GEOLOGICAL AND SEDIMENTARY GEOCHEMISTRY OF MAMFE FORMATION, SOUTH EAST NIGERIA: IMPLICATIONS FOR ECONOMIC MINERALS AND HYDROCARBON POTENTIALS

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Abstract

The present research used inorganic and organic geochemical techniques to evaluate the variations of inorganic constituents, as well as organic matter types to characterize shales of the Mamfe Formation. The aim was to determine its provenance, palaeo-weathering,tectonic setting and paleo-environment condition, and mineral resources potentials. The results revealed a provenance of predominantly terrigenous materials with limited older sediments of passive continental margin setting. Sediment accumulation in Mamfe Formation took place in an oxygen-rich fresh water setting. Shales in the study area are homogenous; they reveal zircon enrichment and a limited influence of mineral sorting. Also, they are enriched in rare-earth element (REE), P, Ba, As, Ce, Cs, Sc, Sr, Th and U, while few samples are enriched with Pb and W. There is moderate to high total organic carbon (TOC) in shales of Mamfe Formation. A wide range in hydrocarbon values of S_1 and S_2 and high hydrogen with oxygen indexes indicate immature to mature organic material and mixed types (Type-II and -III), suggesting good to fair prospect for hydrocarbon source rock. Exploration activities in the Ikom-Mamfe basin should be concentrated more on hydrocarbons and industrial minerals such as REE, phosphate, clay, evaporite, uranium and heavy minerals.

Keyword: Shales, geochemical techniques, total organic carbon, hydrocarbon, industrial minerals, Mamfe Formation.

Introduction

Since the discovery of commercial quantity of petroleum in Oloibiri-Nigeria in 1956, petroleum has remained the main-stay accounting for 95% of foreign exchange earnings, of Nigeria's economy[1]. Globally, the narrative of hydrocarbon as a primary source of energy is given a second lookas many nations currently seek alternatives to remain relevant. Nigeria, in its bid to diversify its economy has begun to focus on different sectors among which geotourisim, agricultureand the mining sector is given much attention.

The Nigerian Government under the 2020 National Integrated Mineral Exploration Project (NIMEP) identified and commissioned about eight (8) critical economic minerals (Au, PGM, Ni, Cr, Co, REE, Pb-Zn-Ag, Ba and Fe) for exploration to foster local and foreign direct investment

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[1]Oyetade O. P. & Abada, O. K., 2020. The application of seismic attribute analyses for enhanced reserve estimation in ''KOA'' field, Niger Delta. *Journal of Iberian Geology, 46*(3), 311-334.

in the mineral and mining sector[2]. This policy aligns sufficiently with the United Nations Sustainable Development Goal 9 that's emphasizes industry, innovation and infrastructural development. This position has stimulated interest in the exploration of frontier basins for their economic resources (hydrocarbon resources and diverse mineral deposits) across the nation especially in the basement complex terrains and the large sedimentary basins - Benue Trough (BT), Sokoto, Borno and Niger Delta Basins. According to Adamu *et al*[3]., little or no attention is given to smaller sedimentary basins such as the Nigerian sector of the Ikom-Mamfe Embayment.

Oden *et al*[4]., reported the occurrence of some critical minerals including barite, lead-zinc, gold, iron-ore and amethyst within fracture systems in Nigerian segment of Ikom-Mamfe Embayment. Also, there are occurrences of base metals, industrial minerals, oil shales and hydrocarbon within the Anambra Basin[5][6]. Occurrences of hydrocarbon have been reported in the southwestern Cameroon segment of Ikom-Mamfe Embayment[7]. These regions have over the geologic past been subjected to similar thermal regimes and therefore it is necessary to assess the economic potential of the Nigerian sector of the Ikom-Mamfe basin. It is also established that hydrocarbon may serve as source and carriers in epigenetic mineralization[8]. Additionally, the presence of basic igneous rocks as extrusive - basalts[9] may have been associated with some level of mineral accumulation whose model depends on a detail geochemical study.

Due to the enormous economic potential and significant information gap in this area, geological and geochemical research has become essential in the Nigerian portion of the Mamfe Basin. Past geological-related studies in this area includes studies by: Fairhead *et al*.,[10] Abolo[11]; Bassey *et*

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al[12]; Oden *et al*., (2015); Nzeuga *et al*.,[13] Otele *et al*.,[14] Essien *et al*., (2018); Arinze *et al*[15]., Ugbor *et al*.,[16]; Njoh *et al*.,[17]; Asi *et al*[18] Emedo et al[19]; and Ogbudu *et al*.,[20]. However, not much work to characterize mineral resources potentials of the basin has been carried out so far. Hence this study intensifies effort towards appraisal of the Nigerian sector of the basin with respect to its mineral deposits and hydrocarbon occurrence, with a view to proffer alternatives for revenue generation within the economy.

For proper understanding of the basins' economic potentials, a combined inorganic and organic geochemical data is required, the weathering patterns, paleo-climate regimes, paleo-productivity, metal enrichment models, and environment of deposition are critical[21]. In most situations, mineral composition of source material are known to be preserved in shale, thus the bulk chemistry approximates the original geochemistry of its provenance[222324]. Hence, the source, tectonics, transportation history, and depositional environment of related minerals of commercial

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relevance are frequently inferred from the elemental makeup of clastic rocks[25262728293031323334]. Due to some important trace elements that help identify small components that are difficult to detect using petrographic analysis, the application of geochemical analysisof sediments become necessary to fathom the sedimentary processes from literature[35 36]. This study examined the geochemistry in the shale rocks unit of the Mamfe Formation within the Ikom-Mamfe Basin using inorganic constituents (major oxides, trace, and rare earth elements) as well as organic matter proxies. This is because quality of the source-rock (shale) and other related mineral assets can be predicted bycharacterization of the sedimentary rock[37].

Geologic settings

The study area lies within the Nigerian sector of Ikom-Mamfe basin (Fig. 1), that extends from Nigeria into the Republic of Cameroon. The basin is situated in the sub-equatorial climate zone of southwestern Cameroon and southeast Nigeria. The studied area falls within latitudes 5° 36' to 6° 12'N and longitudes 8° 24' to 9° 00'E, covering an aerial extent of approximately 24,000 km^2. The basin under study is associated with West and Central African Rift Systems (WCARS). In comparison to other southern Nigerian sedimentary basins, the Ikom-Mamfe Basin is closely associated with the breakup of Gondwana and subsequent parting of Africa and South America continents[38394041]. It is bounded to the south by the Oban Massif, which separates it from the Rio

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[38]Fairhead *et al*., 1991, Op cit.

del Rey Basin; to the north by the Obudu Massif; to the west by the main depositional axis of the Southern Benue Trough[42] (Nwajide, 2022); and to the east and northeast, it narrows and terminates beneath the Cameroon Volcanic Line (CVL) in the Cameroon Republic (Fig. 1). The sedimentary rocks that make up the basin's cover are believed to be Cretaceous in age. Across the borders of Cameroon and Nigeria, the Mamfe Formation lies incongruously on the Precambrian Basement Complex rocks[4344].

The Precambrian rocks that underlie the basin are primarily composed of granite and gneiss. Dykes that cut across the Precambrian and Cretaceous lithologies are made of mafic volcanic rocks of basaltic composition. In some instances, pegmatitic rocks cuts the underlying basement rock but do not intersect the basin; these are exposed along the marginal flanks of the basin. With breaks in the successions brought on by magmatism, erosion, and non-deposition, sedimentation in the Mamfe Basin began in the early Cretaceous and continued until the Neogene[45464748]. Conglomeratic sandstones, mudrocks (mudstones and shales) and calcareous rocks, make up the 4000-meter-thick sedimentary units within the basin (Fig. 2). It is noteworthy the shaly successions become more pronounced in the Cameroonian sector of the Ikom-Mamfe Basin.

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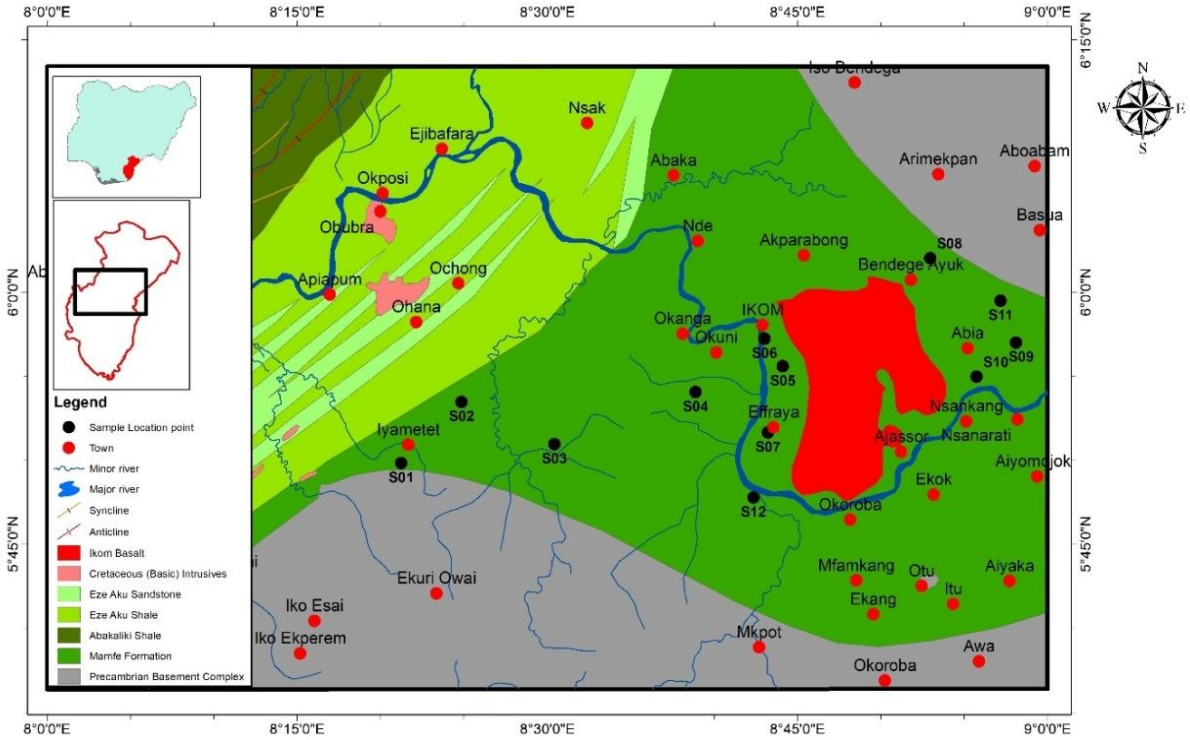


Figure 1. Geological map of the Nigerian sector of the Ikom-Mamfe Basin showing the sample location points

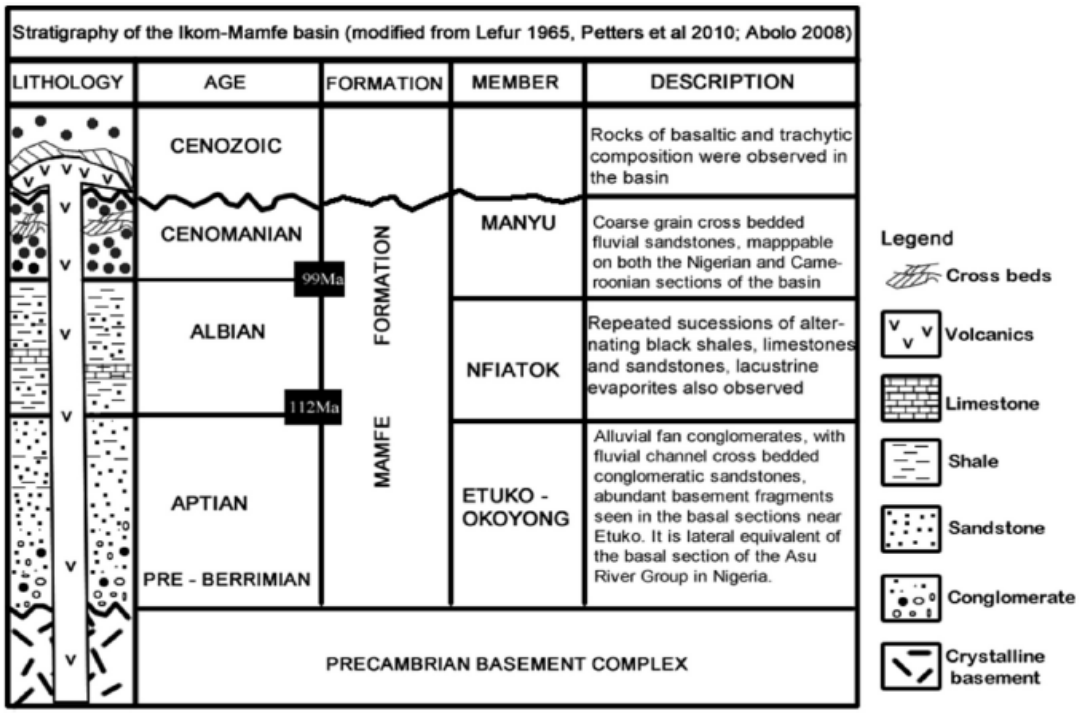


Figure 2. Lithostratigraphy of the Ikom-Mamfe Basin showing the Mamfe Formation and its members (modified after Abolo[49])

The rocks were divided into five units by Le Fur[50], which were named Cg1 through Cg5 in ascending order. The Cg1 to Cg4 are comparable to the Aptian to Albian Asu River Group in southeast Nigeria, whilst the Cg5 is a part of the Cenomanian. Ngeme, Nfaitok (which was further broken into members), Baso, and Cross-River Formations were the four Formations that Eyong[51] identified from bottom to top. All of the sedimentary strata in this basin, however, were categorized by Abolo[52] into a single formation known as the Mamfe Formation, and further divided into the Etoko-Okoyong, Nfaitok, and Manyu Members, in that order. In this study, the description of the lithologic succession as presented by Abolo[53] is adopted because it matches the sedimentary characteristics mapped within the Nigerian sector of the basin and agrees with the study of Petters *et al*[54].

Methodology

The methodology adopted for this research involved desk study, fieldwork and laboratory activities. The desk study involved gathering and analyzing existing information about the Ikom-Mamfe basin from mapsand reports to better understand the geological settings. The study helped in planning the fieldwork in the study area and highlighted areas where gaps to be filled existed within the study area. Field investigations included geological mapping (majorly along road cuts and river sections) and samples collection. During the field mapping exercise,lithofacies and their stratigraphic positions were determined, field relationship as well as observed mineralization patterns were recorded. Also, sampling and properly labeling of shale rocks that facilitated geochemical characterization were carried out. Laboratory activities involved sample preparation (drying, disaggregation, crushing, and pulverization), extraction and geochemical analyses.

The samples collected (12 nos) was prepared using standard procedures including the use of a jaw crusher to pulverize the shale rock. Thereafter, it wasquartered and-homogenized; the samples were put in plastic bags that were sealed for chemical analysis.

In an open beaker, 0.5g of each the powdered sample was digested and left to dry by evaporation and later dissolved in a solution of HNO_3 and HF, after being treated with dilute HNO_3 to react with any carbonate. Ths was repeated three times over the period of three days, concentrated HNO_3 and HF were added to the samples once they were totally dry. The samples were diluted 200 times for Atomic Emission Spectrometry (AES) and 1000 times for Mass Spectrometry

[49]Abolo, 2008, Op cit.
[50]Le Fur, 1965, Op cit.
[51]Eyong, J. T. (2003). Litho-Biostratigraphy of the Mamfe Cretaceous Basin, SW. Province of Cameroon–West Africa. *Ph.D. thesis,* University of Leeds
[52]Abolo, 2008, Op cit.
[53]Abolo, 2008, Op cit.
[54]Petters *et al*., 1987, Op cit.

(MS) after being further dissolved in a 2% nitric double-distilled water solution. For Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), a Varian Vista Pro Radial atomic emission spectrometer was employed, and for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), a Perkin-Elmer Elan DRC-e quadrupole mass spectrometer. ICP-MS was employed to determine the concentrations of trace and rare earth elements (REEs), whereas ICP-AES was used to measure the concentrations of main elements and some trace elements. A blank was added for each of the sample, and USGS standards were utilized for calibration. The accuracy of the analytical procedure was within 10% and precision was 5%. All of the geochemical analyses were carried out by Vancouver, Canada's Bureau Veritas Minerals (BVM) Ltd. The shale-normalized elemental anomalies for Ce and Eu were calculated using the formulae: Ce/Ce* = Ce/(0.5La + 0.5Pr) and Eu/Eu* = Eu/(0.67Sm + 0.33Tb). Anomaly descriptions were based on calculated anomaly ranges (< 0.95 = negative anomaly and > 1.05 = positive anomaly). The geochemical data was interpreted using sensitive major and trace ratios as proxies.The shale samples were further subjected to organic geochemical investigation (Total Organic Carbon, TOC, and Rock Eval Pyrolysis) in order to evaluate the organic richness, maturity, and potential for hydrocarbon generation. Twelve shale samples were analyzed for TOC using the Walkley-Black titration method[55]. This included pulverizing 0.5 g of the dry material and subjecting it to chronic oxidation using a procedure known as the "wet oxidation method." Excess potassium dichromate ($K_2Cr_2O_7$) was heated and then titrated against ferrous ammonium sulphate ($(NH4)_2Fe(SO_4)_2.6H_2O$). The organic content of the sample can be determined by comparing the original and residual potassium dichromate. The formula for this is:

$$\%TOC = 10 * \left(1 - \frac{T}{S}\right) F$$

%TOC is Total Organic Carbon percentage, T is the transmittance (light transmitted through the sample), S is standard reference intensity, F is the correction factor. Each rock sample's hydrocarbon generative potential was calculated using the values in weight percent.

The Rock-Eval pyrolysis was carried out using the method outlined by Espitalie *et al*[56]. This involved heating a small sample (100 mg) at a predetermined temperature in a pyrolysis oven in an inert atmosphere (helium) in order to quantitatively and selectively identify the free hydrocarbons in the sample as well as the hydrocarbon and oxygen-containing compounds (CO_2) that are volatilized during the cracking of the un-extractable organic matter in the sample (kerogen). During the pyrolysis process, which required maintaining the oven isothermally at 300°C for three minutes, the free hydrocarbons were volatilized and measured as the S1 peak (detected by Flame Ionization Detector P87FID). After then, the temperature was raised by 25°C each minute from 300°C to 550°C. This stage involves both the cracking of non-volatile organic

[55]Asi *et al*., 2022, Op cit

[56]Espitalie, M. M., Tissot, B., Mennig, J. J., & Leplat, P. (1977). Source rock characterization method for petroleum exploration. In: *Proceedings of the 9th Annual Offshore technology Conference*, vol. 3, pp. 430–448.

materials and the volatilization of particularly heavy hydrocarbon compounds (> C40). The amount of hydrocarbon generated during this thermal cracking is measured by the S2 peak. The type of the kerogen, and the temperature at which S2 reaches its maximum is used to determine the thermal maturity of the sample. The temperature range in which kerogen cracking produces CO_2 is 300° to 390°C. CO_2 is released from the heated trap and measured on a TCD (S3 peak) while the pyrolysis oven cools. The TOC and the S2 values from Rock Eval were used to calculate the hydrogen index (HI = 100 x S2/TOC in milligrams hydrocarbon per gram of TOC), oxygen index (OI = 100 x S3/TOC in milligrams CO_2 per gram of TOC), and production index (PI = 100 x S1/(S1+S2)).

Results

Major elements

The result of elemental oxide analysis along with calculated values for the chemical index of weathering (CIW), plagioclase index of alteration (PIA), chemical index of alteration (CIA) and index of chemical variation (ICV) is presented in Table 1.

The abundance of major oxide concentrations in the shales of Mamfe Formation varies significantly, ranging from 0.01 to 60.40% (Table 1). SiO_2 (48.60 - 60.40%; mean, 55.78%), Al_2O_3 (19.20 - 24.60%; mean, 20.98%), and Fe_2O_3 (2.20 - 5.20%; mean, 3.46%) have the predominant oxide concentrations in Mamfe Formation shale. The rest of the oxides: CaO, MgO, K_2O, Na_2O, TiO_2 and P_2O_5 have respective percentage ranges; 0.80– 6.60; 0.40– 1.60; 1.66– 5. 40; 0.14- 1.84; 0.05-0.66 and 0.01-0.52 with respective mean percentage values of 1.84; 0.95; 2.96; 0.81; 0.50 and 0.20. The high values of LOI (6.14 - 17.58%; mean, 12.16%) suggest high organic contents or volatile bearing minerals in the shales[57]. The values of CIA, PIA, CIW and ICV range from 65.78 to 85.60; 0.72 to 0.93; 0.27 to 0.87 and 76.88 to 94.20 with mean values of 79.53, 0.88, 0.50 and 89.29 respectively (Table 1).

In comparison to average shales composition from other formations globally, the shale samples used in the current study are often enriched in Al_2O3, P_2O_5, and LOI but significantly depleted in SiO_2, Fe_2O_3, MgO, CaO, Na_2O, and K_2O (Table 2). In addition to being probably caused by quartz dilution, a decreased Na_2O, MgO, and CaO suggests sediments probably experienced severe weathering and recycling[5859]. Since feldspars normally control the amounts of Ca, Na, and K, strong depletion in CaO and Na_2O further suggests that plagioclase was destroyed by chemical weathering at source or during transport. The enrichment in Al_2O_3, P_2O_5 and LOI is an indication of high productivity/carbonate minerals as well as dominance of aluminosilicate minerals suggesting extreme chemical weathering.[6061]

[57]Amajor, L. C. (1987). Major and trace element geochemistry of Albian and Turonian shales from the Southern Benue trough, Nigeria. *Journal of African Earth Sciences, 6*(5), 633-641.
[58] Adamu et al., 2020., Op cit.
[59]Pettijohn, 1957, Op cit.
[60]Pettijohn, 1957, Op cit.
[61]Turekian, K. K. & Wedepohl, H. (1961). Distribution of elements in some major units of the Earth's Crust. *Geological Society of America Bulletin, 72*, 175–192.

Table 1. Major oxides composition in Mamfe Formation shales of Ikom-Mamfe basin

Sample	Concentrations are measured in wt.%											Weathering indices			
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	LOI	Total	CIA	PIA	CIW	ICV
S1	55.20	20.10	3.50	1.20	0.80	2.17	0.23	0.30	0.12	15.60	99.26	84.81	0.93	93.36	0.41
S2	58.50	21.40	2.90	1.50	1.10	1.96	0.14	0.50	0.14	11.80	99.51	85.60	0.92	92.88	0.38
S3	52.20	19.50	5.20	0.80	0.40	2.56	0.40	0.60	0.42	17.20	99.28	83.83	0.93	94.20	0.51
S4	57.00	21.00	3.00	1.50	0.90	2.40	1.72	0.60	0.52	11.20	99.84	78.89	0.85	86.71	0.48
S5	55.40	20.00	3.80	1.20	0.70	2.64	1.84	0.64	0.34	12.80	99.32	77.88	0.85	86.81	0.54
S6	60.00	22.10	2.50	1.60	1.20	4.50	1.00	0.52	0.04	6.14	99.60	75.68	0.87	89.47	0.51
S7	51.50	19.20	4.50	0.90	0.50	4.30	0.80	0.64	0.01	17.60	99.93	76.19	0.90	91.87	0.61
S8	57.30	21.00	3.20	1.40	1.00	2.60	0.42	0.54	0.20	12.10	99.80	82.61	0.91	92.02	0.44
S9	54.00	20.40	4.00	1.20	0.80	3.45	0.52	0.66	0.16	14.60	99.81	79.78	0.91	92.22	0.52
S10	60.40	22.20	2.20	1.60	1.20	1.66	1.60	0.42	0.13	8.56	99.97	82.04	0.87	87.40	0.39
S11	48.60	24.60	3.20	6.60	1.60	5.40	0.80	0.52	0.18	8.26	99.76	65.78	0.72	76.88	0.74
S12	59.20	20.20	3.50	2.60	1.20	1.82	0.24	0.48	0.14	10.00	99.38	81.26	0.87	87.67	0.49
Min	48.60	19.20	2.20	0.80	0.40	1.66	0.14	0.05	0.01	6.14	99.26	65.78	0.72	76.88	0.27
Max	60.40	24.60	5.20	6.60	1.60	5.40	1.84	0.66	0.52	17.60	99.97	85.60	0.93	94.20	0.87
Mean	55.78	20.98	3.46	1.84	0.95	2.96	0.81	0.50	0.20	12.20	99.62	79.53	0.88	89.29	0.50

CIA: Chemical index of alteration, PIA: Plagioclase index of alteration, CIW: Chemical index of weathering, ICV: Index of chemical variation

Table 2. Major oxides of Mamfe Formation shales compared with worldwide shales

Oxides	Present study	AWS	PAAS	NASC	UCC	ASV	1	2	3
SiO_2	55.78	58.9	62.8	64.8	66	58.5	61.26	69.9	44.91
Al_2O_3	20.93	16.7	18.9	16.9	15.2	15	16.88	10	15.71
Fe_2O_3	3.46	6.9	7.22	5.65	5	4.72	3.74	4.04	6.24
TiO_2	0.5	0.78	1	0.7	0.5	0.77	1.74	0.52	0.65
CaO	1.84	2.2	1.3	3.63	4.2	3.1	0.05	3.38	15.32
K_2O	2.96	3.6	3.7	3.97	3.4	3.1	1.39	1.15	2.36
MgO	0.95	2.6	2.2	2.86	2.2	2.5	0.16	0.87	2.58
Na_2O	0.81	1.6	1.2	1.14	3.9	1.3	0.06	0.4	0.42
P_2O_5	0.2	NA	0.16	0.13	NA	0.16	0.08	0.17	0.46

LOI	12.16	NA	6	NA	NA	NA	14.2	9.21	11.1
Total	99.62	93.28	99.59	99.84	100.5	89.15	99.56	99.7	99.75

ASW: Average shale worldwide (Pettijohn[62]) PAAS: Post-Archean Australian Shale (Taylor & McLennan[63]), NASC: North American Shale Composite (Gromet et al.[64]), UCC: Average upper continental crust (Taylor and McLennan, 1985), ASV: Average shale values worldwide (Turekian & Wedepohl[65]), 1. Bida Shale (Okunlola & Idowu[66]) 2. Asu River Group (Amajor[67]); 3. Ezeaku Shale (Amajor[68])

Trace element geochemistry

The result of trace elements geochemistry is presented in Table 3; the result show that the trace element range from below detection limits (BDL) of analytical instrument to 2368.00 ppm (Table 3). The trace element contents and normalized averages of studied shale samples in comparison to the average PAAS (Post-Archean Australian average shale[69]) and UCC (average upper continental crust; Taylor and McLennan,[70]) is also presented (Table 3).The most prevalent trace elements in the shales ofMamfe Formation is phosphorus (P), which ranges from 378.00 to 2368.00 ppm and mean of 1126.17 ppm; Ba, ranges from 376.00 to 1240.00 ppm and mean of 676.13 ppm; Mn, ranges between 221.00 to 980.00 ppm; Sr, with mean of 286.17 ppm; and Ti, ranges between from 120.00 to 340.00 ppm and mean of 243.33 ppm. V 122.50 ppm, Rb 106.38 ppm, Ce 105.00 ppm, Zr 101.75 ppm, Zn 84.92 ppm, Cr 80.17 ppm, Ni 70.50 ppm, and Mo 31.70 ppm, Pb 25.12 ppm, Ag 0.06 ppm and Cd 0.04 ppm are further trace elements with noticeably high mean values. The following trace element concentrations in the shale samples are classified as low mean value elements: Li, which ranges from 32.00 to 51.00 ppm with mean value of 40.25 ppm; Cu, has mean value of 32.28 ppm and ranges from 22.00 to 41.00 ppm; Mo, which ranges from 14.80 to 42.60 ppm and has a mean value of 31.70 ppm; Y, which ranges from 23.70 to 38.00 ppm and a mean value of 29.78 ppm; and Pb which ranges from 19.4 to 35.2 ppm, and has a mean value of 25.12 ppm. Some revealed mean values of 17.75 ppm Co, 17.75 ppm Th, 15.17 ppm Nb, 14.81 ppm Ga, 9.66 ppm W. 9.66 ppm Sc, 5.68 ppm U, 4.13 ppm As, 3.48 ppm Cs, 2.67 ppm Hf, 1.88 ppm Se, 1.87 ppm Sn, 1.59 ppm Ta, and 1.56 ppm Be.

The shales showed very low average values for the following; 0.88 ppm Sb, 0.17 ppm Ge, 0.16 ppm Bi, 0.06 ppm Ag, 0.03 ppm Cd, 0.03 ppm In, 0.02 ppm Te, 0.01ppm Hg and 0.002 ppm Re. The trace elements data revealed comparable distribution outlines on the PAAS and UCC normalized spider plots (Figs. 3a and 3b). A higher detrital flux of feldspar is indicated by the enrichment of shale with large-ion lithophile elements (LILE) like Rb, Sr, and Ba and moderate

[62]Pettijohn, 1957, Op cit.
[63]Taylor, S. R. & McLennan, S. M. (1985). *TheContinental Crust: Its Composition and Evolution*. Blackwell Publishing, Oxford, UK.
[64]Gromet, L. P., Dymek, R. F., Haskin, L. A. & Korotev, R. L. (1984). The "North American shale composite": Its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta, 48*(11), 2469-2482.
[65]Turekian & Wedepohl, 1961, Op cit.
[66]Okunlola, O. A. and Idowu, O. (2012). The geochemistry of claystone-shale deposits from the Maastrichtian Patti Formation, Southern Bida Basin, Nigeria. *Earth Science Research Journal, 16*(2), 1794-6190
[67]Amajor, 1987. Op cit.
[68]Amajor, 1987. Op cit.
[69]Condie, 1993. Op cit
[70]Taylor and McLennan, 1985, Op cit.

transition-trace elements (TTE) like Sc, Co, Cr, Ni, V, and Cu, according to Taylor and McLennan[71]. Due to their high concentration in the shales, high-field-strength elements (HFSEs) such as Zr, Nb, and Ti are probably indicators of industrial mineral reserves in the basin[72]. Trace metal enrichment also points to the major part played by basic rocks as source rocks[73]. Trace metal enrichment also points to the major part played by basic rocks as source rocks[74].

Rare earth elements (REEs)

The result of rare earth elements (REE) is presented in Table 4. REEs concentrations were observed to range between 0.11 to 142 ppm, with the most abundant REE being Cecium (Ce), it has values that range from 77.00 to 142.00 ppm (mean value = 115.08 ppm). Lu has the lowest average value of 0.21 ppm and ranges in concentration from 0.11 to 0.32 ppm. Samples from the shales of Mamfe Formation showed total REE concentration values that range from 217.07 to 295.96 ppm, and mean of 263.27 ppm (Table 4), which is relatively higher than the PAAS normalized value of 210.00 ppm[757677]. This may reflect adsorption and complexation onto clay minerals[78]. Similarly, the shales are enriched in total light REE (ΣLREE, 1 80.00 - 247ppm; mean 218.19 ppm) and total medium REE (ΣMREE, 15.23 – 23.85 ppm; mean 19.01ppm) contents compared respectively to PAAS (166.10 ppm and 10.98 ppm). However, they are depleted in heavy REE (ΣHREE, 3.49 - 5.85 ppm; mean 4.20 ppm) relative to 32.18 ppm of PAAS. In general, PAAS-, UCC- and Chondrite-normalized distributions for REE within the shales investigated from Mamfe-Formation (Figs. 4a, b and c) are observed to be unique for their high light REE (LREE)/heavy REE (HREE) ratio whose values range from 4.29 to 7.53 and an average of 5.57 (Table 4), a flat HREE distribution and prominent positive Ce but negative Eu anomalies. LREEs are segregated, $(La/Sm)_n$ = 3.95 and HREE distributions was nearly flat, $(Gd/Yb)_n$ = 2.00. The negetive Eu anomalies (Table 4), showed Eu/Eu* ranged from 0.13 to 0.42, with a mean value of 0.24 (Figs. 4a and 4b) are attributed to probable Eu-depleted felsic igneous sources, such as granites and granodiorite. While negetive and positive anomalies of Ce (Ce/Ce*= 0.72 - 1.56. mean 1.07) indicate variations in depositional environment (Girtty et al., 1994). The PAAS and UCC normalized plots of REE, further showed depletion in Nd, Dy, Er, Tm and Lu concentration for the shales studied in the Ikom-Mamfe basin. However, only

[71]Taylor and McLennan, 1985, Op cit

[72]Adamu *et a*l., 2020., Op cit.

[73]Rashidi, A., Siddequi, N. A., Ahmed, N., Whahill, A., Jamil, M., Sankoh, A. A. & Olutoki, J. O. (2024). Geochemical and mineralogical characteristics of shales from early-middle Permian Dohol Formation in Peninsular Malaysia: implication for organic matter enrichment, provenance, tectonic setting, Paleoweathering and paleoclimate. *Heliyon, 10*(6), 27553.

[74]Rashidi *et al*., 2024, Op cit.

[75]Adamu *et al*., 2020., Op cit

[76]Girty, G. H., Hanson, A. D., Knaack, C. & Johnson, D. (1994). Provenance determined by REE, Th, and Sc analyses of metasedimentary rocks, Boyden Cave roof pendant, central Sierra Nevada, California. *Journal of Sedimentary Research, 64*, 68–73.

[77]Taylor and McLennan, 1985, Op cit

[78]Pettijohn, 1957, Op cit.

Sample S12 showed distinct rise in concentration of Tm compared with others, but it portrays similar REE distribution outline like other samples (Fig. 4a-c).

Table 3. Trace elements contents (ppm) in Mamfe Formation shales of Ikom-Mamfe basin

Trace elements	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Min	Max	Mean	SD
Al (%)	10.63	11.32	10.32	11.11	10.58	11.69	10.16	11.11	10.79	10.74	13.01	10.69	10.16	13.01	11.01	0.76
K(%)	1.15	1.04	1.35	1.27	1.40	2.38	2.27	1.38	1.82	0.88	2.90	0.96	0.88	2.90	1.57	0.64
Mn	256.00	980.00	720.00	375.00	824.00	298.00	349.00	432.00	221.00	315.00	278.00	318.00	221.00	980.00	447.17	250.12
P	2368.00	2106.00	1962.00	1450.00	1660.00	687.00	608.00	645.00	786.00	452.00	412.00	378.00	378.00	2368.00	1126.17	733.83
Ag	BDL	0.03	0.02	0.01	0.06	0.1	0.1	0.05	BDL	0.08	0.1	BDL	0.01	0.1	0.06	0.04
As	3.3	3.2	4.2	5	4.6	4.6	3.6	5.4	4.6	2.6	2.8	5.6	2.6	5.6	4.13	1.01
Ba	1240	654	1100	764	466	382	437	376	440	890	950	417	376	1240	676.33	305.61
Be	1.45	1.32	1.18	2.06	1.16	2.06	2.3	1.6	2	1.12	1.1	1.32	1.1	2.3	1.56	0.43
Bi	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.2	0.3	0.2	0.1	0.1	0.1	0.3	0.16	0.07
Cd	0.04	0.03	BBL	0.01	0.01	0.03	0.02	0.04	0.03	0.03	0.02	0.04	0.01	0.04	0.03	0.01
Ce	116	120	86	103	94	102	114	106	101	112	98	108	86	120	105.00	9.75
Co	20	17	16	26	13	16	12	14	21	18	15	25	12	26	17.75	4.47
Cr	74	100	90	40	70	59	50	70	102	122	97	88	40	122	80.17	23.89
Cs	3.4	4.4	3.8	1.4	2.4	3.2	6.8	4.2	3.6	2.6	1.8	4.1	1.4	6.8	3.48	1.42
Cu	24.2	38.2	28	22	36	32	25	35	32	41	40	34	22	41	32.28	6.31
Ga	15.1	18.8	13.5	10.2	12.5	12.5	7.4	12.8	20	22.4	18.2	14.3	7.4	22.4	14.81	4.32
Ge	0.18	0.12	0.16	0.3	0.4	0.06	0.1	0.1	0.11	0.13	0.12	0.2	0.06	0.4	0.17	0.10
Hf	3	2	2	5	1	2	4	3	2	2	2	4	1	5	2.67	1.15
Hg	BDL	BDL	BDL	BDL	0.01	0.01	0.01	0.01	BDL	0.01	0.01	0.01	0.01	0.01	0.01	0.00
In	0.03	.P5	0.03	0.01	0.01	BDL	0.02	0.04	0.06	0.01	BDL	0.02	0.01	0.06	0.03	0.02
Li	32	50	42	40	34	36	32	51	48	40	34	44	32	51	40.25	6.88
Mo	36.61	40.9	37.1	14.8	34.4	31.2	24.8	42.6	27.3	23.4	34.9	32.4	14.8	42.6	31.70	7.96
Nb	17	17	15	11	16	15	12	15	17	15	15	17	11	17	15.17	1.95
Ni	41.6	99.7	71.1	57	70	47.61	66.6	85.5	95.5	70.2	64.5	76.7	41.6	99.7	70.5	17.41
Pb	28.6	20.4	21.3	35.2	33	19.4	20.8	22.4	21.9	24.8	28.4	25.2	19.4	35.2	25.12	5.16
Rb	130.4	106.4	122.7	62.3	85	60	156	136	106	61.5	108	142.2	60	156	106.38	33.08
Re	0.003	0.001	0.002	0.002	0.002	BDL	0.002	0.003	0.004	BDL	0.002	0.003	0.001	0.004	0.00	0.00
Sb	0.18	0.22	0.2	8	0.13	0.13	0.3	0.32	0.24	0.21	0.32	0.28	0.13	8	0.88	2.24
Sc	6	11.2	10.4	5.8	7.2	10	8.8	9.6	12	14	11.2	6.5	5.8	14	9.39	2.59
Se	2	3	2	1.6	1	1.2	1.4	2.2	3	1.8	1.8	1.6	1	3	1.88	0.62
Sn	2.5	1.3	1.8	2	1.2	1.4	1.6	2.6	2	1.4	2.2	2.4	1.2	2.6	1.87	0.49
Sr	280	378	220	245	267	278	282	202	266	342	376	298	202	378	286.17	55.44
Ta	1.5	2.1	1	1.4	1.3	1.6	2.2	1.6	2	1	1.4	2	1	2.2	1.59	0.41
Te	0.04	0.04	BDL	0.02	0.03	0.01	0.03	0.03	BDL	0.02	0.01	0.01	0.01	0.04	0.02	0.01
Th	15	20	17	18	18	16	17	19	15	20	20	18	15	20	17.75	1.82
Ti	2.8	3.2	3	3.2	1.2	1.8	2.6	1.4	1.4	2.4	3.4	2.8	1.2	3.4	2.43	0.79
U	3.6	5.4	7	7.2	6.2	6	5.8	6.6	6.2	5.4	4.6	4.2	3.6	7.2	5.68	1.10
V	125	108	120	98	96	115	118	102	212	172	106	98	96	212	122.50	34.84
W	12.8	9.8	7.1	7.9	8.3	7.6	14	9.6	8.4	7.8	12	10.6	7.1	14	9.66	2.25
Y	32.1	25.6	36.3	23.7	38	24.5	27.4	34.5	29.3	33.3	28.7	24	23.7	38	29.78	4.98
Zn	97	68	101	86	75	56	110	76	78	98	66	108	56	110	84.92	17.70
Zr	132	110	81	82	72	130	123	77	96	104	122	92	72	132	101.75	21.52

BDL = Below Detection Limit

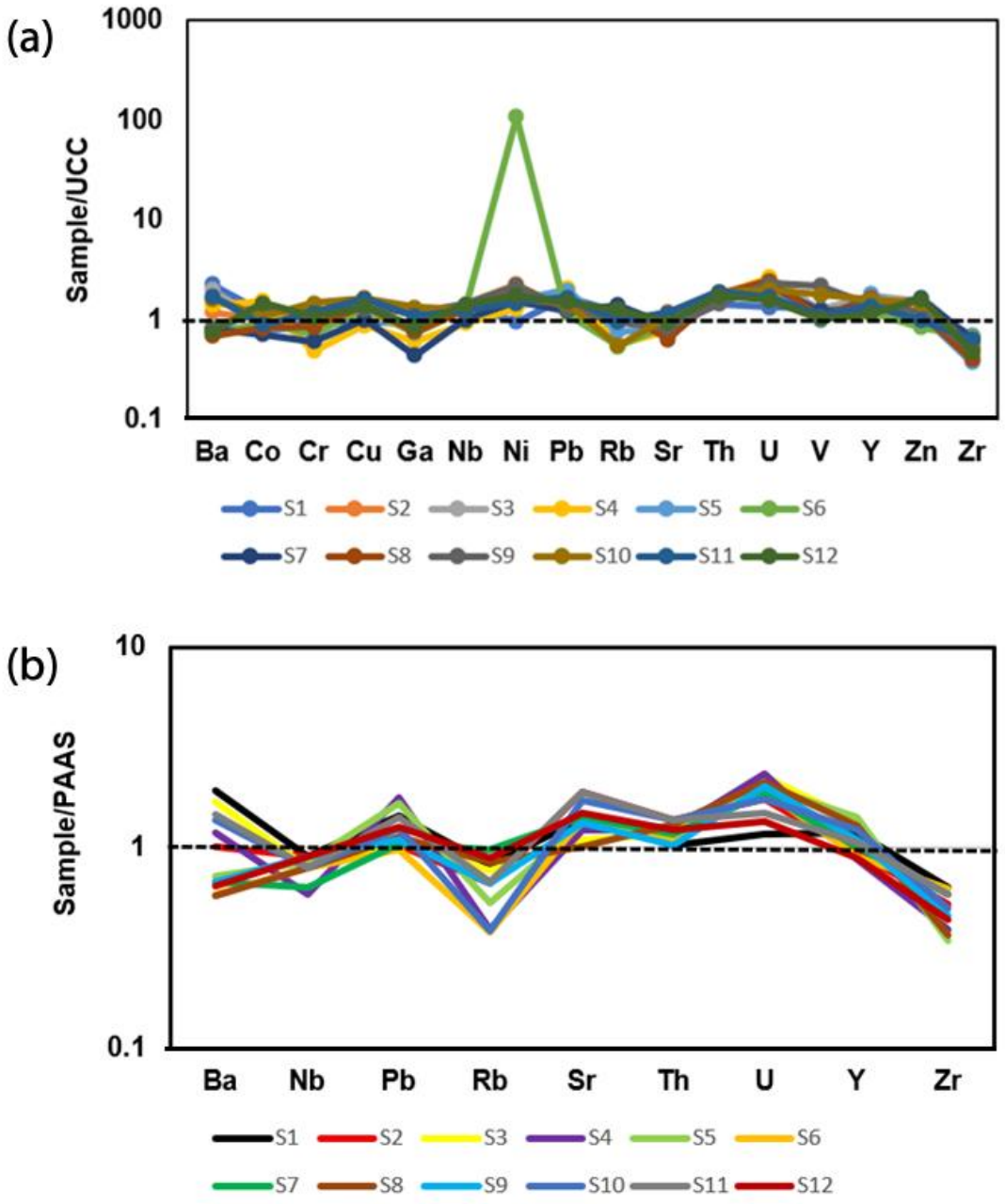


Figure 3. Trace element concentration of shales from Mamfe Formation normalized against (a) Upper Continental Crust (UCC) and (b) Post Archean Australian Shale (PAAS) (after Taylor & McLennan[79])

[79]Taylor and McLennan, 1985, Op cit

Table 4. Rare earth elements concentrations in Mamfe Formation shales of Ikom-Mamfe basin

REE	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Min	Max	Mean	SD
La	34.00	57.00	38.00	36.00	43.00	62.00	60.00	55.00	45.00	36.00	48.00	52.00	34.00	62.00	47.17	9.98
Ce	121.00	87.00	103.00	77.00	116.00	142.00	104.00	124.00	112.00	132.00	127.00	136.00	77.00	142.00	115.08	19.59
Pr	10.20	13.50	20.10	18.30	14.60	12.40	11.60	18.00	14.40	17.50	15.80	13.70	10.20	20.10	15.01	2.99
Nd	25.60	37.20	43.50	41.90	20.00	23.40	39.40	41.30	44.00	18.00	34.30	27.60	18.00	44.00	33.02	9.58
Sm	9.40	6.40	5.30	6.80	9.20	7.20	8.60	7.60	7.00	11.20	5.70	10.60	5.30	11.20	7.92	1.88
Eu	0.43	0.31	0.64	0.58	0.49	0.42	0.30	0.54	0.48	0.40	0.48	0.55	0.30	0.64	0.47	0.10
Gd	4.53	5.45	4.02	3.78	5.07	5.03	5.95	4.52	4.28	5.57	5.42	4.66	3.78	5.95	4.86	0.67
Tb	0.75	1.02	1.15	1.03	0.93	0.64	0.85	1.12	0.96	1.10	0.76	0.87	0.64	1.15	0.93	0.16
Dy	3.46	2.34	3.36	2.98	3.80	2.22	5.44	4.12	5.12	4.45	3.56	4.78	2.22	5.44	3.80	1.03
Ho	1.16	0.87	0.76	1.10	0.92	1.14	1.04	1.12	1.08	1.13	0.96	1.15	0.76	1.16	1.04	0.13
Er	1.89	1.67	2.11	1.72	1.57	1.64	2.00	1.73	1.16	1.78	1.58	1.56	1.16	2.11	1.70	0.24
Tm	0.31	0.22	0.18	0.33	0.20	0.32	0.24	0.20	0.16	0.31	0.18	2.12	0.16	2.12	0.40	0.55
Yb	2.16	1.67	1.84	1.69	1.75	2.04	1.76	1.94	1.87	2.07	1.88	2.02	1.67	2.16	1.89	0.16
Lu	0.24	0.26	0.17	0.16	0.11	0.32	0.14	0.27	0.30	0.17	0.25	0.15	0.11	0.32	0.21	0.07
Y	32.10	25.60	36.30	23.70	38.00	24.50	27.40	34.50	29.30	33.30	28.70	24.00	23.70	38.00	29.78	4.98
ΣREE	247.23	240.51	260.43	217.07	255.64	285.27	268.72	295.96	267.11	264.98	274.57	281.76	217.07	295.96	263.27	21.42
ΣLREE	200.20	201.10	209.90	180.00	202.80	247.00	223.60	245.90	222.40	214.70	230.80	239.90	180.00	247.00	218.19	20.60
ΣMREE	4.96	5.76	4.66	4.36	5.56	5.45	6.25	5.06	4.76	5.97	5.90	5.21	4.36	6.25	5.33	0.59
ΣHREE	42.07	33.65	45.87	32.71	47.28	32.82	38.87	45.00	39.95	44.31	37.87	36.65	32.71	47.28	39.75	5.19
Ce/Ce*	1.56	0.75	0.90	0.72	1.11	1.23	0.95	0.95	1.06	1.26	1.11	1.22	0.72	1.56	1.07	0.24
Eu/Eu*	0.20	0.16	0.42	0.35	0.22	0.21	0.13	0.28	0.27	0.15	0.26	0.24	0.13	0.42	0.24	0.08
(Gd/Yb)n	1.70	2.64	1.77	1.81	2.34	1.99	2.73	1.88	1.85	2.18	2.33	1.87	1.70	2.73	2.09	0.35
(La/Sm)n	2.27	5.60	4.51	3.33	2.94	5.41	4.39	4.55	4.04	2.02	5.29	3.08	2.02	5.60	3.95	1.21
LREE/HREE	4.76	5.98	4.58	5.50	4.29	7.53	5.75	5.46	5.57	4.85	6.09	6.55	4.29	7.53	5.57	0.91
LREE/MREE	40.36	34.91	45.04	41.28	36.47	45.32	35.78	48.60	46.72	35.96	39.12	46.05	34.91	48.60	41.30	4.90
MREE/HREE	0.12	0.17	0.10	0.13	0.12	0.17	0.16	0.11	0.12	0.13	0.16	0.14	0.10	0.17	0.14	0.02

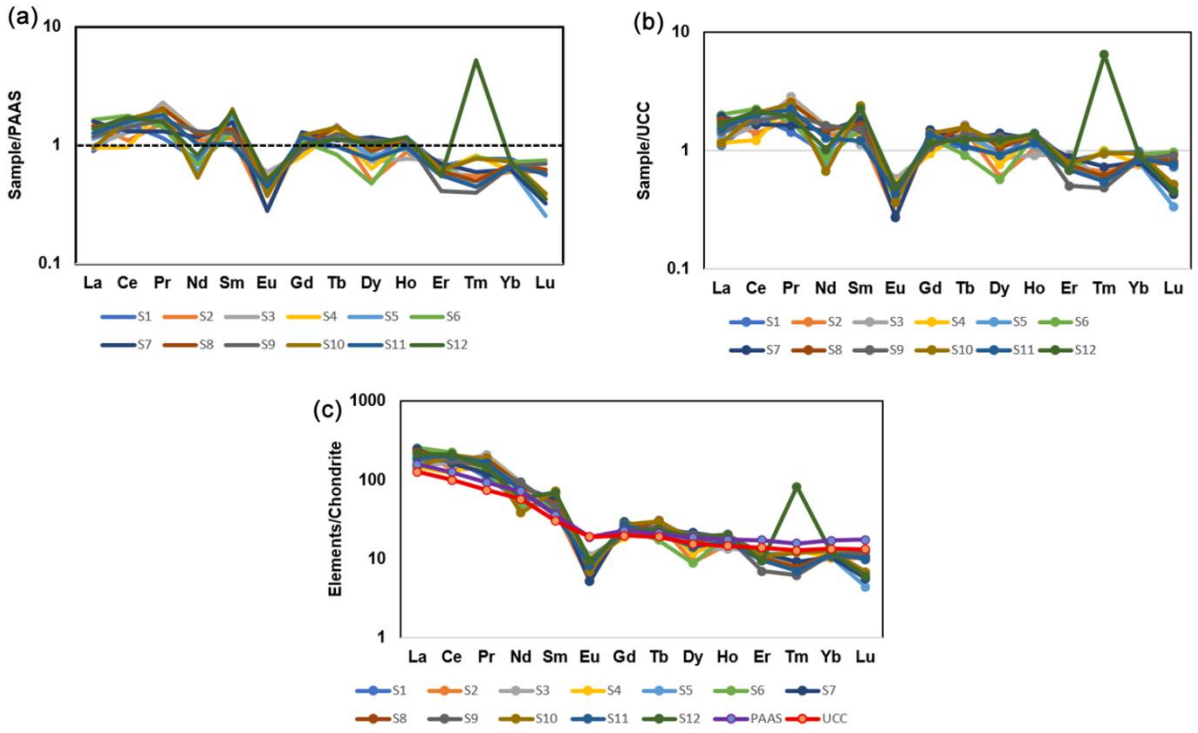


Figure 4 Spider plots of rare earth element contents for shales of the Mamfe Formation normalized against (a) PAAS, (b) UCC and (c) Chondrite data

3.4 Total Organic Carbon (TOC) and Rock Eval Pyrolysis (REP)

The result of organic geochemical analysis is presented in Table 5. One important measure of a rock's capacity to produce hydrocarbons is the amount of TOC in it[80]. The mean TOC (wt%) was 2.32 wt%, with a range of 0.80 to 3.50 wt%. The average value of thermally liberated hydrocarbon (S1) is 0.49 mg HC/g rock, ranged from 0.20 to 0.80 mg HC/g rock (milligram hydrocarbon per gram of rock sample). The average value of hydrocarbon from thermal cracking of the kerogen (S2) is 3.90 mg HC/g rock, with values ranging from 2.40 to 5.60 mg HC/g rock. With an average value of 434.92 °C, the Tmax (maximum temperature of pyrolysis corresponding to peak S2 values) falls between 422 and 476° C.

However, there is a clustering of values observed at temperatures below 450 °C, and just one sample (S7) had a value higher than 450 °C. The average CO_2 production from oxygen-rich organic matter (S3) is 1.48 mg HC/g rock, with a range of 0.90 – 0.91 mg HC/g rock.

The residual hydrocarbon potential, or quantity that can still be produced from the organic matter, is often achieved by cracking kerogen at temperatures as high as 500°C. While the Oxygen Index (OI) varies between 39.29 and 113.33 mg HC/g TOC (av. of 72.10 mg HC/g TOC), the Hydrogen Index (HI) of the Mamfe Formation shales under study ranges from 97.14 to 300.00 mg HC/g TOC (av. = 192.16 mgHC/g TOC). While the Production Index (PI) ranges

[80]Hunt, J. M. (1996). *Petroleum Geochemistry and Geology* (2nded). WH Freeman & Coy, New York.

from 0.03 to 0.19 mg HC/g TOC with an average value of 0.11 mg HC/g TOC, the Genetic Potential (GP = S1+S2), or total richness and potential, of the shale samples varies from 2.80 to 5.80 mg HC/g rock.

Table 5. The total organic carbon (TOC) and rock eval parameters of studied samples

Sample	TOC (%)	S1 (mg/g)	S2 (mg/g)	S1+S2 (mg/g)	S3 (mg/g)	Tmax (°C)	HI	OI	PI
S1	2.50	0.50	3.20	3.70	1.20	435.00	128.00	48.00	0.14
S2	2.80	0.30	2.80	3.10	1.10	428.00	100.00	39.29	0.10
S3	1.50	0.70	4.50	5.20	1.70	438.00	300.00	113.33	0.13
S4	3.20	0.40	3.30	3.70	1.30	429.00	103.13	40.63	0.11
S5	2.10	0.20	5.60	5.80	1.90	425.00	266.67	90.48	0.03
S6	2.60	0.60	3.50	4.10	1.50	436.00	134.62	57.69	0.15
S7	3.50	0.80	3.40	4.20	1.40	476.00	97.14	40.00	0.19
S8	2.40	0.50	4.20	4.70	1.60	432.00	175.00	66.67	0.11
S9	1.60	0.20	4.20	4.40	1.60	422.00	262.50	100.00	0.05
S10	3.00	0.70	4.50	5.20	1.70	430.00	150.00	56.67	0.13
S11	0.80	0.40	2.40	2.80	0.90	436.00	300.00	112.50	0.14
S12	1.80	0.60	5.20	5.80	1.80	432.00	288.89	100.00	0.10
Min	0.80	0.20	2.40	2.80	0.90	422.00	97.14	39.29	0.03
Max	3.50	0.80	5.60	5.80	1.90	476.00	300.00	113.33	0.19
Mean	2.32	0.49	3.90	4.39	1.48	434.92	192.16	72.10	0.11

Discussions

Provenance

The geochemistry of clastic sediments provides valuable information for evaluating sediment provenance and source-rock composition[81][82]. Major, trace, and REEs are particularly useful for identifying the lithological characteristics of shale parent materials. Elements with low mobility during weathering and transport and short residence times in seawater are especially reliable for distinguishing provenance and tectonic settings[83]. These elements are incorporated into sediments during weathering and transport, preserving the primary geochemical signature of the source rocks[84]. The Al_2O_3–TiO_2 relationship is among the most commonly used major-element

[81]Armstrong-Altrin, J. S. & Lee, Y. I. (2004). Geochemistry of sandstones from the upper Miocene Kudankulam Formation, southern India: Implications for provenance, weathering, and tectonic setting. Journal of Sedimentary Research, 74(2), 285-297.
[82]Taylor and McLennan, 1985, Op cit
[83]Pettijohn, 1957, Op cit.
[84]Adamu *et al*., 2020., Op cit

proxies for provenance interpretation. Variations in the Al_2O_3/TiO_2 ratio have been demonstrated to reflect differences in source rock composition. Al_2O_3/TiO_2 ratios of 3–8, 8–21, and 21–70 are generally associated with mafic, intermediate, and felsic igneous rocks, respectively, and are widely used to discriminate source-rock compositions[85]. The Ikom–Mamfe shale samples display Al_2O_3/TiO_2 values ranging from 30.00 to 67.00 (average = 41.09; Table 6), indicating derivation from a weathered felsic (granitic) provenance and reflecting strong clay mineral control within the shale[868788]. This inference is further supported by the TiO_2–Al_2O_3 binary plot (Fig. 5).

Trace element ratios are commonly used in provenance analysis because they clearly differentiate felsic from source rock of mafic origin[899091]. The Th/Sc ratio, in particular, serves as a reliable proxy for source-rock composition. Values ranging from 0.84–20.5 typically indicate felsic sources, whereas lower values of 0.05–0.22 suggest mafic provenance[92]. The Ikom–Mamfe shale samples show Th/Sc ratios of 1.25–3.10, indicating derivation from felsic source rocks (Table 6). The inference is supported by the La/Th–Hf binary diagram (Fig. 6), which places the samples within the acidic arc source field[93].

[85]Hayashi, K. I., Fujisawa, H., Holland, H. D. & Ohmoto, H. (1997). Geochemistry of ~1.9 Ga sedimentary rocks from northeastern Labrador, Canada. *Geochemica et Cosmochimica Acta, 61*, 4115–4137.
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[87]Cullers, 2000, Op cit.
[88]Fazal *et al*., 2022, Op cit.
[89]Cox, R., Lowe, D. R. & Culler, R. L. (1995). The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. *Geochimica et Cosmochimica Acta,* 59, 2919–2940.
[90]Nagarajan, R., Madhavaraju, J., Nagendra, R., Armstronagaltrin, J. S. & Moutte, J. (2007). Geochemistry of Neoproterozoic shales of the Rabanpalli Formation, Bhima Basin, Northern Karnataka, southern India: implications for provenance and paleoredox conditions. *Revista Mexicana de Ciencias Geológicas, 24*(2), 150-160.
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[92]McLennan, S. M. & Taylor, S. R. (1991). Sedimentary-Rocks and Crustal Evolution: Tectonic Setting and Secular Trends. *Journal of Geology, 99*, 1-21
[93]Floyd, P. A. & Leveridge, B. E. (1987). Tectonic environment of the Devonian Gramscatho basin, south Cornwall: Framework mode and geochemical evidence from turbidite sandstones. *Journal of the Geological Society (London, U.K.), 144*, 531–542.

Table 6. Calculated molar ratios of geochemical data in Mamfe Formation shales of Ikom-Mamfe basin

Ratios	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Min	Max	Mean	SD
Al_2O_3/TiO_2	67.00	42.80	32.50	35.00	31.25	42.50	30.00	38.89	30.91	52.86	47.31	42.08	30.00	67.00	41.09	10.84
K_2O/Al_2O_3	0.11	0.09	0.13	0.11	0.13	0.20	0.22	0.12	0.17	0.07	0.22	0.09	0.07	0.22	0.14	0.05
V/Ni	3.00	1.08	1.69	1.72	1.37	1.20	1.77	1.19	2.22	2.45	1.64	1.28	1.08	3.00	1.72	0.58
Ni/Co	2.08	5.86	4.44	2.19	5.38	7.56	5.55	6.11	4.55	3.90	4.30	3.07	2.08	7.56	4.58	1.63
V/Cr	1.69	1.08	1.33	2.45	1.37	1.95	2.36	1.46	2.08	1.41	1.09	1.11	1.08	2.45	1.62	0.49
Zr/Sc	22.00	9.82	7.79	14.14	10.00	13.00	13.98	8.02	8.00	7.43	10.89	14.15	7.43	22.00	11.60	4.19
Sr/Ba	0.15	0.56	0.11	0.32	0.44	0.29	0.43	0.43	0.67	0.27	0.28	0.48	0.11	0.67	0.37	0.16
Sr/Cu	3.32	5.55	3.16	3.93	4.03	3.50	4.03	4.63	5.69	4.03	3.92	4.37	3.16	5.69	4.18	0.79
Sc/Cr	0.08	0.11	0.12	0.15	0.10	0.17	0.18	0.14	0.12	0.12	0.12	0.07	0.18	0.12	0.03	0.03
Th/Cr	0.20	0.20	0.19	0.45	0.26	0.27	0.34	0.27	0.15	0.16	0.21	0.20	0.15	0.45	0.24	0.08
Th/Sc	2.50	1.79	1.63	3.10	2.50	1.60	1.93	1.98	1.25	1.43	1.79	2.77	1.25	3.10	2.02	0.57
Th/U	4.17	3.70	2.43	2.50	2.90	2.67	2.93	2.88	2.42	3.70	4.35	4.29	2.42	4.35	3.24	0.75
Alm	0.84	0.86	0.77	0.85	0.82	0.88	0.81	0.89	0.87	0.84	0.89	0.78	0.77	0.89	0.84	0.12

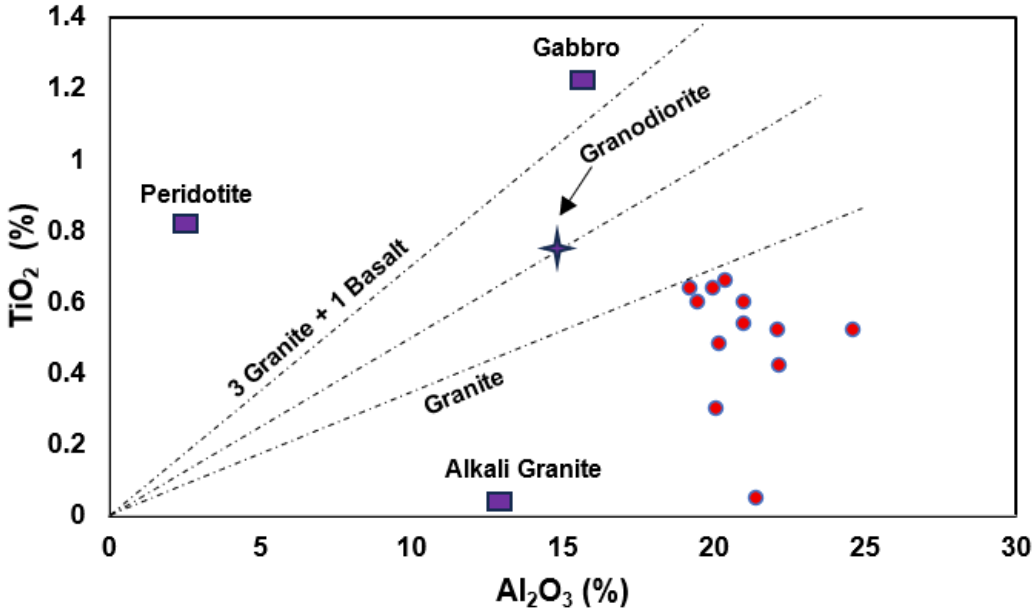


Figure 5 TiO_2 vs Al_2O_3 Discriminant plot for the study (modified after Muller *et al*.,[94])

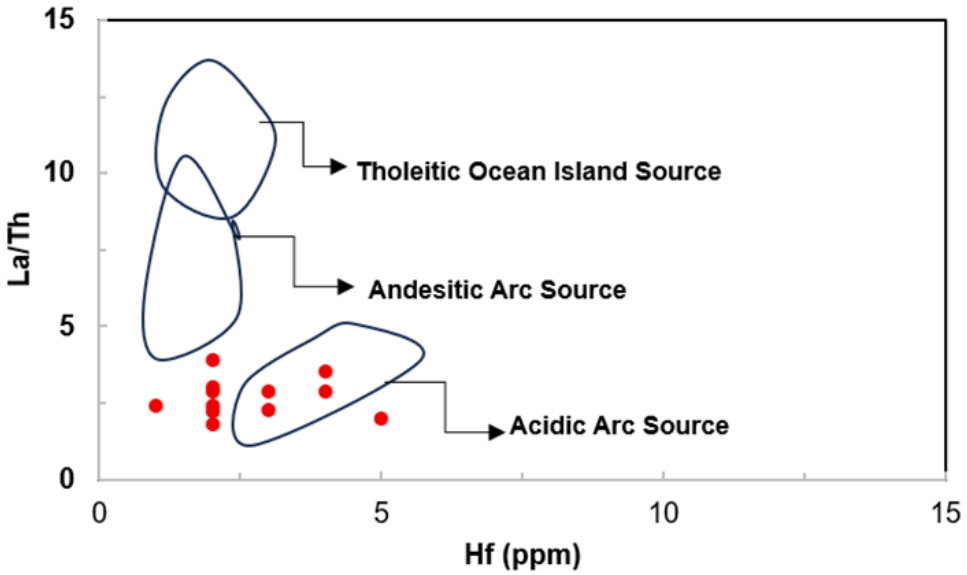


Figure 6 A La/Th vs. Hf bivariate plot for the study (after Floyd & Leveridge[95])

The REE signatures of the Mamfe Formation (shale) samples provide additional support for the provenance interpretations derived from major and trace element geochemistry. Elevated LREE/HREE ratios together with pronounced negative Eu anomalies (Eu/Eu* = 0.13–0.42) are consistent with sediments obtained from a felsic source rock that have undergone plagioclase

[94]Muller, D., Rock, N. M. S. & Groves, D. I. (1992). Geochemical discrimination between shoshonitic and potassic volcanic rocks in different tectonic setting: a pilot study. *Mineralogy and Petrology, 46*, 259–286.
[95]Floyd & Leveridge, 1987, Op cit.

fractionation[96][97][98]. These geochemical indicators collectively affirm a dominantly felsic sediment source from the study area.

Paleo-Weathering, paleoclimate and transportation history

The upper continental crust's weathering processes are largely influenced by climate, and the weathering products that come from these processes are helpful markers of previous weathering regimes and paleoclimatic conditions[99]. During the process of deposition, the distribution, circulation, and fractionation patterns of redox-sensitive elements in both water and sediments are influenced not only by their intrinsic geochemical characteristics but also by the prevailing physical and chemical conditions of the depositional setting and the associated paleoclimatic regime[100][101][102]. Therefore, fluctuations in abundance of major, trace, and REEs that are mobile within aqueous environments can reflect changes in climatic conditions, making them effective geochemical indicators for reconstructing paleoclimate evolution[103].

Geochemical interactions among alkali and alkaline earth metals provide a useful basis for determining the extent and time of weathering processes affecting siliciclastic sediments[104]. Considering that feldspars and volcanic glass are dominant constituents of the upper continental crust[105], chemical weathering processes and soil formation often largely controlled by the breakdown of unstable feldspars and their conversion into secondary clay minerals. The resulting geochemical signatures are preserved in sedimentary records and provide a basis for assessing source composition and weathering conditions. K_2O/Al_2O_3 ratio has been widely employed to infer weathering intensity. A low value suggests intense chemical weathering and higher-ratio points to mild chemical weathering[106]. Low K_2O/Al_2O_3 reported in this study < 1.0 (Table 6), indicates intense chemical weathering, and further reflects control of clay minerals relative to K-

[96]Cullers, 2000, Op cit.
[97]Manikyamba, C., Kerrich, R., Khanna, T. C., Keshav-Krishna, A. & Satyanarayanan, M. (2008). Geochemical systematics of komatiite–tholeiite and adakitic-arc basalt associations: The role of a mantle plume and convergent margin in formation of the Sandur Superterrane, Dharwar craton, India. *Lithos, 106(1–2)*, 155-172.
[98]Taylor and McLennan, 1985, Op cit
[99]Cox *et al*., 1995, Op cit.
[100]Nameroff, T. J., Calvert, S. E. & Murray, J. W. (1989). Glacial–interglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals. *Paleoceanography, 19,* 1010.
[101]Tribovillard *et al.,* 2006, Op cit.
[102]Zhang, Z., Li, S., Suo, Y., Somerville, I.D. & Li X. (2016). Geochemistry of sediments from the Huaibei Plain (east China): Implications for provenance, weathering, and invasion of the Yellow River into the Huaihe River. *Journal of Asian Earth Sciences, 121*, 72–83.
[103]Wei, G. J., Liu, Y., Li, X. H., Shao, L. & Fang, D. Y. (2004). Major and trace element variations of the sediments at ODP Site 1144, South China Sea, during the last 230 ka and their palaeoclimate implications. *Palaeogeography, Palaeoclimatology, Palaeoecology, 212,* 331–342.
[104]Nesbitt, H. W. & Young G. M. (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature, 299,* 715–717.
[105]Tribovillard et al., 2006. Op cit.
[106]Cox *et al*., 1995, Op cit.

bearing minerals, such as K-feldspar and mica, or alternatively indicates a limited contribution of alkali feldspars in the original shale composition[107].

K_2O/Al_2O_3 is often used in conjunction with weathering indices for evaluation of source-rock alteration and paleoclimate. In this study, chemical weathering is quantified using several widely adopted indices, including the "Chemical Index of Alteration (CIA = [Al_2O_3/(Al_2O_3 + CaO* + Na_2O + K_2O)] × 100; Nesbitt and Young[108]), the Plagioclase Index of Alteration (PIA = [(Al_2O_3 − K_2O)/((Al_2O_3 − K_2O) + CaO + Na_2O)] × 100; Fedo *et al*[109]), and the Chemical Index of Weathering (CIW = [Al_2O_3/(Al_2O_3 + Na_2O)] × 100; Harnois[110])". In these computations, CaO* denotes calcium integrated into silicate minerals, and all oxides are stated in molar quantities. According to Nesbitt and Young[111] and Hu *et al*.[112] (2020), CIA values between 50 and 65% typically indicate low chemical weathering, values between 65 and 85% indicate moderate weathering, and values above 85% suggest intense weathering under hot and humid conditions. The respective values of CIA, PIA and CIW for the Mamfe Formation shale ranged from 65.78 to 85.60%, 72.00 to 93.00%, and 76.88 to 94.20%. (see Table 1). This indicates a hot and humid paleoclimate, significant feldspar breakdown during source weathering, moderate to intense chemical weathering within the source area, and a possible source rock rich in felsic rocks[113114115]).

Elevated CIA values further indicate that during weathering processes, CaO, K_2O, and Na_2O leach more readily than the more immobile Al_2O_3 [116]. Trace element geochemistry has been widely employed in paleoclimatic reconstructions[117118119]. The Sr/Cu ratio is particularly responsive to climatic variability, with elevated values generally associated with hot, arid conditions and lower values indicative of warm, humid environments. As proposed by Lerman[120], Sr/Cu ratios in the range of 1.3–5.0 reflect warm and humid paleoclimates, whereas

[107]Cox *et al*., 1995, Op cit.
[108]Nesbitt and Young, 1982, Op cit.
[109]Fedo, C. M., Nesbitt, H. W. & Young, G. M. (1995). Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. *Geology, 23,* 921 – 924.
[110]Harnois L. (1988). The CIW index: a new chemical index of weathering. *Sedimentary Geology, 55*, 319–322
[111]Nesbitt, H. W. & Young, G. (1989). Formation & diagenesis of weathering profiles. *Journal of Geology, 91*, 129-147.
[112]Hu, F., Li, S., Xi, L. & Cao, J. (2020). On the Internal oil Migration in Shale systems and implication for shale oil accumulation: a combined petrological and Geochemical investigation in Eocene Nanxiang Basin China. *Journal of Petroleum Science and Engineering, 184*, 106493.
[113]Adamu *et al*., 2020., Op cit.
[114]Fazal *et al.,* 2022, Op cit.
[115]Fedo *et al*., 1995, Op cit.
[116]Nesbitt & Young, 1984, Op cit.
[117]Lerman, A. (1978). *Lakes: Chemistry, Geology, Physics*. Springer-Verlag, New York, Heidelberg, Berlin, 363p.
[118]Liu, G. & Zhou, D.S. (2007). Application of micro elements analysis in identifying sedimentary environment. *Exploration and Petroleum Geology, 29,* 307–314.
[119]Song, M. S. (2005). Sedimentary environment geochemistry in the Shasi section of Southern Ramp, Donying depression. *Journal of Mineralogy and Petrology, 25*, 67–73.
[120]Lerman, 1978, Op cit.

values exceeding 5.0 are characteristic of hot and arid climatic settings. The Sr/Cu ratio variation from 3.16 to 5.69 with average of 4.18 (Table 6) indicates warm-humid climate with occasional hot-arid conditions.Sediment maturity and transport history was evaluated from the Index of Compositional Variation (ICV), which is computed as ICV = (Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO)/Al_2O_3 [121]. The values decrease from primary minerals to clay minerals, with immature shales showing ICV > 1 and mature shales < 1.The study samples, with ICV ranging from 0.27 to 0.87 (see Table 1), indicate compositionally mature shales that have undergone intense weathering and/or prolonged transport and recycling.

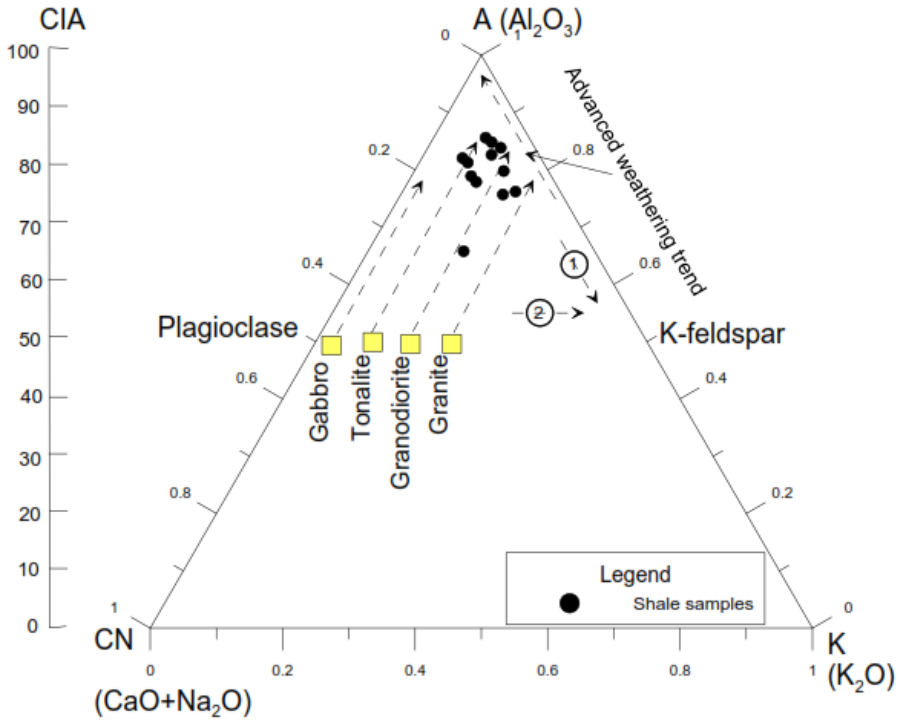


Figure 7. Molecular proportions of Al_2O_3-($CaO+Na_2O$)-K_2O (A-CN-K) ternary diagram for the study (after Nesbitt &Young[122]).

The maturity is most probably associated with the intensive weathering of the felsic rock leading to removal of unstable minerals. The values were reported for muscovite, kaolinite, illite, and plagioclase[123]. The findings agree with the work of Adeigbe and Jimoh[124].

Sediment recycling and/or sorting can be evaluated using Th/Sc versus Zr/Sc bivariate plot. According to this framework, Zr/Sc indicates the concentration of zircon during transport, while

[121]Cox *et al*., 1995, Op cit.
[122]Nesbitt & Young, 1984, Op cit.
[123]Cox *et al*., 1995, Op cit.
[124]Adeigbe, O. C. & Jimoh, T. A. (2013). Geochemical Fingerprints; Implication for Provenance, Tectonic and Depositional Settings of Lower Benue Trough Sequence, Southeastern Nigeria. *Journal of Environment and Earth Science, 3*(10), 2224-3216.

Th/Sc mainly represents source rock composition[125]. Most of the samples show a sub-parallel alignment to trend 1 (Fig. 8) and plot near the average upper continental crust (UCC), indicating uniform composition and little mineral sorting[126][127](Manikyaba & Kerrich, 2006). Only few shales plot between trends 1 and 2 lines, implying minor zircon addition during sediment recycling, which points to the fact that influence of sorting is low to very low[128]. Overall, these results indicate that the shales largely preserve a first-cycle signature, reflecting proximity to the primary source rocks[129].

Palaeo-environment of deposition

The Sr/Ba ratio in shales can be a useful geochemical proxy for interpreting paleo-salinity, paleo environment and sedimentary processes[130]. The interaction between sulfate ions (SO_4^{2-}) present in marine or hypersaline environments and barium ions (Ba^{2+}) found in continental freshwater systems results in barium sulfate ($BaSO_4$) precipitation. In contrast, the comparatively high solubility of $SrSO_4$ enables strontium to remain in solution and subsequently precipitate in central marine or saline lake environments[131].This differential behavior enables the application of Sr/Ba ratios as paleoenvironmental indicators distinguishing marine from terrestrial systems[132]. Generally, Sr/Ba values > 1 signify marine or hypersaline conditions, whereas values below 1 are indicative of freshwater environments[133][134]. The Sr/Ba ratios for the Ikom-Mamfe shales (Table 6) are < 1 (range, 0.11 to 0.67), indicating fresh water conditions. This according to Wang[135], implies that the palaeo-climate as a whole was warm-humid and the water was fresh.

[125]McLennan *et al.,* 1993, Op cit.
[126]Armstrong-Altrin, J. S., Nagarajan, R., Madhavaraju, J., Rosalez-Hoz, L., Lee, Y., Balaram, V., Cruz-Martínez, A. & Avila-Ramírez, G. (2013). Geochemistry of the Jurassic and Upper Cretaceous shales from the Molango Region, Hidalgo, eastern Mexico: Implications for source-area weathering, provenance, and tectonic setting, ComptesRendus Geoscience, 345(4), 185-202.
[127]Mclennan S.M., Back B., Hemming S.R., Hurowitz J.A. & Lev, S.M. (2003). The role of provenance and sedimentary processes in the geochemistry of sedimentary rocks. *Geochemical Sediments and Sedimentary Rocks, 4*, 7-31.
[128]Singh, A. K. & Chakraborty, P. P. (2021). Geochemical and hydrocarbon source rock potentials of shales from the Palaeo-Mesoproterozoric Vindhyan Supergroup, central India. *Energy and Geosciences, 4*(3), 23- 32.
[129]Mclennan, S. M. (1982). On the geochemical evolution of sedimentary reactions. *Chemical Geology, 37 (3-4)*, 335-359.
[130]Zhao, Z. H. (1997). *Principles of Trace Element Geochemistry*, Science Press.
[131]Zhao, 1997, Op cit.
[132]Zhang *et al.,* 2016, Op cit.
[133]Deng, H. W. & Qian, K. (1993). Analysis on Sedimentary Geochemistry and Environment. *Gansu Sci. Tech. Pub. House, Lanzhou*, 15-85
[134]Wang, A. H. (1996). Discriminant effect of sedimentary environment by the Sr/Ba ratio of different existing forms. *Acta Sedimentologica. Sinica, 4,* 169–174.
[135]Wang, 1996, Op cit.

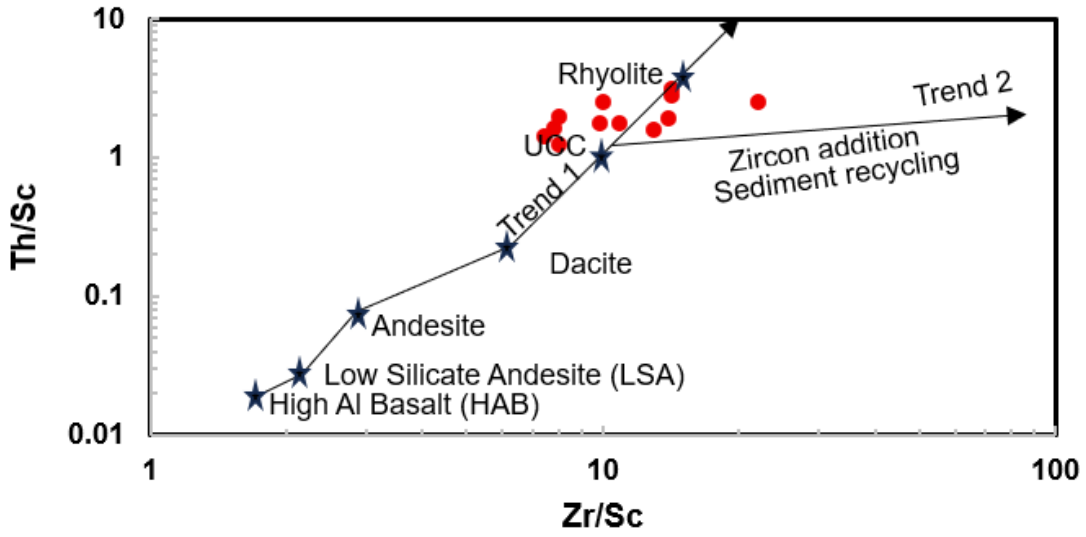


Figure 8 Bivariate plot of Th/SC vs Zr/Scfor the study (after McLennan *et al*[136])

Palaeo-redox conditions during siliciclastic sedimentation can be assessed using bulk geochemical data, particularly redox-sensitive trace metals like V, Cr, Mo, Ni, Co, and U, whose mobility is governed by oxygen availability[137138139140141142143]. Accordingly, elemental ratios including Ni/Co, U/Th and V/Cr are widely used in reconstructing depositional redox environments. Low uranium concentrations are typically associated with sediments deposited under well-oxygenated conditions[144]. The U/Th ratios of the studied shales (0.230.41; mean = 0.32) suggest deposition in an oxic setting dominated by detrital input[145]. In addition, Ni/Co ratios ranging from 2.08 to 7.56 (mean = 4.58; Table 6) indicate predominantly oxic to suboxic

[136]McLennan *et al.,* 1993, Op cit.
[137]Bennett, W. W. & Canfield, D. E. (2020). Redox-sensitive trace metals as paleoredox proxies: A review and analysis of data from modern sediments. *Earth-Science Reviews, 204*, 103175.
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[145]Crusius *et al.,* 1996, Op cit.

conditions, according to Jones and Manning[146], where values < 5.00 reveals oxic environments and values from 5.00 to 7.00 denote suboxic conditions. Additionally, the samples' V/Cr ratios, which range from 1.08 to 2.45 with an average of 1.62, show that they were deposited in an oxic environment with sporadic anoxic conditions[147].

In addition, many authors have linked Ce anomalies in shales to redox conditions[148149150151152153]. According to them, Cerium (Ce^{4+}) exhibits variable mobility under different redox regimes, being relatively immobile under oxic conditions but more soluble and depleted in sediments deposited under anoxic conditions. The Ce/Ce* ratios for the samples under study has an average value of 1.07 and fall between 0.72 and 1.56 (see Table 4). This suggests a mixed redox (suboxic to oxic) conditions. The collective evidence from the multiple redox proxy parameters reveals that shale deposition within the Mamfe Formation occurred primarily under oxygenated paleoenvironmental conditions, punctuated only by brief intervals of suboxic and anoxic fluctuations.

Tectonic setting

The assessment of petroleum potential and other economically significant mineral resources requires an understanding of the tectonic setting within a sedimentary basin. Several studies have emphasized the usefulness of major element geochemical data from sedimentary formations in reconstructing tectonic regimes, particularly through the application of discrimination diagrams (for example, (McLennan & Taylor[154]; Bose *et al*[155],Singh & Chakraborty[156]; Rashidi *et al*.,[157]). Plate tectonic processes are known to influence the geochemical composition of sediments by controlling both provenance characteristics and sedimentary processes associated with different

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[154]McLennan & Taylor, 1991, Op cit.
[155]Bose, P. K., Sarkar, S., Chakrabarty, S. & Banerjee, S. (2001). Overview of the meso-to Neoproterozoic evolution of the Vindhyan Basin, central India. *Sedimentary Geology, 141,* 395-419.
[156]Singh & Chakraborty 2021, Op cit.
[157]Rashidi *et al*., 2024, Op cit.

tectonic settings[158]. It was evaluated using the discrimination scheme of Bhatia and Crook[159], specifically through the La/Y versus Sc/Cr bivariate plot (Fig. 9). The shales studied plotted within close proximity to passive continental margin field. This tectonic interpretation is further substantiated by the distribution of REE, similar to the average UCC and PAAS which are marked by prominent negative europium anomalies (Eu/Eu* = 0.13–0.42, average 0.24).

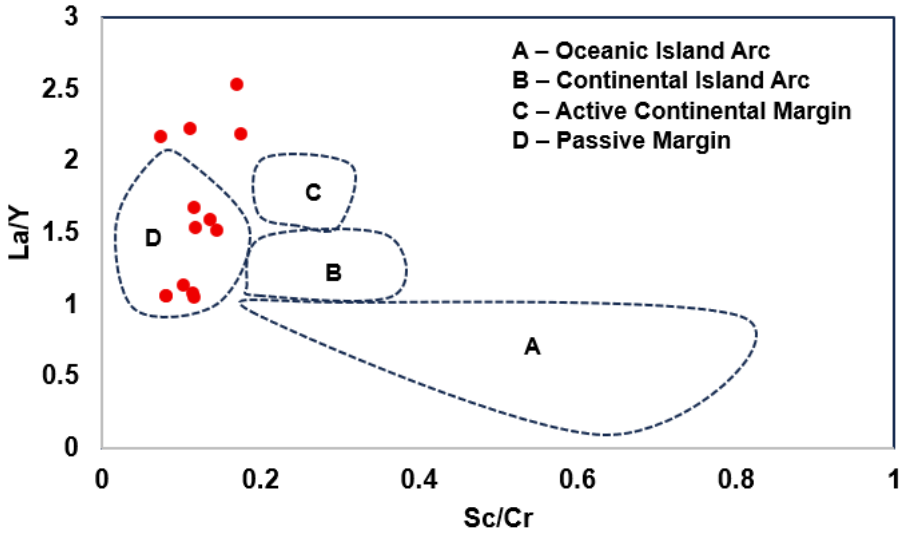


Figure 9 Discriminant plot of La/Y versus Sc/Cr (fields after Bhatia & Crook[160])

Comparable tectonic inferences have been reported the tectonic setting of some nearby sedimentary basins within the Southern Benue Trough; among such include passive to active continental margin setting for sediments of the Awi Formation, Calabar Flank[161][162][163]. Similarly, Oni et al. (2014) classified the Niger Delta sediments as having been deposited within a passive continental margin tectonic regime. They linked such a setting to the development of a failed arm of a triple junction associated with the Cretaceous rifting of West and Central Africa. A comparable tectonic framework may therefore be inferred for the depositional setting of the sediments investigated in the present study as corroborated by the data acquired n interpreted.

[158]Oni, S. O., Olatunji, A. S. & Ehinola, O. A. (2014). Determination of Provenance and Tectonic Settings of Niger Delta Clastic Facies Using Well-Y, Onshore Delta State, Nigeria. *Journal of Geochemistry, 1*, 960139.
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[162]Okon *et al*., 2017, Op cit.
[163]Okon *et al.,* 2023, Op cit.

Hydrothermal activity signatures

The Sc/Cr proxy was used by Xue *et al*.[164] to assess hydrothermal activity signatures, because Chromium is commonly mobilized during sediment transportation and therefore the Sc/Cr ratio presents a suitable tool to evaluate the response of the sediments to hydrothermal activities. When hydrothermal fluids interact with crustal rocks, they can leach Cr from the rocks, leading to an increase in Cr concentrations in the fluids. This can result in a decrease in the Sc/Cr ratio in the rocks[165]. According to Xue *et al*[166]. (2020) Sc/Cr ratio below 0.120 are interpreted to reflect hydrothermal influence during deposition, whereas values exceeding 0.144 are considered characteristic of deposition under normal water conditions. In this study, Sc/Cr ratios ranges from 0.07 to 0.18, with an average value of 0.12 (Table 6), suggesting that the shales of Mamfe Formation were deposited under predominantly normal water conditions, with minor contributions from hydrothermal processes. This interpretation is further corroborated by the presence of negative europium and positive Cerium anomalies[167168169170171]). The lack of intensive hydrothermal influence in the Ikom-Mamfe basin indicates lack of deep-seated metallic ores in the basin. Therefore, exploration efforts in the Ikom-Mamfe basin should focus more on industrial minerals (Bua, 1991).

Organic matter enrichment and hydrocarbon potentials

TOC combined abundance of organic matter present as kerogen and bitumen, is the key parameter used in the generation potential of hydrocarbon from petroleum source rocks[172173]. The potential for producing hydrocarbon increases with the TOC value measured in wt%. Source rocks with 0.0 < TOC < 0.5 are considered to have poor potentials for the generation of hydrocarbon; those with 0.5 < TOC < 1.0 are considered to have fair potentials; those with values between 1.0 < TOC < 2.0 are of good potentials; and those with 2.0 < TOC < 3.0 are

[164]Xue, C. J., Zhao, X. B., Zhao, W. C., Zhao, Y., Mo, X. X., Zhang, G. Z., Nurtev, B. & Pok, N. (2020). Deformed zone hosted gold deposits in China-Kazakhstan-Kyrgyzstan-Uzbekistan Tian Shan: metallogenic environment controlling parameters, and prospecting criteria. *Earth Science Frontiers, 27*(2), 294-319.
[165]Bau, M. (1991). Geochemistry of rare earth elements and scandium in hydrothermal systems. *Chemical Geology, 93*(1-2), 59-74.
[166]Xue, *et al*., 2020, Op cit.
[167]Bau, M. & Dulski, P. (1996). Distribution of Yttrium and Rare-Earth Elements in the Penge and Kuruman Iron-Formations, Transvaal Supergroup, South Africa. *Precambrian Research, 79*, 37-55.
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[170]Sverjensky, D. A. (1984). Europium redox equilibrium in aqueous solution. *Earth and Planet Science Letters, 67*, 70-78.
[171]Xue *et al.,* 2020, Op cit.
[172]Hunt, 1996, Op cit.
[173]Peters, K. E. & Cassa, M. R. (1994). Applied source rock geochemistry. In: L. B. Magoon, & W. G. Dow, (Eds). *The petroleum system from Source to Trap.* American Association of Petroleum Geologists Memoir 60, 93-120.

considered to have very good potentials. Exceptionally rich source rocks with excellent hydrocarbon generation potential are characterized by TOC values exceeding 5.0 wt%. The TOC analyzed in this study ranged in value from 0.80 to 3.50, and a mean value of 2.32 wt%. Therefore, all the shale showed good to very good potential for hydrocarbon source rocks (Table 5). This finding is supported by the relatively high genetic potential values (GP > 2.5, Hunt[174]) and it was corroborated by Asi *et al*[175]. (2022). Source rock quality was appraised by means of the classification criteria[176] established for source rock of continental origin (Fig. 10). The plot indicates that over 70% of the analyzed samples fall within the fair to good source rock category, while more than 20% are categorized from fair to very-good. However, one sample plotted as fair source rocks. Majority of the studied shale have high organic matter and a required capacity to generate hydrocarbon.

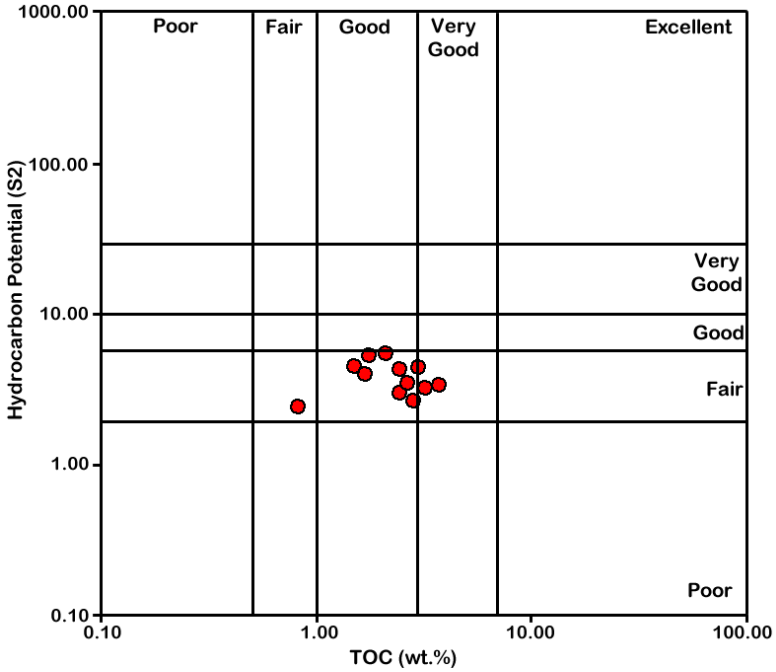


Figure 10 Rock Eval S2 vs TOC for determination of hydrocarbon potential (modified after Jackson et al., 1985)

Geochemical indicators have used biophilic elements (Co, Ni, and V) to trace organic matter origin in shale[177178179180]. The ratios derived from these elements are particularly useful for assessing organic matter provenance, depositional conditions and often times, thermal maturity.

[174]Hunt, 1996, Op cit.
[175]Asi *et al.,* 2022, Op cit.
[176]Huang, D.F. & Li, J.C. (1982). X Diagram of Kerogen Type Classification. Geochemistry, 1, 21-30.
[177]Adamu *et al*., 2020., Op cit.
[178]Akinlua, A., Olise, F. S., Akomolafe, A. O. & McCrindle R. I. (2016). Rare earth element geochemistry of petroleum source rocks from northwestern Niger Delta. *Marine and Petroleum Geology, 77*, 409-417.
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[180]Zhao, 1997, Op cit.

V/Ni ratios lower than 1.9 is generally associated with terrestrially derived organic matter. The values between 1.9 and 3.0 reflect mixed terrestrial as well as marine sources, while ratios exceeding 3.0 are indicative of predominantly marine organic matter. Shale from Mamfe Formation exhibit V/Ni ratios ranging from 1.08 to 3.00 (Table 6), suggesting a heterogeneous origin of terrestrial and marine organic materials. Furthermore, association between hydrogen index (HI) and oxygen index (OI) provides insight into kerogen type. The HI–OI plot (Fig. 11) indicates that the kerogen within the Mamfe Formation source rocks is dominated by marine oil/gas prone (Type II) kerogen, with a subordinate contribution from terrestrially derived, gas-prone (Type III) kerogen. These results are consistent with those derived from the inorganic proxies.

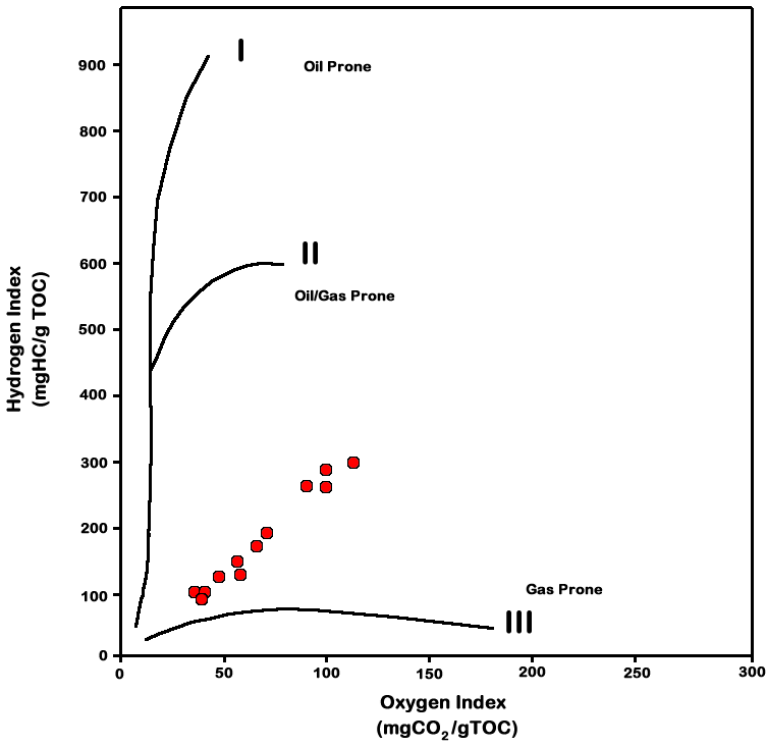


Figure 11 The HI–OI plot for the shales of Mamfe Formation (Espitalie *et al*[181])

In addition to the abundance and quality of organic matter, its thermal maturity constitutes a critical factor in hydrocarbon generation, as organic matter must undergo sufficient thermal evolution to generate petroleum[182]. Thermal maturity is commonly assessed using T_{max} values, which allow organic matter to be classified into immature, mature (oil window), transitional, and overmature stages. T_{max}< 435 °C implies a thermal immature organic matter, whereas 435 °C <T_{max}< 455 °C correspond to an oil-generation window. Temperature range between from 455 to 470 °C is interpreted as transitional, while Tmax values exceeding 470 °C reflect over-mature or

[181]Espitalie et al., 1977, Op cit.
[182]North, F. K. (1985). *Petroleum Geology*. Allen & Unwin, Boston, 607p.

super-mature conditions[183][184]. Thermal maturity of organic matters from Ikom-Mamfe shales shows a wide variation (Table 5). The Tmax values range from a thermally immature organic matter (422 °C) to a super mature organic matter (476 °C). To verify this finding further, Tmax was plotted against values of productivity index, PI (Fig. 12) in modified Van Krevelen diagram[185][186][187]. It confirms that > 50% the shale obtained for this study, plotted within the immature source rock region that has not been subjected to high enough heat to generate significant hydrocarbons; one thirds (more than 30%) plotted in the zone of mature source rock actively generating hydrocarbons; and one sample plots in the dry gas zone where oil has been cracked into gas or from type III kerogen[188].

Economic potential

The presence of high organic matter in shales suggests potential for hydrocarbon generation. Studies have shown that shales deposited in fresh oxic water during warm-humid climates can be rich in kerogen Type-II and -III, favorable for hydrocarbon generation[189]. The high organic matter content in shales can also make them suitable for carbon sequestration, providing a potential revenue stream through carbon credits[190].The clayey nature of the shales, combined with high organic matter, makes them a potential source for shale gas and oil. The passive continental margin setting and minimal hydrothermal activity indicate lack of deep-seated metalliferous deposits and suggest a high-risk environment for exploration[191]. The felsic source rocks and clayey shales may indicate the presence of minerals like kaolin, bentonite, or other industrial minerals. These minerals have economic value for various industrial applications[192].

[183]North, 1985, Op cit.
[184]Tissot, B. & Welte, D. H. (1978). *Petroleum Formation and Occurrence*. Springer-Verlag, Berlin, 538 p.

[185]Hunt, 1996, Op cit.
[186]Tissot & Welte, 1978, Op cit.
[187]Van Krevelen, D. W. (1961). *Coal: typology, chemistry, physics, constitution.* New York, Elsevier Pub. Coy. 514p
[188]Hunt, 1996, Op cit.
[189]Peters & Cassa, 1994, Op cit.
[190]Bachu, S. (2008). Mineralogical and Geochemical characteristics of Caprock Formations used for storage and sequestration of carbon dioxide. *Progress in Energy and Combustion Science, 34*, 254-273.
[191]Kvenvolden, K A. (1993). Gas hydrates-geological perspective and global change. *Reviews of Geophysics, 31,* 2.https://doi.org/10.1029/93RG00268
[192]Klein C. & Hurlbut C.S. (1993). *Manual of Mineralogy,* 21st Ed. Xii. John Wiley' Sons, Inc., New York, Chichester, Brisbane, Toronto, Singapore, 1 – 681.

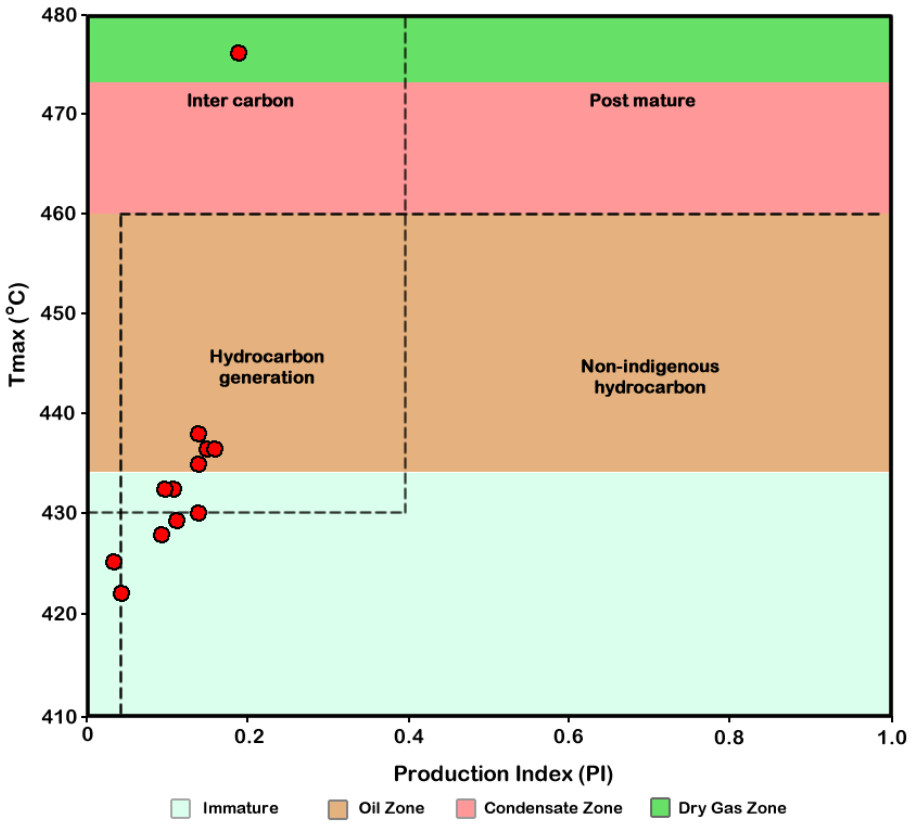


Figure 12 Thermal maturity indicators with a plot of PI vs Tmax (Modified after Peters, 1986)

According to Rogers[193], organic-rich shales commonly contain metal concentrations that may be of economic significance. The geochemical make-up of shale evaluated in this study was compared with average UCC, PAAS, and the metalliferous shale standards of the United States Geological Survey (USGS) in order to evaluate patterns of metal enrichment and depletion. The examined shale samples show relative enrichment in rare earth elements (REE), although to a lesser degree, when compared to UCC and PAAS reference values (Figs. 4 and 13). The high REE and trace element contents can make the shale a potential source for these critical elements, which are essential for various high-tech applications and energy.

Metalliferous shales contain a wide range of metallic constituents, including alkali, alkaline earth-metals, metalloids, trace metals, and REEs[194]. When compared with reference values provided, the studied shales exhibit elevated concentrations of P, As, Ba, Ce, Cs, Pb, Sc, Sr, Th, U, and W. These enrichments indicate that the shales may serve as a viable source of industrial minerals[195196].

[193]Rogers, N. (2016). Volcanism. In: *Encyclopedia of Geochemistry*, Springer, Cham,p. 1-6.
[194]Rogers, 2016, Op cit.
[195]Bhatia, 1983, Op Cit.
[196]Bokanda et al., 2018, Op Cit.

According to Calvert and Piper[197], Aluminum module (Alm) = Al/(Al + Mn + Fe), is a geochemical tool used to distinguish sediment source primarily by differentiating between terrigenous (detrital) and hydrothermal (metalliferous) origins. The proxy is based on the fact that Al is a key indicator of terrigenous component. It is a refractory element and least susceptible to alteration. The Fe and Mn are enriched components of hydrothermal fluids. Values of Alm > 0.16 and Alm < 0.16, agrees with terrigenous and hydrothermal sources respectively. The Alm obtained for this study is from 0.77 to 0.89, with an average of 0.84 (Table 6) classifying the shales as terrigenous sediments.

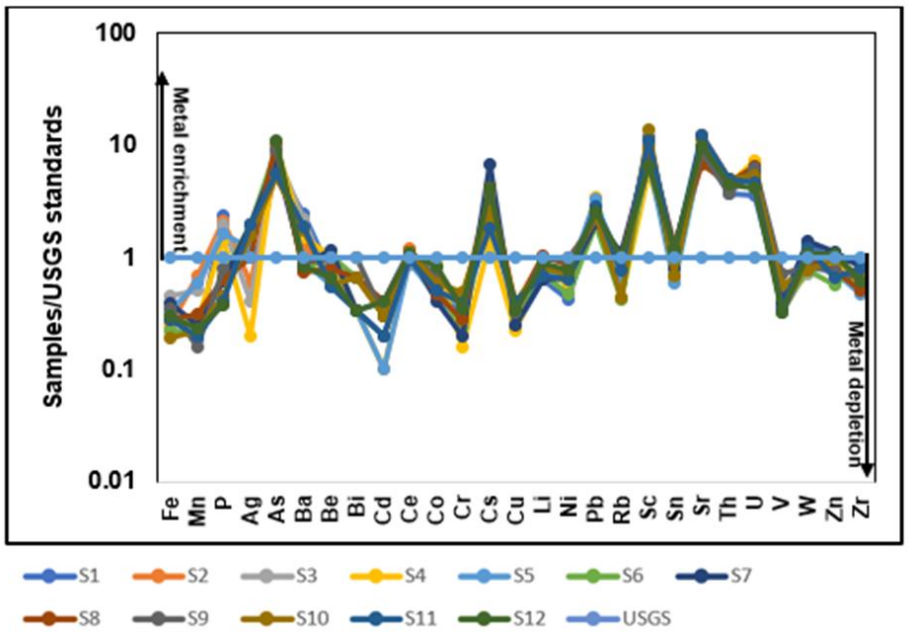


Figure 13 Spider plots of element contents for Mamfe Formation shales normalized against USGS standard for metalliferous sediments

The Al-Fe-Mn triangular diagram (Fig. 14) further confirms typical pelagic/terrigenous sediments for the Ikom-Mamfe basin. The dominance of terrigenous sediments also supports minimal hydrothermal exhalations, metal precipitation or diagenetic enrichment associated with ore formation[198][199]. Passive margins can host various mineral deposits beyond hydrocarbon including heavy mineral, phosphate, clay and evaporite deposits[200][201].

[197]Calvert, S. E. & Piper, D. Z. (1984). Geochemistry of Ferromanganese Nodules from DOMES Site A, Northern Equatorial Pacific: multiple diagenetic metal source in the deep sea. *Geochimica et Cosmochimica Acta, 48,* 1913-1928.
[198]Adamu *et al*., 2020., Op cit.
[199]Xue *et al*., 2020, Op cit.
[200]Bokanda *et al*., 2019, Op Cit.
[201]Fazal *et al*., 2022, Op cit.

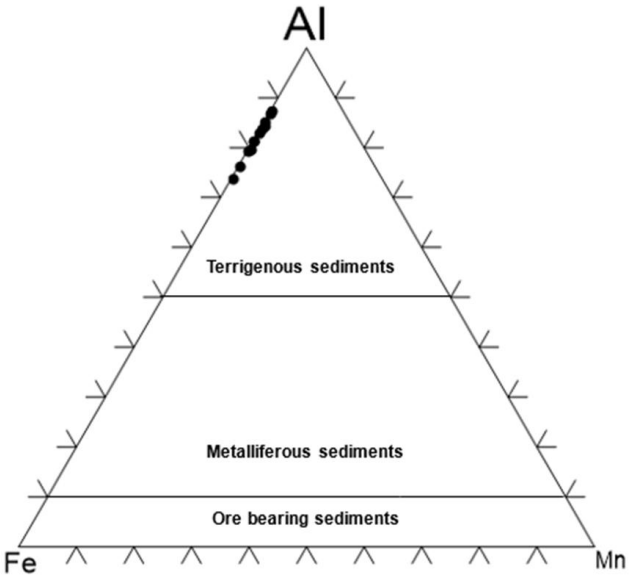


Figure 14 Triangular plot of Al-Fe-Mn for evaluating the relative contributions of hydrothermal vs terrigenous materials within the Mamfe Formation shales

Conclusion

The study aimed at characterizing the inorganic and organic geochemical compositions of shale from Mamfe Formation in Ikom-Mamfe basin. The data was used to infer their provenance history, environment of deposition and mineralization potentials. Major oxide compositions reveal high SiO_2 content with Al_2O_3 exceeding Fe_2O_3 in all samples studied, while other oxides occur in lower concentrations, suggesting that clay minerals dominate the shale. Rare earth element (REE) distributions indicate enrichment in light REEs relative to medium and heavy REEs without showing any significant enrichment for ecomonic conentration. Geochemical ratios such as Al_2O_3/TiO_2, Th/Sc, and LREE/HREE suggest that the shales originated predominantly crystalline basement sources. Moreover, the similarity of trace and REE distribution patterns compared with UCC and PAAS further supports an upper continental crust origin. Discrimination diagrams, such as the La/Y versus Sc/Cr bivariate plot and the REE patterns, suggest that the shale deposition occurred along a passive continental margin. The K_2O/Al_2O_3, CIA, PIA and CIW data, as well as the A - CN - K plot, collectively reveal chemical weathering to be moderate to intense in the source area. The ratios: Sr/Ba, U/Th, Ni/Co, V/Cr and Ni/Co, REE patterns and anomalies, and other related geochemical proxies, indicates shale to be deposited in oxic to sub-oxic fresh waters during warm humid climatic conditions. Most of the Ikom-Mamfe shales have uniform geochemical composition and limited influence of sediment recycling and zircon enrichment. Comparisons with metalliferous shale standards indicate that the Mamfe Formation shales are enriched in REE, P, Ba, As, Ce, Cs, Sc, Sr, Th, and U, with a few samples showing elevated Pb and W contents. The Alm, V/Ni ratio and ternary plot of Al–Fe–Mn showed that shale are largely land-derived in origin, through minimal hydrothermal inputs.

The shales are categorized by values of TOC up to 3.50 wt %asfair to good quality source rocks; the S2 which ranged from 2.4 to 5.6 mgHC/g, also suggest good to very good source rocks. The shales are thermally immature to mature, with kerogen Type-II and Type-III of oil/gas prone generation potential.

Exploration activities in the Ikom-Mamfe basin should concentrate more on hydrocarbons and industrial minerals such as REE, phosphate, clay, evaporite, uranium and heavy minerals, than metalliferous deposits. The investigation demonstrated that inorganic and organic geochemical analysis proved to be a valuable method for characterizing shale deposits. Future studies should incorporate additional geochemical data from a wider range of locations to enhance and deepen our understanding of metallogenic enrichment processes.

Credit author statement: C. I. Adamu and T. N. Nganje: conceived and designed the research; E. E. Okon, E. A. Kudamnya and I. K Adebayo: wrote the proposal; C. I. Adamu; T. N. Nganje; E. E. Okon; E. A. Kudamnya and I. K Adebayo: carried out the fieldwork, analyzed, interpreted the data, and wrote the paper.

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