /Al2O3 are

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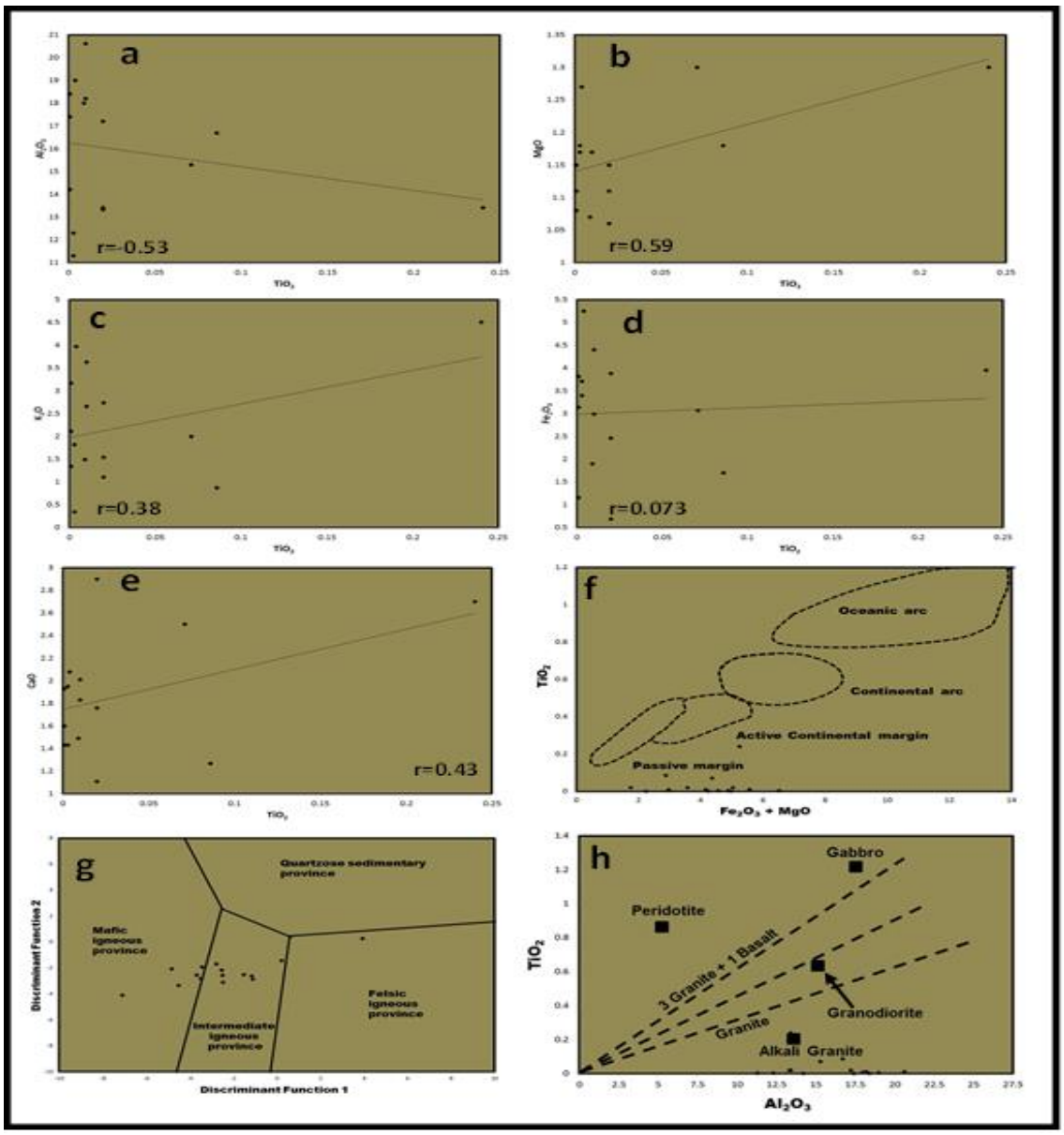

Figure 5a-e: Correlation coefficient plots for TiO2 against other major oxides, f-h) provenance models for Gongila formation

Proven indexes to original composition of ancient mudrocks, with values ranging from 0.0 – 0.3 claystones and 0.3 – 0.9 for feldspars [18]. A range of 0.06 – 0.2 herein may suggest that contribution for the shales of the Gongila Formation are generally from claystones.

5. Discussion

Source Rocks and Tectonic Setting

Chemical compositions of silicilastic rocks are largely controlled by tectonic settings of provenance and as a consequence, they exhibit specific signatures with strong affinities to different tectonic provinces [19-21]. The inferences on provenance types and tectonic setting of ancient sedimentary basin are usually made from established bivariate models for geochemical species.

ISSN- 2350-0530(O), ISSN- 2394-3629(P)
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The plots of Fe2O3+ MgO versus TiO2 discriminant model for shale tectonic provenance (Bhatia, 1983) indicated a skewed plot of geochemical species of the Gongila Formation around the passive margin field, which is quite consistent with earlier works on the Chad Basin that was established to have developed under passive tectonic setting [8, 12, 22] (Fig. 5f). Provenance analysis on the basis of ratio of major oxides [23] for characterizing the source material for the geochemical effluents indicated a dominant intermediate igneous provenance (Fig.5g). Mafic contributions are also notable but felsic are generally few. Considering immobile nature of Al and Ti, its provenance affinity in constraining siliciclastic rocks source using Al2O3 versus TiO2 bivariate discriminant diagram indicated a plot along the granite line for the shales of the present study (Fig.5h).

Palaeoweathering

Disintegration of rocks and the subsequent mobility of contained labile elements are preserved records of intensities of weathering in sedimentary units, thus providing an invariable tool for evaluating source area weathering conditions [28-29]. The measure of the intensities of the geochemical alterations are determined from formulated alteration indexes comprising of Chemical Index of Alteration, [28], Plagioclase Index of Alteration [26], Chemical Index of Weathering [27]. The Chemical Index of Alteration is the most widely employed in determining the degree of source area weathering of formation. This index is established on the basis of molecular proportions of major oxides in relationship where, CIA = (Al2O3/Al2O3+CaO*+Na2O+K2O)*100, and the CaO* is the amount of CaO associated with the silicate frac¬tion of the rock. Anomalous CaO values are generally ignored in CIA calculation because it gives the relative proportions of secondary aluminous clay minerals to primary silicate minerals like feldspars [24]. Therefore, the method are considered in this context, where if the content of CaO was less or equal to that of Na2O content, then we deploy the CaO value for further calculation, and if the CaO content was higher than Na2O, then Na2O value was considered as CaO* value [28-29]. In this present study, the shales show lower concentra¬tion of CaO (1.11 – 2.90%), and using these values indicated moderate CIA average values (76) out of range (62 to 84) in the sedimentary rocks (Table 2). This suggest dominantly moderate intensities associated with few pulse intense chemical weathering in the source region e.g. [30-31].

CIA values herein are higher than the average NASC value of 57 [32] and slightly lower than the typical shale values [33], hence, affirming the moderate chemical weathering intensity in the source rocks. Chemical Index of Weathering (CIW) determined from molecular proportions equating CIW = {Al2O3 / (Al2O3 + CaO + Na2O)} x 100 indicated values in the range of 77 – 91 (av.84) (Table 2). This suggests moderate – high degree of source area weathering, largely agreeing with the findings of the Chemical Index of Alteration (CIA). The Plagioclase Index of Alteration (PIA) monitors and quantifies progressive weathering of feldspars and volcanic glass to clay minerals [26]. Therefore, it is indicative of intensity of destruction of feldspars during the course of source weathering, fluvial transport, sedimentation and diagenesis and calculated as PIA = [(Al2O3 - K2O)/ (Al2O3+Na2O+CaO*-K2O)] × 100 (molecular proportions). The PIA values for the shales of the Gongila Formation ranged from 71 – 90 (av.82) (Table 2) indicating a dominantly moderate intensity of chemical weathering intercalated with few phases of intense conditions which are in consonance with the earlier inferences.

Paleoclimate

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Bulk-rock mineralogy and clay fraction in any environmental settings are records of paleoclimatic changes and diagenetic overprint imposed through the processes of weathering and metasomatic alterations [34]. Diagensis generally obscure paleoclimatic signatures, therefore evaluation of its degree is imperative for reliable paleoenvironmental deductions. The paragenesis of detrital clay minerals records inherent complex interaction of environmental factor (temperature, pressure, Eh, Ph, humidity etc.), synchronously operating within depositional setting, culminating in preferential evolution of mineral phase with specific climatic conditions. Under burial diagenesis, original detrital fabric and compositions are commonly transformed and changed to authegenic forms, with kaolinite altering to dickite, haloysite and nacrite morphologically and to illite chemically, while smectite evolves to chlorite [35-36]. Literarily these geochemical alterations have not been observed in this study, and coupled with the general absences of illite /smectite mixed layers, may account for a very low diagenetic overprint [37]. Furthermore, the absence of continuous variations in clay mineral content across the down dip profile of the study area are in consonance with the earlier inference, pointing to low diagenetic modulations [38]. Hence, the reliability of the clay mineral assemblage of the Gongila Formation for paleoenvironmental interpretations. The occurrence of solely smectite and kaolinite in clay mineral assemblage of this formation is indicative of a generally warm climate interchanging between hot dry and humid condition [39-40], with the latter superseding because of the dominance of smectite mineralization. This mineral commonly forms in a basic medium enriched with Ca and Na under mild hydrolysis, promoted by low water – rock interaction, a common phenomenon characterizing semi-arid to arid climatic settings [41]. This condition characterizes much of the Turonian of the Bornu Basin signaling periods of low chemical weathering [42-43]. Intermittent increase in the intensity of the chemical weathering were also recorded from the relative kaolinite mineralization, depicting high rainfall favored ionic transfers and pedogenic development typically supported by humid sub – tropical to tropical climatic conditions [43].

6. Conclusion

The geochemical characterization of the shales of the Gongila Formation revealed that the formation solely formed in a passive continental margin. Provenance evaluation indicated that the sediments were sourced from intermediate igneous rocks with few felsic and mafic materials in a generally granite province. This setting is generally characterized by moderate weathering, but pulses of intense conditions are also common. The Turonian of the Bornu Basin is dominantly defined by arid to semi- arid climatic condition superposed with relatively few periods of pronounced tropical to subtropical climate.

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