

Mineralogy and geochemical signatures for provenance and palaeoweathering conditions of the upper Albian Abakaliki Shale in south-eastern Nigeria

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Abstract

Mineralogical and geochemical studies of the Abakaliki Shale have been undertaken in order to constrain source rock composition and palaeoweathering conditions, as well as to deduce the provenance terrane types. The mineralogical analysis using X-ray diffraction has revealed an abundance of quartz and clay minerals (illite, chlorite and illite/smectite mixed layer) with a minor content of albite and gypsum. Geochemical data have demonstrated a depletion in SiO₂, MnO, Y, Zr, Hf, U, Y, Cu, Ni, V, Ba and Cr and an enrichment in Rb, Sr, Th, Sc, Co, Zn and Pb in the Abakaliki Shale in comparison to the Post-Archean Australian Shale (PAAS; a proxy for the upper continental crust). Rare earth element contents generally show LREE fractionation and enrichment (LaN/YbN = 16.08–35.75 and LaN/SmN = 3.61–6.16, respectively) with a strong negative Europium anomaly (Eu/Eu* = 0.56–0.73). These geochemical characteristics suggest that the provenance of the Albian Abakaliki Shale lay in ancient upper continental crust composed mainly of felsic basement rocks with a minor contribution from mafic rocks. This is in contrast to earlier studies which suggested possible contribution of mafic components from Jurassic volcanogenic terrane as source rocks of the Albian shale in the southern Benue Trough. Moderate chemical weathering of the source rocks with mixed granite-granodiorite compositions is indicated by the value of the chemical index of alteration (average CIA 76.60); the plagioclase index of alteration (average PIA 85.20) and the index of compositional variability (average ICV 0.88), as well as by the Rb/Sr (0.32–0.92), K/Rb (125.36–193.55) and K/Na (1.13–2.70) ratios.

Key words: Abakaliki Formation, Benue Trough, chemical weathering, source rock

Introduction

Mineralogical and chemical compositions of siliciclastic sedimentary rocks are known to provide important information regarding source rock composition/terrane type (McLennan, 1989; McLennan et al., 1993; Armstrong-Altrin et al., 2012, 2017), weathering/recycling conditions (Cox et al., 1995;

Fedoet et al., 1995; Ghandouret et al., 2003; Zhang et al., 2013) and tectonic evolution of depositional basins (Deruet et al., 2007; Verma and Armstrong-Altrin, 2013). Clay mineralogy has been used to distil information on terrigenous sediment provenance as well as to obtain useful data on weathering regimes, palaeoclimatic variability and diagenetic overprint (Petschickett et al., 1996; Thiry, 2000; Dou et al., 2010;

Westermann et al., 2013; Ghosh et al., 2019). For example, an abundance of kaolinite in clastic sediments indicates possibly felsic source rocks. It also suggests intense weathering of source rocks under wet palaeoclimatic conditions (Chamley, 1989; Thiry, 2000). However, source rock interpretation from clay mineralogy has to be done with caution because authigenic clay minerals may be formed during burial diagenesis, thereby limiting the use of clay mineral composition in provenance studies (Kubler & Jaoyedoff, 2000; Godet et al., 2008). The geochemical approach complements data from clay mineralogy as it preserves both the provenance and diagenetic signatures (Madhavaraju, 2015; Armstrong-Altrin et al., 2013, 2015). The geochemistry of fine-grained sedimentary rocks such as shale is widely accepted to represent the mean composition of the upper continent crusts better than any other sedimentary rock and as such can provide more valuable information on the geological past (McCulloch & Wasserburg, 1978; DaPenget et al., 2012). Immobile major, trace and rare earth element abundances in sediments are good indicators of source rock geochemistry, since these are little-fractionated by sedimentary processes (McLennan, 1989; Taylor & McLennan, 1985), while more mobile elements are helpful for understanding weathering regimes and palaeoenvironmental conditions (Nesbitt & Young, 1984; Sensarmaet et al., 2008).

The upper Albian Abakaliki Formation forms part of the basal Asu-River Group in the southern Benue Trough. The formation consists predominantly of folded lead-zinc mineralised shales, with lenses of sandstone and limestone (Reyment, 1965; Petters, 1978). This shale-dominated unit has generally been noted as a shallow- to deep-marine deposit (Petters, 1978, 1983; Ojoh, 1992). Previous clay mineralogical and geochemical studies of this Albian shale (Amajor, 1987; Agumanu & Enu, 1990; Akande & Viczian, 1996; Adeigbe & Jimoh, 2013; Bolarinwa et al., 2022) were done mostly on surface exposures which may have been weathered due to extensive tropical weathering. The clay mineralogical studies by Agumanu & Enu (1990) and Akande & Viczian (1996) presented contrasting results. Agumanu & Enu (1990) reported abundances of kaolinite (47%), illite (33%), chlorite (19%) and illite/smectite mixed layer (I/S; 1%), while Akande & Viczian (1996) recorded abundances of illite (5–37%) chlorite (12–16%) and I/S (2–4%). However, both studies attributed the controls of clay mineral abundances to burial diagenesis. Based on major and trace elements, Amajor (1987) characterised the composition of Albian and Turonian shales in the southern Benue Trough in order to clarify as-

pects of their origin and provide geochemical criteria for distinguishing both shale units. That study noted that the shale units were derived from basement rocks of granitic and basaltic compositions. However, it also pointed out the need for further geochemical and mineralogical studies in order to deduce whether the basaltic source is from Upper Cretaceous pyroclastic or Precambrian basement rocks. The geochemical studies by Adeigbe & Jimoh (2013) and Bolarinwa et al. (2022) also revealed the composition source rock of the Albian shale (felsic and basic basement rocks) without deducing provenance components. Although the mineral and chemical compositions of the Abakaliki Shale are known, studies of geochemical and mineralogical constraints on provenance components/terrane types and palaeoweathering conditions were still lacking. Hence, the present study intends to evaluate the mineralogical and geochemical characteristics of the Abakaliki Shale with the aim to infer possible source rock composition and palaeoweathering conditions, as well as deduce provenance components or terrane types. The information provided in the present study will be useful for further interpretation of the stratigraphical evolution of the southern Benue Trough, especially with regard to the controversy surrounding the stratigraphical position of the Abakaliki pyroclastic.

2. Geological setting

The Benue Trough is a NE–SW trending, intracratonic rift structure in Nigeria that extends for about 1,000 km in length and is up to 250 km in width (Fig. 1A). The basin is considered to have formed as a failed arm (aulacogen) of a triple junction developed as a result of separation of the African and South American plates and the opening of the South Atlantic during the Early Cretaceous (Grant, 1971; Burke et al., 1972; Olade, 1975; Whiteman, 1982). Various lines of geomorphic, structural, stratigraphical and palaeontological evidence detailing the sequence of events leading to the formation of Benue Trough can be found in Olade (1975), Offodile (1976), Petters (1978), Wright (1976, 1981), Benkhelil (1989) and Guiraud & Bellion (1995). The Benue Trough is geographically subdivided into three main areas (i.e., Northern, Central and Southern Benue Trough), corresponding to areas of differing geological features (Nwajide, 1990; Obaje et al., 2004).

The southern Benue Trough is the southernmost part with a lateral extent of about 250 km. It includes mainly the Abakaliki Anticlinorium

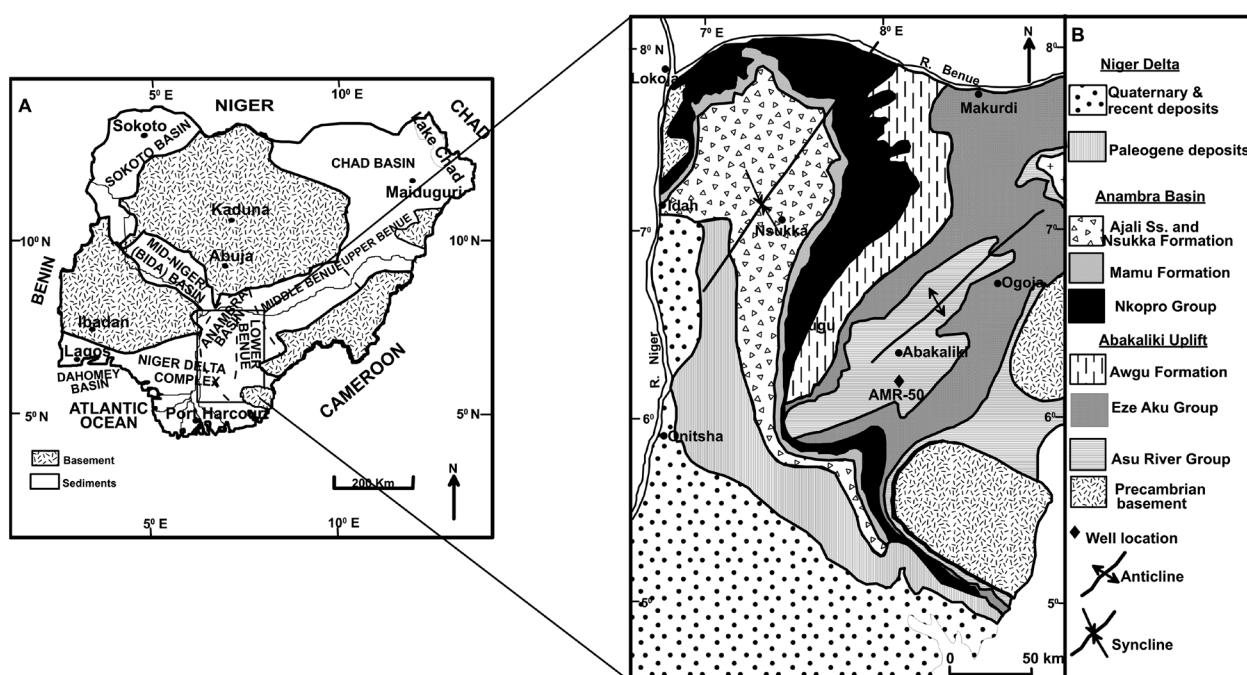


Fig. 1. A - Geological map of Nigeria showing the location of the southern Benue Trough; B - Geological map of the southern Benue Trough showing the location of the studied well (modified after Nwajide, 2013).

and Anambra Basin (Benkhelil, 1989). Reviews of the geology and stratigraphical succession of the southern Benue Trough with details on stratigraphical units, bed thicknesses, lateral extensions and stratigraphical equivalents may be found in Petters (1978), Ofoegbu (1985), Wright et al. (1985), Ojoh (1992) and Nwajide (2013). The present study follows the most recent review by Nwajide (2013). The Cretaceous sedimentary succession of the southern Benue Trough comprises three unconformity-bounded sequences that were deposited within the accommodation space created by transcurrent fault systems in the Precambrian to Lower Palaeozoic Basement Complex rocks. These infills consist of Albian-Cenomanian, Turonian-Coniacian and Campanian-Maastrichtian transgressive cycles (Petters, 1977; Agagu & Adighije, 1983). In the Abakaliki sub-basin, erosion and continental sedimentation during the Aptian, coupled with the Albian marine transgression, led to the deposition of thick sandstones and shales of the Asu River Group. The second marine transgressive cycle led to the deposition of Turonian laminated shales and calcareous siltstones of the Eze-Aku Formation and Coniacian black shale and limestones of the Awgu Formation (Fig. 1B). The mid-Santonian compressional folding and faulting led to uplift of the Abakaliki Basin to become Abakaliki Anticlinorium and subsequent

subsidence of the adjacent area to become the Anambra Basin which then became the focus of sedimentation. This led to the deposition of the Enugu/Nkporo Shales and Mamu Formation during the Campanian-Maastrichtian transgressive cycle.

In the Abakaliki-Ogoja areas, sediments of the Asu River Group are broadly subdivided into the non-marine, coarse-grained Ogoja Sandstone and the blue-black Abakaliki Shale. The Ogoja Sandstone is the basal, non-marine, conglomeratic and arkosic sandy unit of the Asu River Group that unconformably overlies the Basement Complex in both Ikom and Ogoja areas (Uzuakpunwa, 1980; Petters et al., 1987). The Abakaliki Formation at its type locality within the town of Abakaliki consists of folded, lead/zinc mineralised shales, with lenses of sandstone and limestone (Reyment, 1965). The Abakaliki Shale belongs to the transgressive phase of the Albian-Cenomanian depositional cycle (Petters, 1978). The Asu River Group is unconformably overlain by the transitional Eze-Aku Group, which consists of flaggy, grey-black calcareous shales and siltstones, shelly limestones and calcareous sandstones. This in turn is overlain by the marine Awgu Formation, which consists of about 900 m of shales, bluish-grey with some limestone bands. These represent sediments of the Turonian-Coniacian depositional cycle.

3. Material and methods

3.1. Core sampling

Core samples of the Abakaliki Shale retrieved from an exploratory well (AMR-50; 6°10.6' N, 8° 8.2'E) drilled to a total depth of about 163 m were utilised for the present study (Fig. 1B). The core samples were measured and carefully examined for their colour, structural features and rock boundary. The well penetrated about 1.3 m of brownish muddy top soil, underlain by about 161 m of dark grey, thickly laminated shale with thin calcitic veinlets (Fig. 2), which was assigned to the shale unit of the upper Albian Abakaliki Formation, locally referred to as Abakaliki Shale. The shale is underlain by about 1.7-m-thick, yellowish, medium-coarsely grained sandstone. The base boundary of this sandstone unit could not be established as the well terminated within the sandstone unit. A total of 12 sub-samples (labelled S1 to S12) from depths ranging between 11.5 m and 161.6 m (Fig. 2) were used for elemental geochemical analyses, while mineralogical analysis was conducted on three samples (S1, S6 and S11).

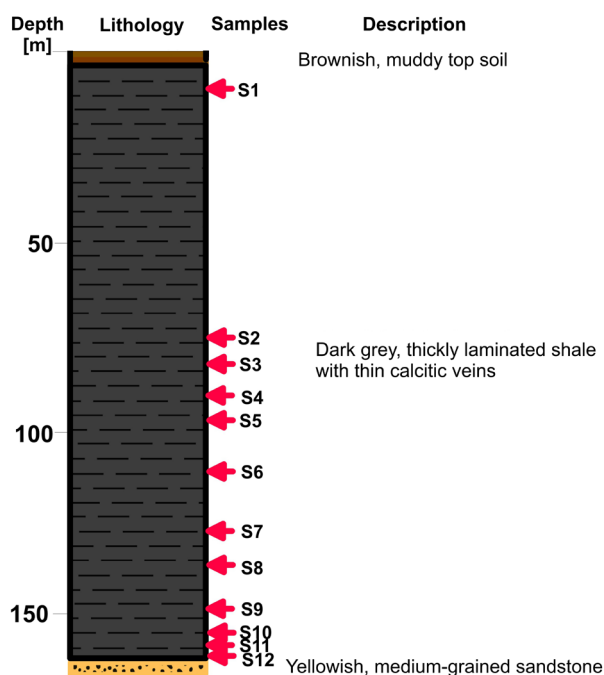


Fig. 2. Lithological section showing the core samples from well AMR-50 described in the present study.

3.2. X-ray diffraction (XRD) analysis

Selected samples of the Abakaliki Shale were analysed qualitatively for bulk rock and clay minerals

by XRD using a Bruker D8 ADVANCE diffractometer. Sample preparations were done following the standard procedures outlined by Brindley & Brown (1980) and Moore & Reynolds (1997) for X-ray diffraction (XRD) analysis. Bulk rock powder samples packed into a glass cavity mount were analysed using X-ray radiation from a CuK α anode at 40kV and 40 mA, scanned between 2° to 65° (2 θ) at a step size of 0.025°2 θ /s. For the clay size (<2 μ m) mineral separation, completely dispersed solute of powdered samples were centrifuged after which the fine suspensions were decanted into a beaker. The clay fractions were later mounted on glass slides after the dilute suspensions of <2 μ m particle sizes were concentrated by evaporation in an oven at 60°C. Oriented mounts of clay fraction were then scanned under three separate conditions: air-dried (AD), after saturation with ethylene glycol (EG) and after heating to 550°C for four hours. Heat treatment to 550°C was used to identify chlorite type and also distinguish between chlorite and kaolinite (Moore & Reynolds, 1997). X-ray scans were run between 2° and 35° (2 θ) at 40kV and 40mA using CuK α at 0.025°2 θ /s step size. Identification of mineral phases and indexing of diffraction peaks were achieved using Philips "Xpert High Score Plus®" software and comparing the X-ray diffraction patterns from the samples with an internationally recognised database. Semi-quantitative estimates of the whole rock and clay mineralogy were calculated using characteristic peak area ratios with the aid of Fityk software (Wojdyr, 2010).

3.3. Geochemical analysis

Whole-rock elemental analysis for major oxides, trace and rare earth elements contents in samples of the Abakaliki Shale were carried out using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma-Emission Spectrometry (ICP-ES) at the Bureau Veritas Analytical Laboratory, Canada. Samples were first washed to remove any contamination, air dried and then powdered to 230 μ m mesh in an agate mortar. Two methods of digestion were employed; a lithium borate fusion digestion to analyse for major oxides, refractory trace elements (Ba, Co, Cs, Hf, Nb, Rb, Sr, Ta, Th, U, V, Zr and Y) and REE (La-Lu) by Inductively coupled plasma emission spectrometry (ICP-ES) using a simultaneous/sequential ThermoJarell-Ash Enviro II ICP equipment, and an aqua regia digestion to analyse for Cu, Mo, Ni, Pb and Zn using a Varian Vista Pro ICP-MS. Calibrations were performed using USGS and CANMET certified reference materials coded STD SO-18 for ICP-ES, and STDs DS9 and OREA-

S45EA for ICP-MS. Relative deviations between measured and certified values are generally less than 5%. Loss on ignition (LOI) was determined by heating dried samples to 1,000°C for two hours.

To evaluate the enrichment and source of the elements in the samples analysed, the major and trace element contents of the samples were normalised with the average contents of the Post-Archean Australian Shale (PAAS; Taylor & McLennan, 1985), while the rare earth element concentration was normalised with the average chondrite values (Sun & McDonough, 1989) and average values of Post-Archean Australian Shale (PAAS; Taylor & McLennan, 1985). Also, in order to investigate the relationships between various geochemical variables and identify the main factor(s) that played a dominant role in the distribution of the variables, Pearson bivariate correlation coefficient statistical analysis was carried out on the log-transformed compositional data (major, trace and rare earth elements) using Statistical Package for Social Sciences (SPSS; version 16.0) software.

4. Results

4.1. Bulk and clay mineralogy

The bulk rock diffraction patterns (Fig. 3) show that the samples are composed mainly of quartz and

clay minerals associated with feldspar (albite) and gypsum. Quartz, albite and clay minerals represent 53, 10 and 36% (average of the bulk samples), respectively. Gypsum is present in small amounts (5%) in a sample from the top section of the core. Microcline and orthoclase feldspars are completely absent in the samples studied. Diffraction patterns of the clay fraction (Fig. 4) indicate high contents of illite (67%), chlorite (32%) and a low abundance of illite/smectite (I/S; 4%). The illite peaks are sharp and characterised by 001, 002 and 003 reflections at 9.94 Å, 4.99 Å and 3.34 Å, respectively in air-dried patterns. These peaks remain invariably unaffected by ethylene glycol solvation, but are slightly modified by a little shift in position when heated to 550°C (Fig. 4). Chlorite is identified in air-dried X-ray patterns by diagnostic peaks 001, 002, 003 and 004 at 14.22 Å, 7.06 Å, 4.71 Å and 3.53 Å, respectively. The 002 and 004 peaks are more intense than 001 and 003 peaks. The chlorite peaks remain unaltered when treated with ethylene glycol. However, upon heating to 550°C, the 001 chlorite peak showed an increase in intensity, while other peaks weakened and almost disappeared (Fig. 5). This is typical dehydroxylation behaviour of chlorite and is used indisputably to identify chlorite especially from kaolinite in which its peaks overlap with the 002 and 004 peaks of chlorite (Moore & Reynolds, 1997; Sordon, 2013). The I/S mixed layers are identified by the asymmetry peaks between 10–10.5 Å

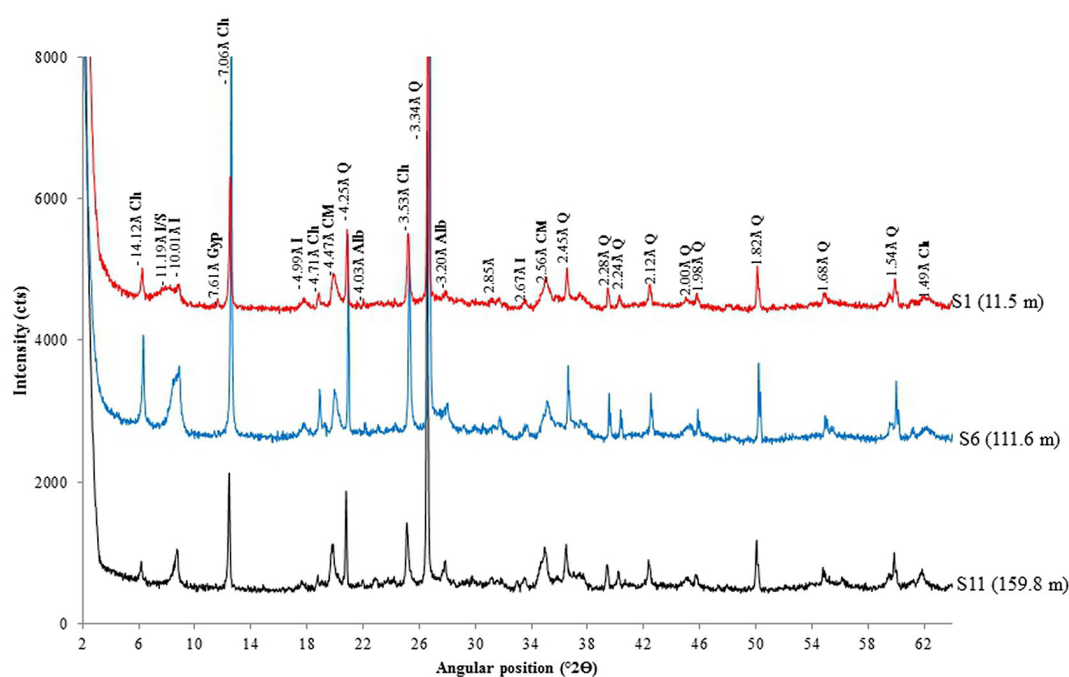


Fig. 3. Bulk rock X-ray diffraction patterns of samples of the Abakaliki Shale. Ch – chlorite, I/S – illite/smectite, I – illite, Gyp – gypsum, CM – clay minerals, Q – quartz, Alb – albite.

in air-dried patterns and collapsed to double peaks between 9.74–10.5 Å upon ethylene glycol solva-

tion. Kaolinite and smectite are absent in the samples analysed.

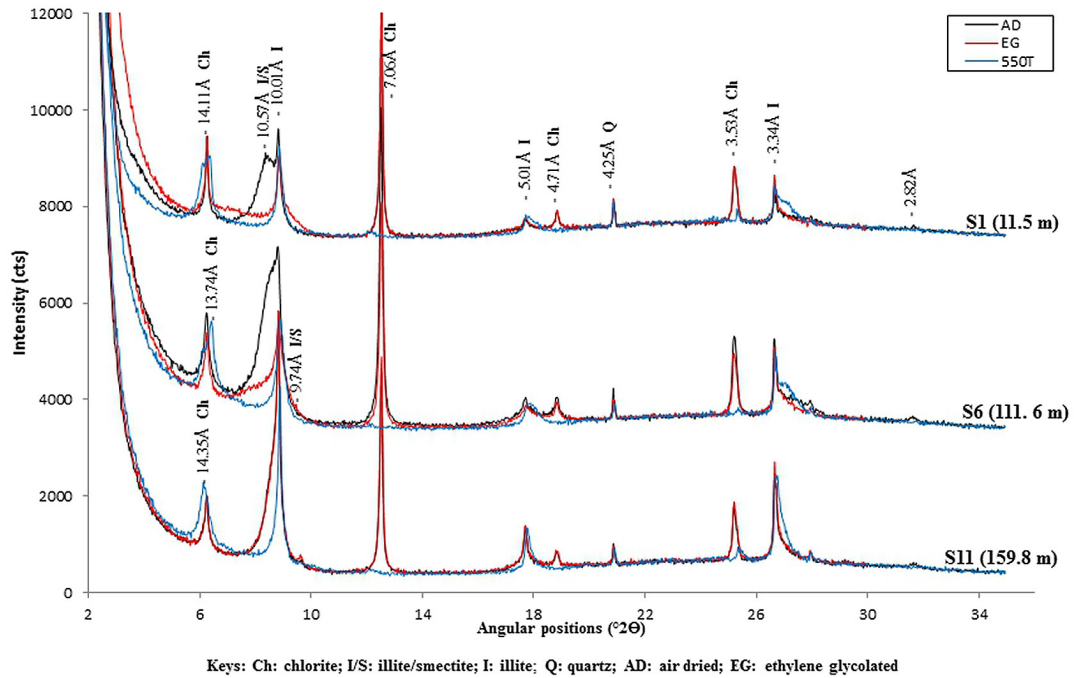


Fig. 4. X-ray diffraction patterns for the clay fraction from the samples of the Abakaliki Shale. Ch - chlorite, I/S - illite/smectite, I - illite, Q - quartz, AD - air dried, EG - ethylene glycolated.

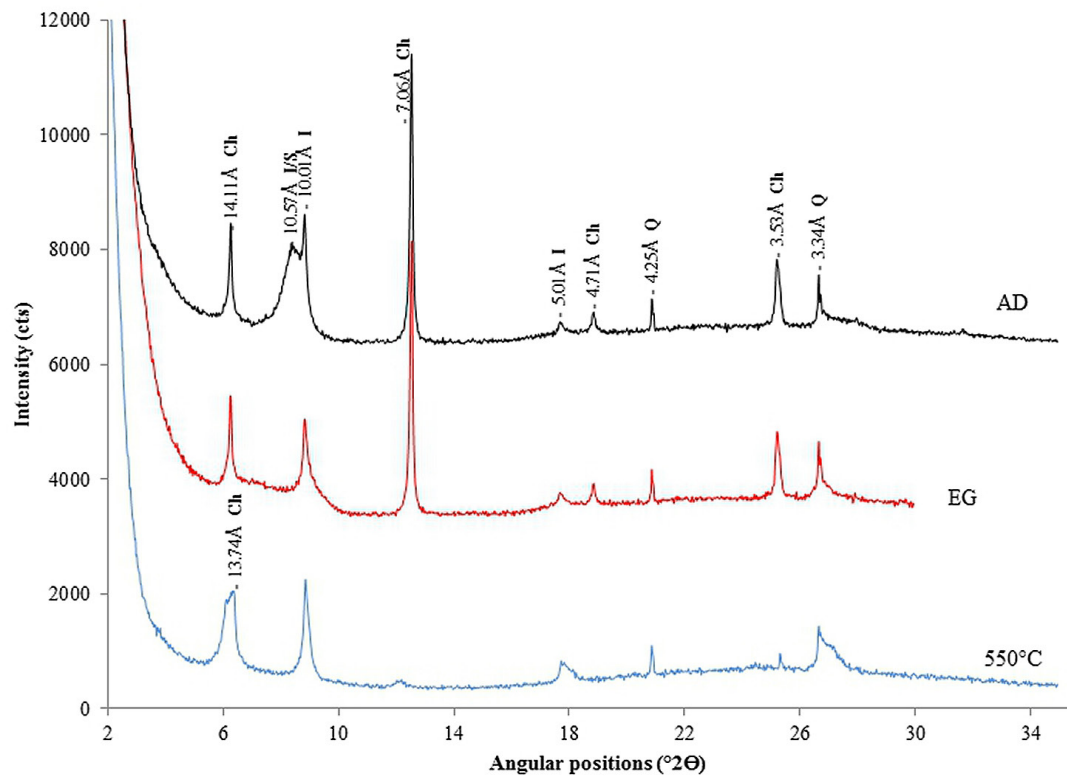


Fig. 5. X-ray diffraction patterns for air-dried, glycolated and heated (550°C) clay mineral fraction for sample S1. Ch - chlorite, I/S - illite/smectite, I - illite, Q - quartz, AD - air dried, EG - ethylene glycolated.

4.2. Major oxide contents

The summary of the concentrations of major and trace elements in samples of the Abakaliki Shale analysed are presented in Table 1 (for details see Table 4 – Supplement in the electronic version of the manuscript). The samples are high in SiO_2 (44.25–48.45 wt. %), Al_2O_3 (15.85–23.04 wt. %), Fe_2O_3 (6.56–9.36 wt. %), loss-on-ignition (LOI; 8.39–17.77 wt. %) and low in K_2O (1.84–3.96 wt. %), MgO (1.19–2.19 wt. %), Na_2O (0.90–1.38 wt. %), TiO_2 (0.76–1.04 wt. %), P_2O_5 (0.05–0.24 wt. %), MnO (0.03–0.07 wt. %). The CaO content shows a wide range between 0.15 and 14.62 wt. % (Table 1). The major oxide contents of the analysed samples, in comparison to those of the Abakaliki Shale reported by Adeigbe & Jimoh (2013), are lower in SiO_2 , but comparable in Al_2O_3 , Fe_2O_3 , MgO and K_2O . Major oxide concentrations normalised to the average Post-Archean Australian Shale (PAAS; Taylor & McLennan, 1985) show that the shale samples are slightly depleted in SiO_2 , MnO and comparable in Al_2O_3 , Fe_2O_3 , MgO , Na_2O , TiO_2 (Fig. 6), but variable in CaO , K_2O and P_2O_5 compared to PAAS. The samples analysed also exhibit lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ (2.04–3.06) and higher $\text{Al}_2\text{O}_3/\text{TiO}_2$ (19.60–23.67) ratios, but a variable $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (1.18–2.70) ratio compared to PAAS 3.32, 18.97 and 2.03, respectively. The correlation matrix for the major element contents of the shale samples reveals strong, positive correlations of Fe_2O_3 , K_2O and TiO_2 with Al_2O_3 ($r = 0.65, 0.64$ and 0.83 , respectively), and of LOI with Al_2O_3 , Fe_2O_3 and TiO_2 ($r = 0.79, 0.68$ and 0.80 , respectively). Calcium oxide (CaO) contents display strong positive correlations with SiO_2 and MnO ($r = 0.54$ and 0.95), weak positive correlations

with MgO and P_2O_5 ($r = 0.27$ and 0.39), but strong negative correlations with Al_2O_3 , Fe_2O_3 , Na_2O , TiO_2 and LOI ($r = -0.67, -0.69, -0.51, -0.57$).

4.3. Trace elements

Trace element contents of samples of the Abakaliki Shale reveal high abundances of Ba (380–704 ppm), Sr (209–367 ppm), Rb (117.40–213.30 ppm), Zn (94.80–221.50 ppm) and low contents of Hf (1.09–1.45 ppm) and U (2.20–3.00 ppm). The correlation matrix shows strong positive correlations of Sc, V, Cr, Ni, Nb, Rb, Th and Ga with Al_2O_3 ($r = 0.94, 0.88, 0.67, 0.67, 0.56, 0.69, 0.79$ and 0.95 , respectively), and with TiO_2 ($r = 0.75, 0.73, 0.50, 0.66, 0.81, 0.59, 0.80$ and 0.87 , respectively)

4.3.1. High Field Strength Elements: HSFE (Y, Zr, Hf, Nb, Ta)

In comparison with the PAAS, the Abakaliki Shale shows a depletion in Y, Zr, Ta and Hf (but comparable in Nb; Fig. 7). Similarly, the Abakaliki Shale samples show lower Zr/Hf (30.00–32.93), Zr/Y (1.91–3.09) and Zr/Nb (1.92–2.60) ratios relative to those of PAAS (42.00, 7.78 and 11.67, respectively).

4.3.2. Large Ion Lithophile Elements: LILE (Rb, Sr, Ba, Th, U)

Most studied samples of the Abakaliki Shale are relatively enriched in Rb, Sr, Th and Ga, but slightly depleted in U (~ 0.8 PAAS) and variable in Ba (380–684 ppm) compared to those in PAAS (Fig. 7). Compared to PAAS, all samples of the Abakaliki Shale show lower K/Rb (125.38–161.23) and higher

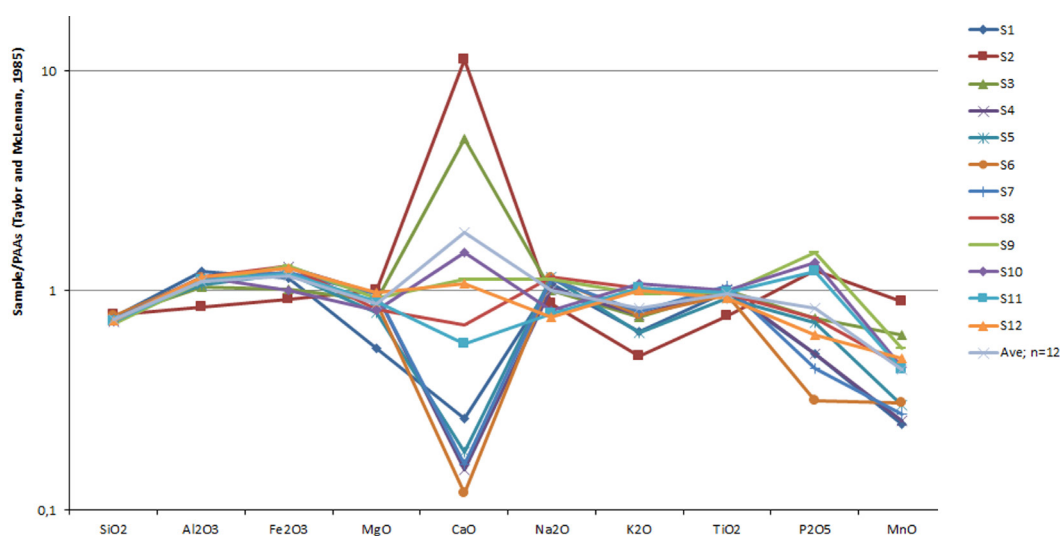


Fig. 6. PAAS-normalised major oxide plot for the samples of the Abakaliki Shale (PAAS values from Taylor & McLennan, 1985).

Table 1. Average, range and standard deviation values of the major and trace elements concentrations (wt% and ppm, respectively) in samples of Abakaliki Shale.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	LOI	Sc	V	Co	Cr
Min	44.25	15.85	6.56	1.19	0.15	0.90	1.84	0.76	0.05	0.03	8.39	11.30	87.00	14.60	61.60
Max	48.45	23.04	9.36	2.19	14.62	1.38	3.96	1.04	0.24	0.10	17.77	21.20	150.00	35.60	136.80
Avg	46.19	20.76	8.38	1.91	2.37	1.19	3.07	0.95	0.13	0.05	14.96	18.08	125.92	23.84	20.80
Stdev	1.30	1.80	0.91	0.27	4.22	0.18	0.68	0.07	0.06	0.02	2.51	2.70	15.03	6.95	20.73
	Ni	Cu	Zn	Y	Zr	Nb	Hf	Rb	Sr	Ba	Pb	Th	U	Ga	Ta
Min	37.30	21.61	94.80	14.20	33.90	16.42	1.09	117.40	209.00	380.00	13.86	17.60	2.20	23.65	0.10
Max	60.40	44.96	221.50	21.10	44.20	20.49	1.45	213.30	367.00	704.00	47.34	29.20	3.00	34.44	0.90
Avg	50.08	32.81	121.68	17.15	39.52	18.74	1.25	170.01	268.83	521.50	25.43	24.22	2.59	31.42	0.50
Stdev	7.34	7.24	38.75	2.34	2.60	1.31	0.09	25.98	43.91	120.99	9.58	3.43	0.19	2.91	0.30

Min - minimum; Max - maximum; Avg - average; Stdev - standard deviation.

Table 2. Average, range and standard deviation values of the rare earth elements concentrations (ppm) in samples of Abakaliki Shale.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Min	1.30	1.80	0.91	0.27	0.15	0.18	0.09	0.07	0.05	0.02	2.51	2.70	0.19	2.91	0.10
Max	60.40	44.96	221.50	21.10	44.20	20.49	3.96	213.30	367.00	704.00	47.34	29.20	150.00	35.60	136.80
Mean	36.91	21.01	62.74	7.54	17.70	7.58	1.68	66.19	111.15	215.84	17.48	15.97	48.24	21.68	30.22
Stdev	21.18	13.64	78.44	8.46	18.53	9.16	1.27	87.68	148.19	281.31	13.85	9.51	62.74	12.42	47.91

Min - minimum; Max - maximum; Avg - average; Stdev - standard deviation.

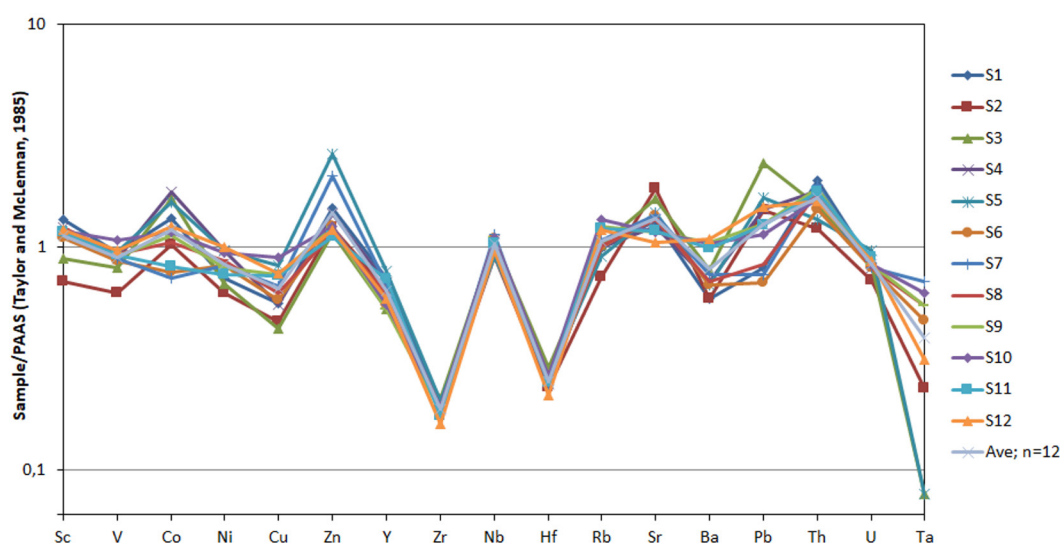


Fig. 7. PAAS-normalised trace elements plot for the samples of the Abakaliki Shale (PAAS values from Taylor & McLennan, 1985).

Th/U (6.50–11.23) ratios, but a variable Rb/Sr ratio. However, the last four samples represent the base of the core and show higher Rb/Sr values (>0.80) than PAAS (0.80).

4.3.3. Transition Trace Elements: TTE (Sc, V, Co, Cr, Ni, Cu)

A great deal of variability exists in the PAAS-normalised patterns of transition trace element (TTE) contents in the samples studied (Fig. 7). On average, samples of the Abakaliki Shale analysed are comparable in Co (23.84 ppm) and Ni (50.08 ppm) contents to those of PAAS (Fig. 7), but depleted in V, Cr, and Cu (125.92, 96.35, 32.81 ppm, respectively)

and higher in Sc (18.08 ppm). In addition, the Abakaliki Shale exhibit a higher average Ni/Co (2.25), but lower Cr/V (0.76) and V/Ni (2.53) ratios than PAAS.

4.4. Rare Earth Elements (REE)

The summary of REE (La-Lu) compositions of samples of the Abakaliki Shale analysed is presented in Table 2 (for details see Table 5 - Supplement in the electronic version of the manuscript). The Σ REE content (134.67–354.15 ppm) of the samples shows significant variations. The mean Σ REE value for the

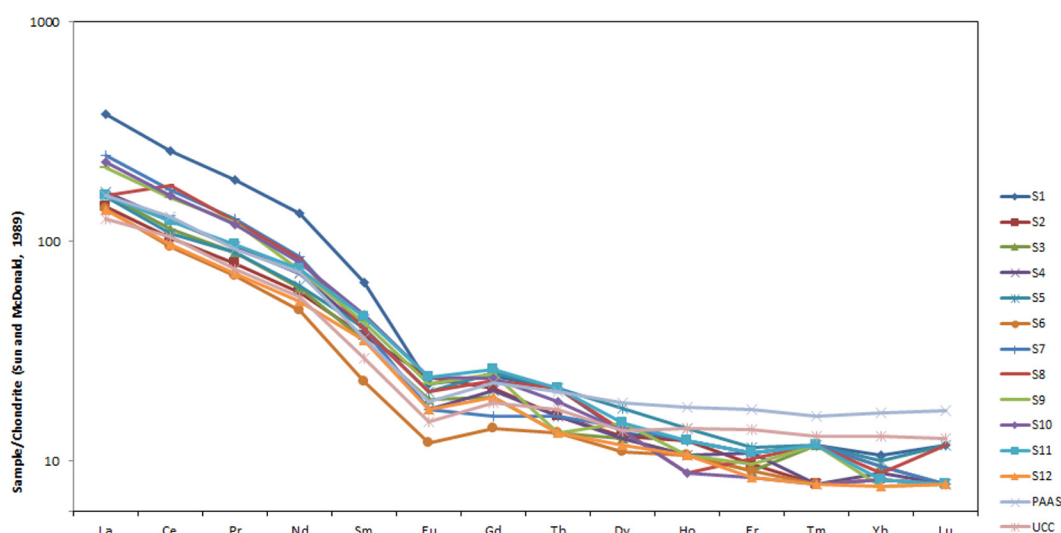


Fig. 8. Chondrite-normalised REE plot for the samples of the Abakaliki Shale (chondrite values after Sun & McDonough, 1989). For comparison, averages of UCC and PAAS (Taylor & McLennan, 1985) are also plotted. Note the uniformity in REE patterns for the studied samples of the Abakaliki Shale and a similarity to UCC and PAAS.

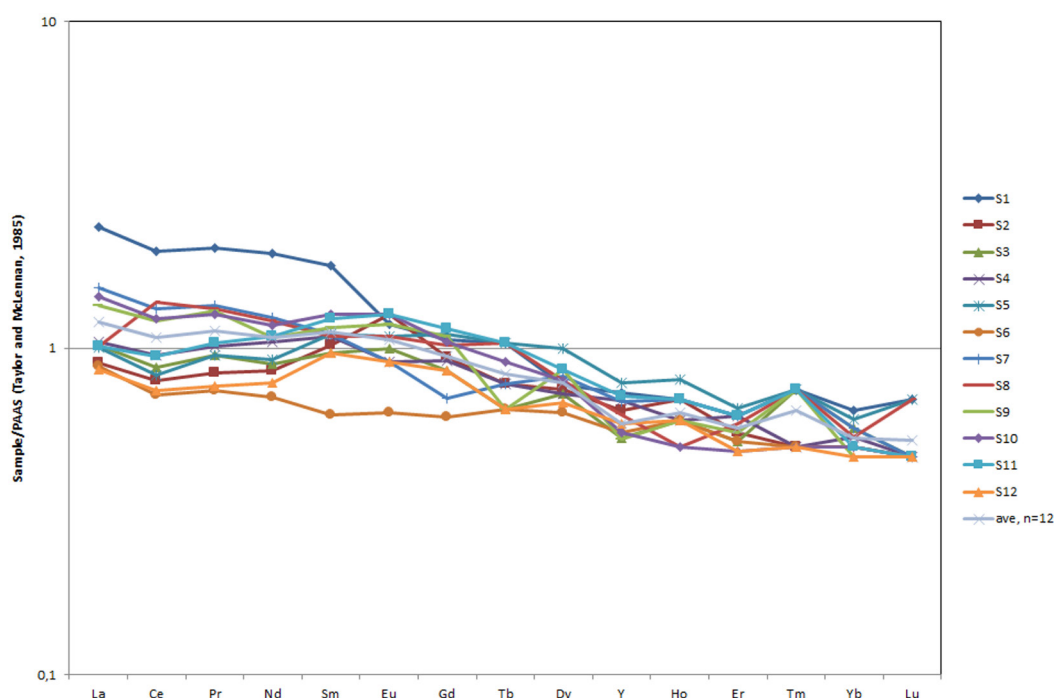


Fig. 9. PAAS-normalised rare earth element plot for the samples of the Abakaliki Shale (PAAS values from Taylor & McLennan, 1985).

present analysed samples (197.99 ppm) is lower than that reported for the same shale in a previous study (239.98 ppm; Bolarinwa et al., 2022), but higher than that of the Post-Archean Australian Shale (Σ PAASREE = 183.03 ppm, Taylor & McLennan, 1985). The chondrite-normalised REE patterns of the samples analysed are similar with overlapping abundances and follow closely the average composition of PAAS (Fig. 8). They are characterised by pronounced LREE fractionation and enrichment as shown by $(La/Yb)_N$ and $(La/Sm)_N$ ratios ranging from 16.08–35.75 and 3.61–6.16, respectively (Table 2, see also Table 5 in Supplement); where N represent chondrite-normalised value), Heavy REE (HREE) depletion ($(Gd/Yb)_N = 1.71$ – 3.25) and consistent negative europium anomaly ($Eu/Eu^* = 0.56$ – 0.73 ; details for calculation are provided with the full dataset in the electronic version).

The PAAS-normalised REE+Y plot for the samples of Abakaliki Shale (Fig. 9) also shows REE fractionation patterns of high LREE/HREE ratios ($(LaN/YbN = 1.65$ – 3.67) signifying LREE enrichment (~ 2 PAAS), depleted HREE, weak negative Ce anomaly ($Ce/Ce^* = 0.85$ – 1.19 ; ave 0.93) and positive Eu anomaly ($Eu/Eu^* = 0.86$ – 1.30 , ave 1.04).

The correlation matrix shows a weak positive correlation of Al_2O_3 with Σ REE ($r = 0.49$), strong positive correlations of Th with Σ REE (0.72) and Light REE (La: 0.66; Ce: 0.74; Pr: 0.72; Nd: 0.71 and Sm: 0.52), and good positive correlations of Heavy

REE with Zn (Dy: 0.56; Ho: 0.63; Er: 0.60 and Yb: 0.64) and Y (Tb: 0.72; Ho: 0.69; Er: 0.86; Yb: 0.60 and Lu: 0.53).

5. Discussion

5.1. Mineralogical characterisation

The XRD patterns of the Abakaliki Shale show a quartz-albite-illite-chlorite-gypsum-illite/smectite association with illite and chlorite as the most abundant clay minerals. The results also indicate the complete absence of microcline and orthoclase feldspars, kaolinite and smectite. This observed mineralogical association is similar to those reported for outcropping samples of the Abakaliki Shale by Akande & Viczian (1996). In contrast, Agumanu & Enu (1990) recorded an abundance of kaolinite (47%), illite (33%) and chlorite (19%) with traces of illite/smectite mixed layer (1%) in samples of the Abakaliki Shale designated as the Lower Asu River Group.

The predominance of quartz (> 50%), with a subordinate amount of total clay (average 36%) and trace amount of feldspar (10%) in the bulk mineralogy, characterises the Abakaliki Shale as a siliceous-argillaceous mudstone (Si-Ar; Lazar et al., 2015). The high intensity of the 002- and 004-chlo-

rite peaks suggests Fe-rich chlorites (Moore & Reynolds, 1997; Akande & Viczian, 1996). No other Fe-mineral is found in the samples analysed. However, Akande & Viczian (1996) noted an abundance of siderite (3–25%) and traces of pyrite and goethite in some shale samples from the Ishiagu and Enyigba mining districts. The collapse of I/S peaks in EG patterns to double peaks suggests the presence of long-range ordered R3 illite/smectite (Figs. 4, 5). Illite and chlorite may have been derived from the degradation of muscovite and biotite from metamorphic rocks under hot and dry climatic conditions. Both minerals may also have formed diagenetically through smectite to illite transformation during burial diagenesis. The high contents of illite and Fe-chlorite, as well as the trace amount of regularly ordered I/S mixed layer and the absence of smectite in samples of the Abakaliki Shale, are suggestive of an advanced stage of smectite-illitization at high temperatures (Velde & Vasseur, 1992). The smectite-illitization process involves a gradual conversion of smectite to illite via illite/smectite layer, leading to loss of smectite during sediment burial (Hillier et al., 1995; Berger et al., 1999). The process is temperature controlled and mainly dependent on potassium ion availability (Berger et al., 1999; Meunier & Velde, 2004). Therefore, the absence of K-feldspars (e.g. microcline and orthoclase) in the studied samples of the Abakaliki Shale probably reflects their complete dissolution and replacement by albite (albitization). The potassium ion is then released for smectite-illitization (Pollastro, 1993). Furthermore, the presence of Fe-chlorite in the samples suggests a source from altered clays such as smectite. The conversion of smectite during the illitization process could have released the iron and magnesium needed for precipitation of the Fe-chlorite in the pore space (Ehrenberg, 1993; Hillier, 1994). Accordingly, the clay mineral characteristics of the

studied samples of the Abakaliki Shale suggest strong diagenetic control, thereby constraining the use of the clay mineral contents to interpret source composition as well as weathering intensity.

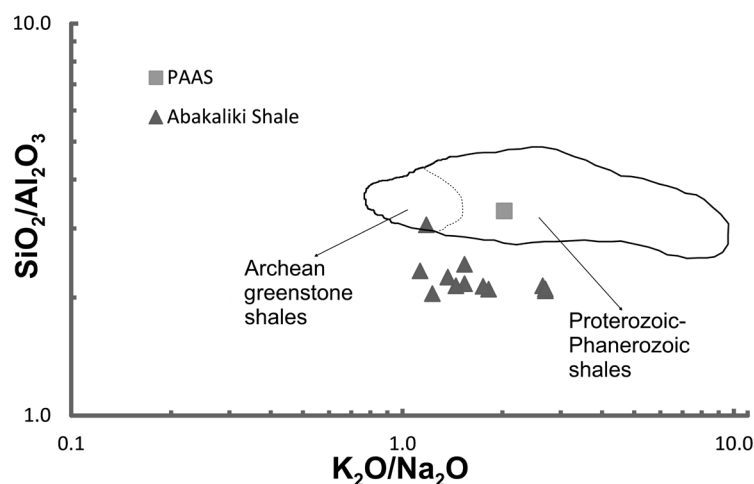
5.2. Geochemical characterisation

The high content of SiO_2 and Al_2O_3 in the compositional data confirms a mineralogy dominated by quartz and clay minerals as reflected in XRD bulk mineralogy (section 4.1). The high CaO content (> 2%) observed in two samples (S2 and S3; full dataset in the electronic version) is possibly related to the presence of gypsum as reflected in the mineralogy result. However, the low contents of K_2O and Na_2O in the samples studied reflect the near-absence of feldspars. This is confirmed by the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio for the samples (0.10–0.18), which suggest the dominance of clay minerals over feldspars in the original composition of these Albian sediments (Cox et al., 1995).

Samples of the Abakaliki Shale studied exhibit a small range of SiO_2 (44.89–48.45%) content, relatively uniform REE chondrite-normalised patterns (Fig. 8), weak correlations of Zr with Al_2O_3 and SiO_2 ($r = -0.12$ and 0.27 , respectively) and lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio compared to Proterozoic-Phanerozoic shales (Fig. 10), suggesting that hydraulic sorting and quartz dilution might have had no significant control on the chemistry of the Abakaliki Shale. The homogeneous relationship between Th/Sc and Zr/Sc ratios (Fig. 11) for the Abakaliki Shale samples further support that sedimentary sorting and recycling had no important control on the chemistry, but that REE and trace element contents are controlled by input from first-cycle material (Fig. 11).

The strong positive correlations of Fe_2O_3 , K_2O and TiO_2 contents with Al_2O_3 suggest that their

Fig. 10. $\text{SiO}_2/\text{Al}_2\text{O}_3$ vs. $\text{K}_2\text{O}/\text{Na}_2\text{O}$ plot showing a lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the Abakaliki Shale in comparison to PAAS, Greenstone shales and Proterozoic-Phanerozoic shales. Boundaries for Proterozoic-Phanerozoic and Archean Greenstone shales are from Wronkiewicz & Condie (1987). Data for PAAS are from Taylor & McLennan (1985), while those for the Abakaliki Shale are from the present study.



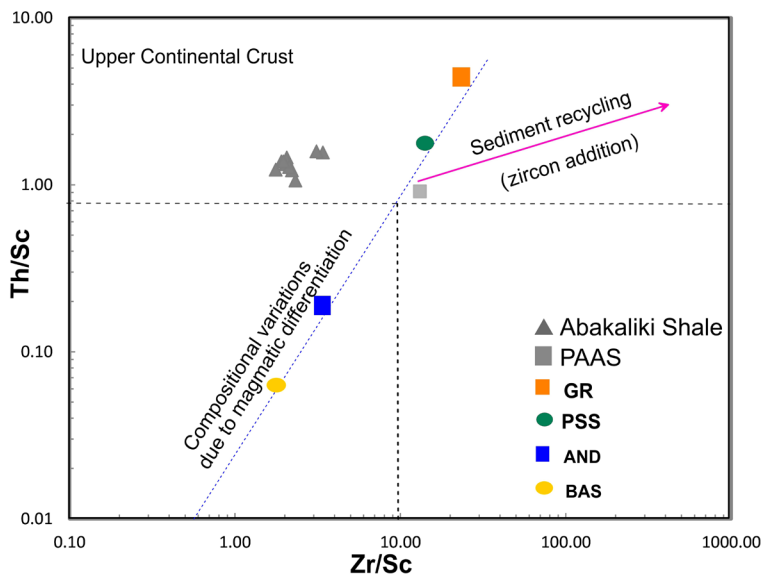


Fig. 11. Th/Sc vs. Zr/Sc plot (after McLennan et al., 1993) showing the homogeneous relationship of ratios, interpreted as depletion of zircon (low Zr/Sc) due to insignificant control of sedimentary sorting on the chemistry of the Abakaliki Shale. Data on GRA, PSS, AND, BAS and PAAS (granite, Proterozoic sandstone, andesite, basalt and post-Archean Australian Shale) are after Taylor & McLennan (1985).

abundances are significantly controlled by the dominant clay mineral (Nesbitt et al., 1980). The relatively comparable TiO_2 content of the PAAS (0.99; Taylor & McLennan, 1985) and that of the studied samples of the upper Albian Abakaliki Shale (avg. 0.95; Table 1) suggest similar mafic contents of their source rocks. Therefore, the strong positive correlations of TiO_2 contents with Al_2O_3 , Fe_2O_3 , K_2O , Sc, V, Cr, Nb, Rb, Th and Ga contents suggest their concentrations in the Abakaliki Shale are relatively from the source rocks. The plot of Th/Sc vs. Zr/Sc for samples of the Abakaliki Shale also suggests significant contribution of parent rocks to the chemical composition (Fig. 11). Similarly, the comparable abundances of Al and Ti relative to PAAS (Fig. 6) and their strong positive correlation suggest that they are controlled by clay mineral abundances. Illite, the most dominant clay mineral in the studied shales, accommodates only K, Si and Al. The negative correlation of Na_2O with K_2O ($r = -0.35$) and the positive correlations of K_2O with Al_2O_3 , Fe_2O_3 and TiO_2 also suggest that the K_2O content is controlled by the dominant clay mineral, not by feldspar content. This therefore underscores the importance of weathering of the source rocks in the enrichment of these elements.

5.3. Source rock composition

Geochemical approaches have proved powerful in identifying source rock composition of clastic sediments (Taylor & McLennan, 1985; Cullers et al., 1988; Condie et al., 1992). Hayashi et al. (1997) considered the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of mudrocks as suitable of source rock composition and suggested an

$\text{Al}_2\text{O}_3/\text{TiO}_3$ ratio of 3–8 for mafic source rocks, 8–21 for intermediate source rocks and 21–70 for felsic igneous rocks. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio (19.6–23.7) for the analysed samples of the Abakaliki Shale are relatively comparable to those of Precambrian shales and sandstones in Egypt (15–25; Willis et al., 1988) and Neoproterozoic shales in India (13–25; Nagarajan et al., 2007), which were interpreted to be sources from granulitic rocks of intermediate to felsic composition. A similar inference is also supported by the TiO_2 vs. Ni bivariate plot (Fig. 12). Most samples of the Abakaliki Shale plotted outside, but close to the acidic source rock field, suggesting that these shales were derived mainly from intermediate to felsic source rocks.

Trace elemental ratios such as Th/Sc, Th/Co, La/Sc, La/Co and Th/Cr are significantly differ-

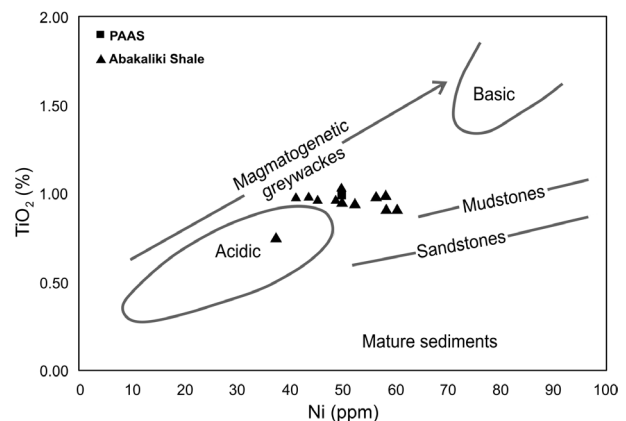


Fig. 12. TiO_2 vs. Ni bivariate plot for samples of the Abakaliki Shale showing an enrichment in TiO_2 and Ni contents similar to PAAS depicting components from acidic to intermediate source composition (fields after Floyds et al., 1989).

Table 3. Range of elemental ratios of the shale samples in this study compared to the ratios in sediments derived from felsic rocks, mafic rocks, upper continental crust (UCC) and post-Archean Australian shale (PAAS).

Elemental ratio	Range for samples of Abakaliki Shale ¹		
	min	max	average
Eu/Eu*	0.56	0.85	0.68
La/Sc	1.71	4.23	2.53
La/Co	1.11	4.00	2.06
Th/Sc	1.06	1.58	1.35
Th/Co	0.61	1.90	1.11
Th/Cr	0.19	0.39	0.26
Cr/Th	2.55	5.28	4.01

	Range for sediments ² derived from:		UCC ³	PAAS ⁴
	felsic rocks	mafic rocks		
Eu/Eu*	0.40–0.94	0.71–0.95	0.63	0.66
La/Sc	2.50–16.30	0.43–0.86	2.21	2.40
La/Co	1.80–13–80	0.14–0.38	1.76	1.65
Th/Sc	0.84–20.50	0.22–0.25	0.79	0.90
Th/Co	0.67–19.40	0.04–1.40	0.63	0.63
Th/Cr	0.13–2.70	0.02–0.05	0.13	0.13
Cr/Th	4.00–15.00	25–500	7.76	7.53

¹Present study, n = 12; ²Cullers et al. (1988), Cullers (1994, 2000), Cullers & Podkovyrov (2000); ³, ⁴Taylor & McLennan (1985).

ent in felsic and basic rocks; such have been used to constrain the average provenance composition of ancient and modern clastic sediments (Taylor & McLennan, 1985; Cullers et al., 1988; Fralick & Kronberg, 1997; Hayashi et al., 1997). The Th/Sc (1.06–1.58), Th/Co (0.61–1.90), La/Sc (1.17–4.23), La/Co (1.11–4.00) and Th/Cr (0.19–0.39) ratios for samples of the Abakaliki Shale are within the range of sediments derived from felsic rocks rather than mafic rocks (Table 3). More importantly, the La/Sc, Th/Sc and Th/Cr ratios of the studied shales are relatively similar to those of PAAS, hinting at the felsic nature of the source rocks. These interpretations are also supported by the triangular plot of La-Th-Sc (Fig. 13) which reveals that the composition of most of the analysed samples closely resembles Phanerozoic shales, suggesting their derivation from old and well-differentiated upper continental crustal sources dominated by felsic metavolcanic-plutonic terranes with a minor contribution from mafic rocks (McLennan et al., 1990). The incorporation of a mafic component in the source rocks of the Abakaliki Shale is further shown by a higher Sc content as well as higher Th/Co and Ni/Co ratios than those of PAAS.

REE chondrite-normalised patterns and a europium anomaly of clastic sedimentary rocks have

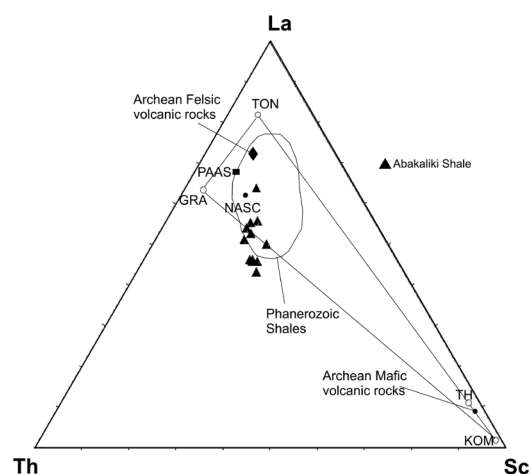


Fig. 13. La-Th-Sc ternary plot for the samples of the Abakaliki Shale (after Jahn & Condie, 1995). Fields of Phanerozoic shales, Archean felsic volcanic rocks and Archean mafic volcanic rocks after Taylor & McLennan (1985). PAAS - post-Archean Australian Shale, NASC - North American Shale Composite, GRA - granite, TON - tonalite, TH - tholeiite, KOM - komatiite are also plotted as reference.

been used to provide important clues regarding the source rock composition (Taylor & McLennan, 1985; Wronkiewicz & Condie, 1987). Mafic rocks show less fractionated chondrite-normalised patterns with low LREE/HREE ratios and no or weak Eu anomalies, whereas felsic rocks usually show fractionated chondrite-normalised patterns with high LREE/HREE ratios and negative Eu anomalies (Cullers, 1994; Cullers & Graf, 1984; Taylor & McLennan, 1985). The fractionated chondrite-normalised REE patterns (i.e., high normalised concentration of LREE and nearly flat REE; Fig. 13) as well as high LREE/HREE ratios (16.08–35.75) and pronounced negative Eu anomalies (0.56–0.85; average 0.68) of the Abakaliki Shale samples suggest that they were derived from predominantly felsic rocks of the upper continental crust.

The above assertions that the Abakaliki Shale was derived from crustal rocks dominated by felsic components and minor mafic rocks is in agreement with studies by Adeigbe & Jimoh (2013) and Bolarinwa et al. (2022), but diverge from the view by Amajor (1987) that the shales of the Albian Asu River Group (equivalent of the Abakaliki Shale) were sourced from more basic rocks than felsic ones. In addition, the negative Eu anomaly (ave. 0.68), the high Th/Sc (>1.0) and Th/U (4.0) ratios as well as high CIA value (~76) hint at Precambrian upper continental crust terrane as provenance of the Abakaliki Shale. This forecloses any contribution from

younger Cretaceous volcanics or pyroclastics as suggested by Amajor (1987).

5.4. Palaeoweathering conditions

A number of different geochemical proxies have been proposed for evaluating weathering processes and intensity on continents (Parker, 1970; Nesbitt & Young, 1982; Harnois, 1988; Fedo et al., 1995; Price & Velbel, 2003). The Chemical Index of Alteration (CIA; Nesbitt & Young, 1982) and Plagioclase Index of Alteration (PIA; Fedo et al., 1995) were used to quantitatively measure the degree of source area weathering condition for the Albian Abakaliki Shale. CIA and PIA were calculated as molecular proportion of $[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100]$ and $[\text{Al}_2\text{O}_3 - \text{K}_2\text{O} / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} - \text{K}_2\text{O}) \times 100]$ respectively, where CaO^* represents the amount of CaO incorporated in the silicate fraction of the rock. CIA and PIA values of samples of the Abakaliki Shale analysed range from 71.5–81.6 and 79.3–88.8, with mean values of 76.6 and 85.2, respectively (Table 4 in Supplement). CIA and PIA values of the Abakaliki Shale samples are lower than the average values (95 and 93, respectively) for suspended sediments of the Niger River (Martin & Meybeck, 1979) which happens to flow through the same geographical region and experience the same climatic condition as the present-day Benue valley. These suggest that the Abakaliki Shale and the Niger River sediments are products of different weathering intensities, possibly under different climatic conditions. On the other hand, the CIA and PIA values of the Abakaliki Shale are comparable

to the CIA and PIA values of average shale (70–75 and 77–85 respectively; Fedo et al., 1996) and Taiwan coastal and offshore sediments (71–75 and 80–90 respectively; Selvaraj & Chen, 2006), suggesting that the studied samples of the Abakaliki Shale are product of similar silicate weathering intensity as the average shale and Taiwan sediments. Therefore, the CIA and PIA values of the Abakaliki Shale samples indicate that they are possibly product of rocks that underwent intermediate chemical weathering.

Similarly, on the A-CN-K [$\text{Al}_2\text{O}_3 - (\text{CaO}^* + \text{Na}_2\text{O}) - \text{K}_2\text{O}$] ternary plot (Fig.14), the compositional data of the Abakaliki Shale samples plotted between CIA 70 and 81 (CIA scale shown on the left side of the diagram) above the feldspar line and fall on two weathering trends parallel to A-CN line. The first weathering trend (arrow 1 in Fig. 14) falls on the line similar to the weathering trend of PAAS and intersects the Pl-Ks join at UCC point, suggesting derivation from a moderately weathered source rock of granodioritic composition. The second weathering trend (arrow 2 in Fig. 14) falls on a line to the right of PAAS trend, intersecting Pl-Ks join at a point x and suggests that the parent rock is slightly richer in k-feldspar compared to upper crustal rock. Therefore, these two weathering trends indicate that the Abakaliki Shale samples are products of moderate chemical weathering of basement rocks with mixed granite-granodiorite compositions.

The Index of compositional variability (ICV; Cox et al., 1995) is another proxy that can be used to deduce the degree of chemical weathering of mudrocks and shales. ICV is a measure of aluminium abundance relative to other oxides and is calculated as $[(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Fe}_2\text{O}_3 + \text{MgO} + \text{MnO} +$

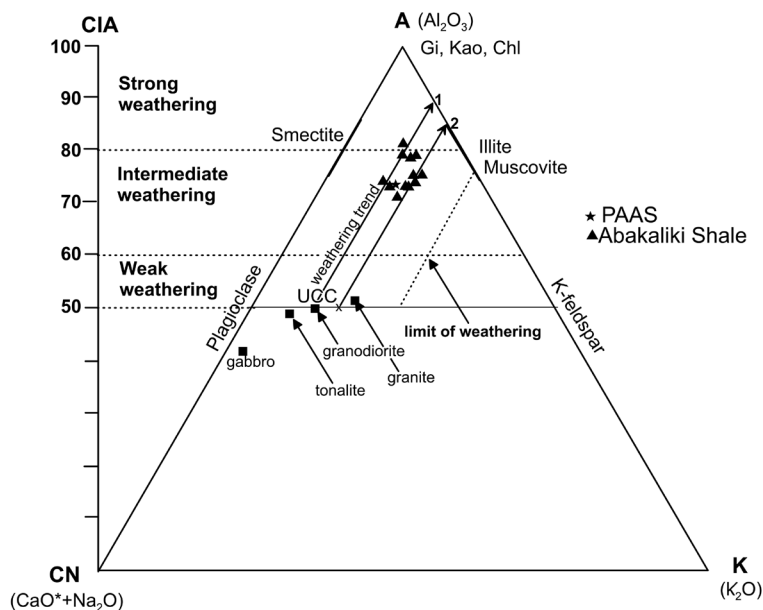


Fig. 14. $\text{Al}_2\text{O}_3 - (\text{CaO}^* + \text{Na}_2\text{O}) - \text{K}_2\text{O}$ (A-CN-K) ternary plot showing the weathering trend for the samples of the Abakaliki Shale. Gi - gibbsite, Kao - kaolinite, Chl - chlorite, UCC - upper continental crust, PAAS - post-Archean Australian Shale (after Fedo et al., 1995, 1996; Nesbitt & Young, 1984, 1989; Nesbitt et al., 1997).

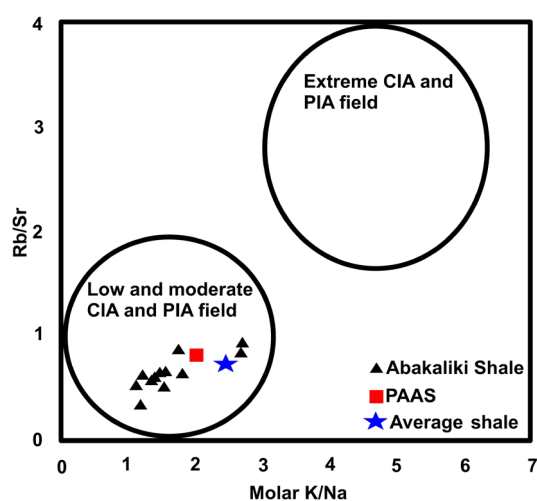


Fig. 15. Scatter plot of Rb/Sr *vs.* molar K/Na ratios for the samples of the Abakaliki Shale and other reference compositions. Fields of low, moderate and high values of chemical and plagioclase index of alteration (CIA and PIA) after Selvaraj & Chen (2006).

TiO₂)/ Al₂O₃; Cox et al. (1995)]. Non-clay silicates have lower content of Al₂O₃ and hence, higher ICV (0.54–0.87) than those of clay minerals (0.03–0.78) (Cox et al., 1995). The ICV values for the samples of Abakaliki Shale (0.63 to 1.71 average 0.880.31, Table 4 in Supplement) are higher than those for the Permian Barakar Formation (0.33–0.62), which is interpreted to be product of intense chemical weathering (Ghosh et al., 2019). Cox et al. (1995) suggested that sediments with high ICV values are compositionally immature and derived by weak to moderate weathering of source rocks, whereas sediments with low ICV are compositionally mature and derived from source rocks under strong weathering conditions. Therefore, the high ICV values of the Abakaliki Shale indicate compositionally immature mudrock which were derived by weak to moderate chemical weathering of source rock.

Some elemental ratios such as Rb/Sr, K/Rb and molar K/Na have also been widely used as proxies to examine the degree of weathering based on the fact that these elements commonly display remarkably different mobilities and are fractionated to different degrees during weathering (Nesbitt & Young, 1982; Ma et al., 2000; Ding et al., 2001; Yang et al., 2004; Roy et al., 2008). An increase in chemical weathering intensity rapidly depletes Sr and Na compared to Rb and K, and K compared to Rb (Nesbitt & Young, 1982; Wronkiewicz & Condie, 1989; Ma et al., 2000). Therefore, high ratios of Rb/Sr and K/Na, and low ratio of K/Rb have been suggested to indicate extreme chemical weathering. The Rb/Sr, K/Na and K/Rb ratios for the samples

of Abakaliki Shale range from 0.32 to 0.92, 1.13 to 2.70 and 125.36 to 193.55, respectively (Table 4 in Supplement). The mean Rb/Sr and K/Rb ratios (0.70 and 176 respectively) of the studied samples are consistently close to the Rb/Sr and K/Rb ratios of post-Archean Australian Shale (0.80 and 192 respectively; Taylor & McLennan, 1985) and average shale (0.82 and 190, respectively; Turekian & Wedepohl, 1961), corroborating that the degree of silicate weathering was intermediate. Similarly, the scatter plot of Rb/Sr *vs.* molar K/Na ratios (Fig. 15) shows the relationship between both ratios. Samples of the Abakaliki Shale plotted in the low and moderate CIA and PIA field, corroborating the intermediate weathering intensity.

6. Conclusions

Mineralogical and geochemical compositions of the upper Albian Abakaliki Shales in the southern Benue Trough are presented in order to infer possible source rock compositions and deduce palaeoweathering conditions. The mineralogical analysis has revealed an abundance of quartz, albite and clay minerals (illite, chlorite and illite-smectite). Clay mineral composition may be the end product of diagenesis and therefore constrain their use in interpreting rock-source compositions as well as weathering conditions. Major oxide and trace element compositions of the shales studied have shown an enrichment of Al₂O₃, Fe₂O₃, Sc, Nb, Sr, Sc, T and LREE, and a depletion of Si, K, P, Mn, V, Ni, Cu, Y, Zr, Hf, Ba and HREE with regard to PAAS. Source rock characteristics and chemical weathering are the major factors that controlled the geochemical composition of the Abakaliki Shale. The provenance area of the upper Albian Shale in the southern Benue Trough is ancient Upper Continental Crusts composed predominantly of felsic basement rocks with a minor mafic component. The chemical weathering indices characterise the Abakaliki Shale as an immature rock derived by moderate chemical weathering of source rocks with mixed granodiorite-granite compositions. The present study further concludes that the upper Cretaceous volcanics of the southern Benue trough did not contribute to the sediment source of the Abakaliki Shale.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial and non-profit sectors. The work was supported by the Department of Earth Sciences, Ladoke Akintola University of Tech-

nology, Nigeria as part of staff development. The authors wish to thank the management of the Rock Salt Mining and Exploration Company for releasing the core samples for this study, as well as Olabode M. Bankole of the Université de Poitiers for assisting in carrying out the XRD analysis and to the late Dr Mike Akaegbobi for his comments and guidance during the course of this study. We thank also two anonymous reviewers for their comments and suggestions, which contributed to improving the content of this paper.

Supplement available on <http://www.geologos.com.pl/>

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Manuscript submitted: 10 December 2023

Revision accepted: 5 May 2024