Elemental Geochemistry of the Late Paleocene Shales from Dange and Gamba Formations, Sokoto Basin, Northwest Nigeria

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ABSTRACT

An essential aspect of petroleum exploration is the analysis of elemental geochemistry, which can provide valuable information about the provenance, source facies, and depositional paleoenvironments. The present study utilized inductively coupled plasma-mass spectrometry (ICP-MS) to explore the geochemical significance of elements in shales from Sokoto Basin. The study identified and quantified a total of fifteen elements. The results showed that Fe was the most abundant trace element in the shale samples, indicating a siliciclastic facies. Mn and Co followed in abundance, while Ni was the least detected trace element in the shales. The low metal content recorded in some of the samples suggests that they have reached a state of thermal maturity. The variations in concentrations observed among the shales suggest that the samples have mixed origins but with higher contribution from marine organic matter. The values of various ratios computed from the elements indicated mixed input of terrestrial and marine origins, deposited in lacustrine-fluvial/deltaic environments. This study showed that elemental geochemistry can be used to determine the provenance, tectonic setting and depositional conditions of the shales from the Sokoto Basin, North West, Nigeria.

Keywords: Provenance, source facies, depositional conditions, elements, ICP-MS

Nomenclature list

Sb: Antimony; Co: Cobalt; Cr: Chromium; Cs: Cesium; Cu: Copper; Ga: Gallium; Fe: Iron; ICP-MS: Inductively coupled plasma-mass spectrometry; La: Lanthanum; La/Sc: Lanthanum/Scandium; La/Co: Lanthanum/Cobalt; Mn: Manganese; Mo: Molybdenum; Ni:

Nickel; Ni/Co: Nickel/Cobalt; Ni/Mo: Nickel/Molybdenum; Rb: Rubidium; Sc: Scandium; ΣREEs: Summation of rare earth elements; TTM: Total trace metal; V/Ni: Vanadium/Nickel; V/Fe: Vanadium/Iron; V/(V+Ni): Vanadium/(Vanadium + Nickel); Zr: Zirconium; Zr/Cr: Zirconium/Chromium.

INTRODUCTION

Nigeria possesses an abundance of sedimentary basins, aside from the Niger Delta Basin, which is one of the sources of current petroleum production. These basins include the Anambra, Bida, Sokoto, Bornu (Chad), and Dahomey Basins, as well as the Benue Trough, which is comprised of the Lower, Middle, and Upper Benue Troughs. These basins share structural and stratigraphic similarities with contiguous intracratonic rifted basins of Chad Republic, Niger Republic, Sudan, Tanzania, Uganda, and Kenya, where commercial oil accumulations have been discovered [1, 2] (Figure 1). The Sokoto Basin, also known as the Iullemenden basin, is situated in northwestern Nigeria and is depicted in Figure 2. The stratigraphic succession is demonstrated in Figure 3. The basin is primarily composed of a great undulating plain, with an average elevation that varies between 250 and 400 meters above sea level, occasionally interrupted by low mesas. The most prominent feature in the basin is a low escarpment, referred to as the "Dange Scarp," which is closely related to the geology [3]. The sediments of the Iullemenden basin were accumulated during four primary phases of deposition. The Iiio and Gundumi Formations, consisting of grits and clays, constitute the pre-Maastrichtian continental intercalaire of West Africa, overlying the pre-Cambrian Basement unconformably. They are overlain uncomformably by the Maastrichtian Rima Group, consisting of mudstones and friable sandstones (Taloka and Wurno Formations) separated by the fossiliferous Dukamaje Formation. The Paleocene Sokoto Group is made up of the Dange and Gamba Formations (mainly shales), separated by the calcareous Kalambaina. The Dange Formation, which is of Late Paleocene age, comprises slightly indurated bluish-grey shales with bands of gypsum and numerous irregular phosphatic noodles and pellets. The shales are interbedded with thin layers of yellowish-brown limestone. The Dange Formation is a sedimentary rock that boasts plenty of fossils. The formation's type section is located in Dange village, approximately 28 kilometers south of Sokoto, along the Sokoto-Gusau road.

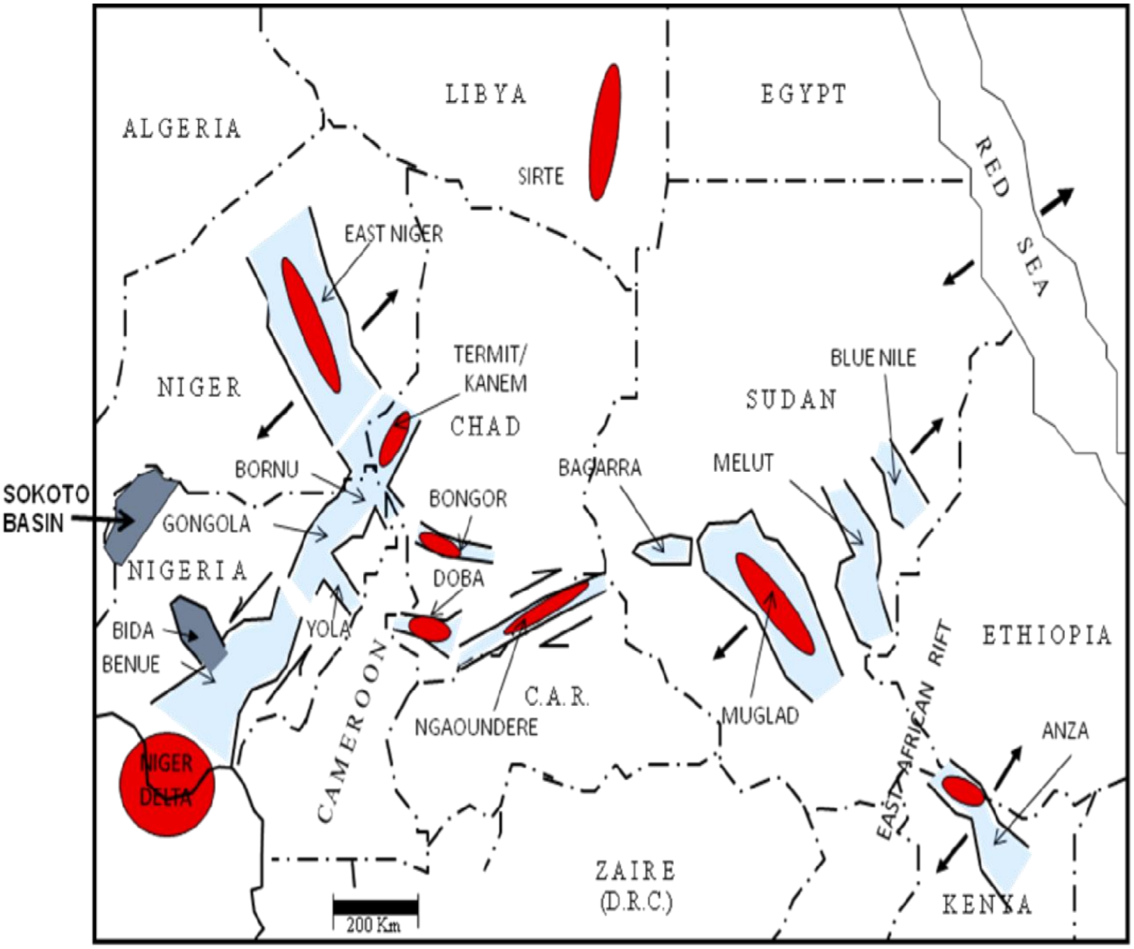


Fig.1: The Regional tectonic map of western, central, and eastern African rifted basins showing Sokoto basin and other related African basins (modified from Obaje et al. [4]).

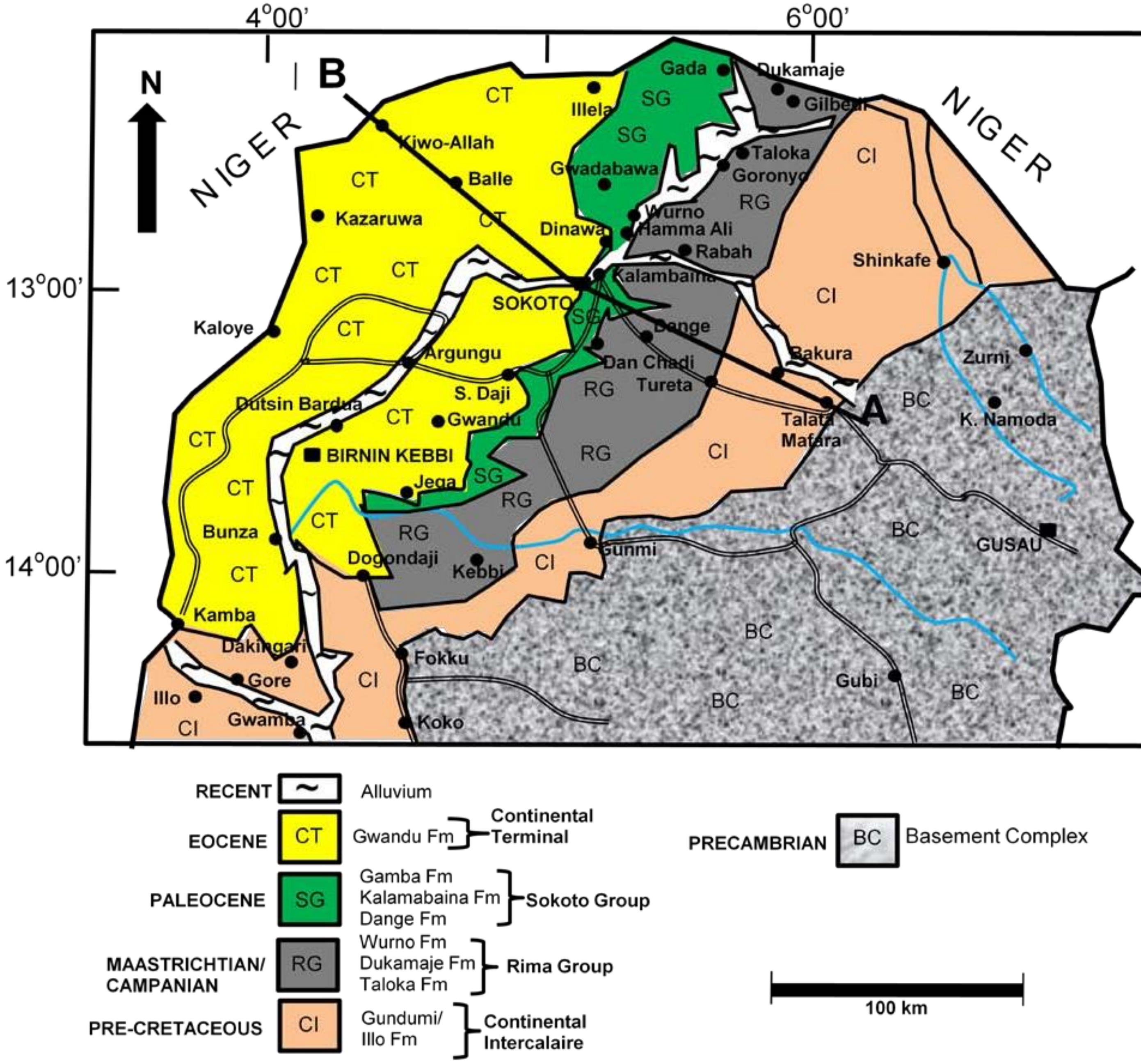


Fig. 2: Generalized geological map of the Nigerian sector of lullemmeden Basin (Sokoto Basin) adopted from Obaje et al. [4].

The thickness of the formation is approximately 45 meters. Okosun [5] discovered agglutinated benthic foraminifera and ostracods, indicating that the Dange Formation could have been a transitional marine, shallow marine, or inner neritic environment.

The Kalambaina Formation is comprised of white clayey limestones interbedded with shales, which were deposited in a marine environment. The limestone is classified as bioclastic wackestone. The formation is abundant in fossils and has a thickness of 20 meters. The Gamba Formation is composed of grey shale that is rich in fossils and gypsum, with phosphatic pellets and coprolites. The formation also contains thin phosphatic micro-conglomeratic intercalations that hold fish teeth and scales, as well as moulds of bivalves. The type section is located within a Cement Company and the type locality is Gamba. Nwajide [6] posits that the formation's folded appearance is the result of slumping, which occurred due to solution cavities in the underlying limestones of the Kalambaina Formation. The formation is capped by ferruginous oolite, dated Upper Paleocene by Kogbe [7]. A similar assemblage of calcareous benthic foraminifera and ostracods found in Kalambaina are also present in this formation, albeit with lower diversity and abundance [5].

Shale is one of the most commonly found sedimentary rocks in records and constitutes about two-thirds of all well-known argillaceous rocks. It is believed that trace elements' behavior is affected by sedimentary processes, which depends on several factors such as weathering, physical sorting, adsorption, provenance, diagenesis, and metamorphism [8-12].

The assessment of sediment sources in marine and terrestrial basins is a traditional practice that can be achieved through trace element geochemistry, particularly via provenance studies. This involves using the relative abundances of rare earth elements (REEs) and trace elements to define parent materials. In marine environments, certain elements actively participate in geochemical processes that occur during deposition; the availability of free oxygen during this period may lead to the authigenic enrichment or depletion of these elements in sediments. The distribution patterns of such elements are widely applied to comprehend variations in paleoredox conditions in modern marine sediments and ancient rocks [13-19]. The exploration of shale oils and gas in recent years has brought about increased attention to the trace elemental compositions of shales in reconstructing paleoenvironments, which is crucial for organic matter accumulation [20-23]. Immobility of trace elements and REEs renders them resistant to chemical weathering and less susceptible to leaching compared to major oxides during sediments denudation and weathering [24]. The ratios of Cr/Th, La/Th, Co/Th, La/Sc, and Th/Sc are commonly used to infer the provenance of sedimentary rocks [23-26] Therefore, trace elements and REEs are widely analyzed to distinguish detritus provenance and tectonic background [24, 27-28].

A lot of studies have been undertaken in Sokoto Basin [2,4,7,29-34] Toyin et al. [34-35] have reported on the lithostratigraphical, paleontological, and sedimentological characteristics, as well as the reservoir potential of carbonate rocks derived from various parts of this basin. It also worth noting that Kogbe [7,29-30] and Reyment [36] have previously documented the general geology of the larger Iullemmeden basin. Additionally, the Nigerian government's pursuit of hydrocarbon reserves in the inland basins of Nigeria has prompted the research of Obaje et al. [4]. However, the majority of these studies have primarily concentrated on topics such as regional geology, stratigraphic sequence, sedimentology, geological mapping, and aeromagnetic geophysical investigation. Unfortunately, these investigations have failed to furnish sufficient insights into the petroleum generative potential of the shales from the basin which is very crucial to petroleum exploration. Only a limited number of reports on elemental geochemistry regarding the shales from the basin have been documented [37]. Therefore, samples were collected to study the provenance, origin, depositional environments, and discriminate the tectonic setting of the shales from Dange and Gamba Formations by applying a more detailed elemental proxy. The aim is to decipher the provenance, depositional conditions, and tectonic background for the formation of the shales in the Sokoto Basin during the Late Paleocene. This may provide valuable insights for exploration of shale oil and gas in this area.

MATERIALS AND METHODS

Sampling

A total of thirty (30) outcrop shale samples were collected from two formations, namely, Dange and Gamba Formations in Sokoto Basin, Northwestern Nigeria. The geological map and stratigraphic sequence are shown in Figures 2 and 3.

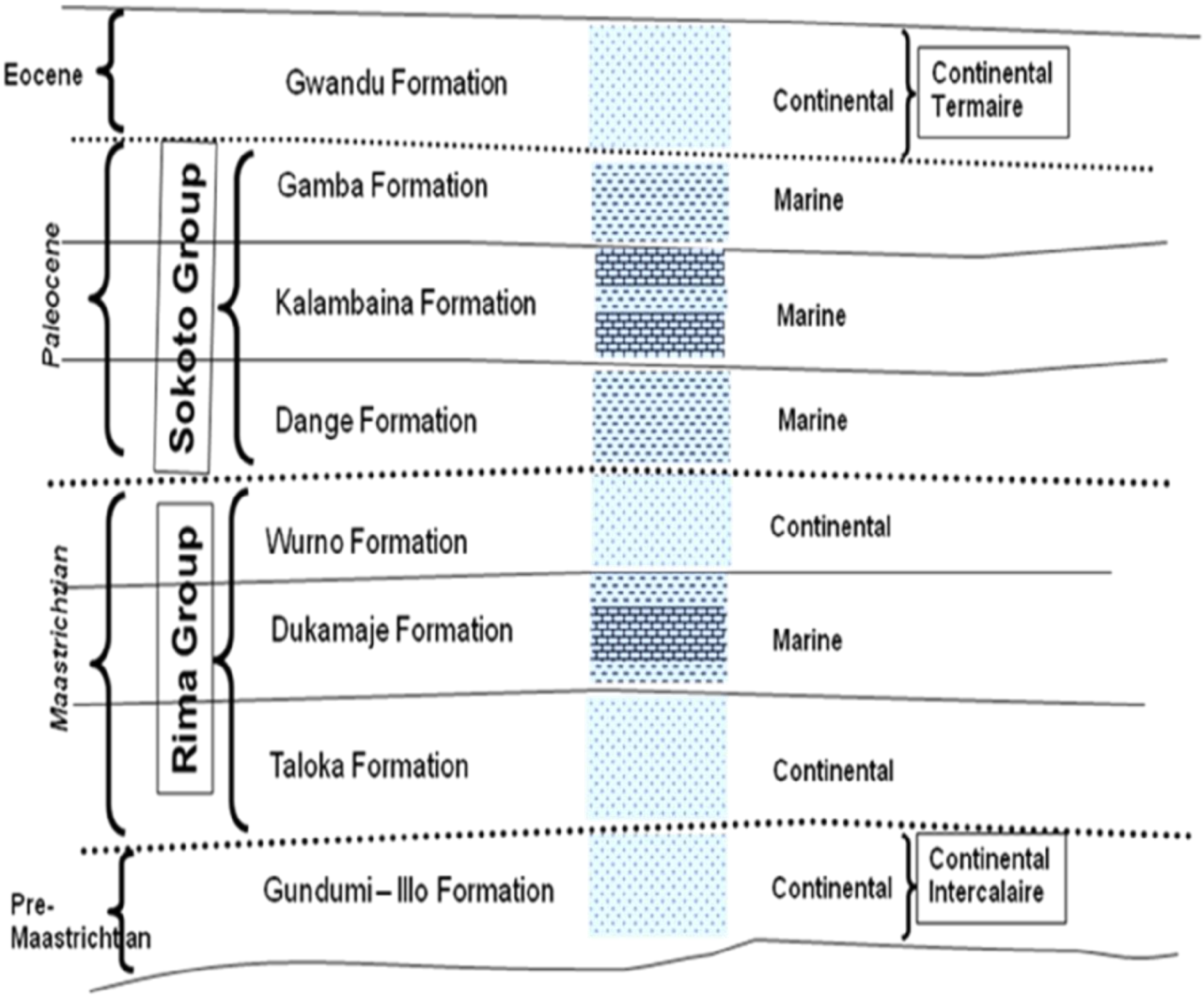


Fig. 3: Stratigraphic successions in the Nigerian sector of lullemmeden Basin (Sokoto Basin) adopted from Obaje et al. [4].

Sample Preparation

All glassware utilized in the experiment underwent thorough washing and rinsing with distilled water. They were then immersed in a chromic acid solution for 24 hours. Subsequently, they were rinsed with deionized water and then, dried in an oven at a temperature of 110 ˚C. Finally, they were placed in desiccators to cool. The samples were subjected to grinding with an agate mortar. The pounded samples were sifted through a

100 µm-size sieve. To avoid cross contamination, the pestle and mortar were cleaned following the grinding of each sample.

Inductively coupled plasma-mass spectrometry (ICP-MS) analysis

The shale samples were subjected to analysis after undergoing a process of digestion utilizing a concentrated tetraoxosulphate (VI) acid and 30% hydrogen peroxide according to Akinlua et al. [38-39]. In order to extract the water soluble salts of metals from the shales, three milliliters of deionized water were added to 2.0 grams of each shale sample and vigorously shaken. Proper separation of the two phases was achieved through centrifugation of the samples. The organic phase (shale) underwent digestion with 3 milliliters of concentrated H_2SO_4 which charred the sample for complete decomposition, followed by the addition of 4 milliliters of 30% hydrogen peroxide for oxidation. The resulting aqueous solution was made up to 10 milliliters with deionized water and was found to be a colourless solution compatible with standard ICP-MS instrumentation. A multi-element standard solution was then prepared from the stock solutions of the elements, which were subsequently diluted with deionized water to prepare each working solution for calibration.

A Perkin Elmer-Sciex Elan 6100 system was used to analyze the digested shale samples using inductively coupled plasma-mass spectrometry technique at the BGI laboratory services, Port-Harcourt, Rivers State, Nigeria. The system was equipped with a quartz spray chamber and a concentric glass nebulizer as the sample introduction system. ICP-MS is a highly efficient technique that allows for the simultaneous determination of multiple trace metals within crude oil samples. The operating conditions of ICP-MS were set to an RF incident power of 1.2 kW, a plasma gas flow rate of 13 L min-1, an auxiliary gas flow rate of 1.4 L min^{-1}, a nebulizer gas pressure of 40 psi, a counting precision of 0.1, a dwell time of 0.05 s, and a sample flow rate of 60µls^{-1}[40].

RESULTS AND DISCUSSION

Seven trace elements and eight rare earth elements were ascertained in the shale samples originating from the Dange and Gamba Formations, located within the Sokoto Basin, Nigeria. The trace elements that were determined encompassed Co, Cr, Cu, Fe, Mn, Ni, and V, while the rare earth elements included Cs, Ga, La, Mo, Rb, Sb, Sc and Zr. The concentrations of both trace and rare earth elements in the shale samples, total trace metals (TTM), and total rare earth elements (ΣREEs) are presented in Tables 1 and 2.

Distribution of trace and rare earth elements

The concentrations of cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), and vanadium (V) in the shales ranged from 14.4–75.6, 3.0–17.3, 0.8–11.3, 350.6–1099.0, 30.1–334.9, 1.5–3.0, and 1.1–25.9 mg/kg, respectively (Table 1). The most abundant trace element in the samples was Fe, which is indicative of siliciclastic facies (Table 1, Fig. 4). Mn was found to be next in abundance to Fe, followed by Co, while Ni was the least detected trace element in the shales. This trend is in agreement with the previous reports on trace metals [41,42]. However, between V and Ni, which are metals of proven relationship with organic materials, V predominated over Ni, contrary to previous reports [41, 42]. The TTM values for the shale samples ranged from 479.9 to 1415.7 mg/kg (Table 1). A comparison among the shale samples using TTM showed that some samples had low trace metal content compared with others due to their thermal maturity [43].

Additionally, the results of the analysis also showed that the concentrations of La, Cs, Ga, Mo, Rb, Sb, Sc, and Zr ranged from 1.7 to 5.0, 0.8 to 1.9, 0.4 to 1.8, 3.0 to 19.0, 0.1 to 8.2, 6.9 to 22.1, 1.5 to 28.5, and 0.8 to 31.1 mg/kg, respectively (Table 1). The total rare earth elements values for the shale samples ranged from 25.3 to 63.7 mg/kg (Table 1). Mo, Sb, and Zr had relatively high concentrations compared to other REE. The relatively high Mo, Sb, and Zr values were probably due to the fact that in the ocean, Mo, Sb, and Zr are oxidized to form insoluble compounds that are preferentially precipitated. The precipitated Mo, Sb, and Zr were probably incorporated into the organic matter from which the shales were formed, especially during the processes that took place at the water–sediment interface. The low REE contents of these shales is in agreement with the fact that geological samples with significant terrestrial input usually have low metal contents [43], of which Sokoto Basin shale is a good example [44].

Table 1: Concentrations of trace and rare earth elements in the shale samples from Sokoto Basin.

Sample	Concentration (Mg/Kg)														
	Co	Cs	Cu	Fe	Ga	La	Mn	Cr	Mo	Ni	Rb	Sb	Sc	V	Zr
DG 01	14.4	0.8	7.3	350.6	0.4	1.7	36.4	6.7	19	1.5	0.4	17.7	1.5	1.1	22.2
DG 02	20	1.9	11.3	374.7	0.7	2.3	35.4	10.1	10.1	1.6	1.5	7.8	1.6	9	10.7
DG 03	35.6	1.5	10.7	356.9	0.7	2.5	30.1	3.6	3.6	1.7	0.03	9.2	1.7	10.1	12
DG 04	33.3	1.7	3.2	372.8	0.5	2.7	68.2	3.7	3.7	1.9	0.2	6.9	2	7.7	9.1
DG 05	44.4	1.6	3.3	477.3	0.8	3	200.2	10.2	10.2	1.9	0.2	7.6	1.6	4.8	14.7
DG 06	38.9	1.4	6.7	690.7	1.2	3.1	167	7.2	7.2	1.9	0	9.7	1.7	5.3	12.2
DG 07	34.4	1.5	2.9	532.4	1.7	1	268	3.5	3.5	2.1	1.1	14.6	1.9	4.4	17
DG 08	53.3	1.6	2.7	362	0.8	3.5	302.2	7	7	2.2	0.2	15.3	2	1.4	28.5
DG 09	41.1	1.7	6.2	448.3	0.5	3.5	334.9	3.6	3.6	2.2	0	8.4	2	1.3	5.6
DG 10	43.3	1.7	6.8	351.2	1.7	3.1	167.6	3.7	3.7	2.3	0.1	16	2.3	8.7	2.8
DG 11	48.9	1.7	7.5	702.5	1	2.1	234.7	13.5	13.5	2.2	0.1	11.5	2.6	10.2	7.9
DG 12	56.7	1.7	2.6	589.4	0.9	3	136.6	7	7	2.2	0.2	16.5	2.3	10.7	12.2
DG 13	54.4	1.7	2.9	509	1.1	3.6	201.8	13.7	13.7	2.6	0	14.9	2.3	8.6	4
DG 14	55.6	1.6	3.5	680.6	1.2	3.6	100.3	10.3	10.3	2.2	0.4	22.1	2.7	5.2	2.9
DG 15	64.4	1.8	2.2	844.9	0.6	3.7	134.5	3.8	3.8	2.4	0.1	17.9	2.8	13.1	0.8
GB 01	60	1.7	1.8	725.5	0.7	3.8	300.3	3.7	3.7	2	0.4	14.9	2.9	15.5	18
GB 02	55.6	1.6	3	1099	0.6	3.9	201.6	7.1	7.1	2.5	0.3	15.2	3	5.7	9.5
GB 03	66.7	1.8	3.4	963.6	0.6	4.4	67	3.3	3.3	2.5	0.2	14.5	2.9	2.3	1.7
GB 04	54.4	1.7	7.7	1018	0.9	3.6	135.8	4.3	4.3	2.5	0.2	11.3	28.5	3.8	4.7
GB 05	75.6	1.6	3.2	735.1	0.8	5	170.1	3.1	3.1	2.5	0.9	18	3.8	25.9	29.7
GB 06	57.8	1.8	2.6	675.5	0.9	4.1	135.4	3.8	3.8	2.7	2	14.8	3	10	25.2
GB 07	46.3	1.7	0.8	668.9	0.9	3.5	202.4	4	4	2.5	0.8	15.5	3.3	10.5	31.1
GB 08	74.4	1.7	0.9	836.4	0.8	3.4	101.7	4.2	4.2	2.4	0.4	14.8	3.3	8.4	2.2
GB 09	53.3	1.7	3	357.6	0.7	2.3	134.7	13.8	13.8	2.7	0.2	11.5	3.2	10.3	0.8
GB 10	35.6	1.3	3.1	680.8	0.6	1	34.2	17.3	17.3	2.5	1.2	15	3.6	10.2	1.1
GB 11	63.3	1.4	1.3	479.3	1.8	5	68	13.8	13.8	2.8	2.8	11.2	3.4	10.5	2.2
GB 12	58.9	1.5	1	543.5	1.6	4.7	67.3	10.2	10.2	2.7	0.7	11.1	3.5	10.4	12.4
GB 13	32.2	1.5	2.7	545.6	1.4	4.7	101.1	4.3	4.3	2.7	1.4	17.9	3.9	6	14.3
GB 14	70	1.5	4.2	677.2	1.3	3.1	133.4	3.3	3.3	3	1.5	18.5	3.6	8.7	7.8
GB 15	64.4	1.5	4	546.4	1.8	3.6	101	3	3	2.8	8.2	14.8	4	9.4	1.4

Table 2: Geochemical parameters calculated from the concentrations of trace and rare earth elements in the shale samples from Sokoto Basin

Sample	TTM (mk/kg)	V/Ni	V/(Ni + V)	Ni/Co	Ni/Mo	Zr/Cr	La/Sc	La/Co	V/Fe	V/Cr	ΣREEs
DG 01	481.7	0.7	0.4	0.1	0.1	3.3	1.1	0.1	0.003	0.2	63.7
DG 02	498.7	5.6	0.8	0.1	0.2	1.1	1.4	0.1	0.024	0.9	36.6
DG 03	479.93	5.9	0.9	0.02	0.5	3.3	1.5	0.1	0.028	2.8	31.23
DG 04	517.6	4.1	0.8	0.1	0.5	2.5	1.4	0.1	0.021	2.1	26.8
DG 05	781.8	2.5	0.7	0.01	0.2	1.4	1.9	0.1	0.010	0.5	39.7
DG 06	954.2	2.8	0.7	0.02	0.3	1.7	1.8	0.1	0.008	0.7	36.5
DG 07	890	2.1	0.7	0.1	0.6	4.9	0.5	0.0	0.008	1.3	42.3
DG 08	789.7	0.6	0.4	0.03	0.3	4.1	1.8	0.1	0.004	0.2	58.9
DG 09	862.9	0.6	0.4	0.1	0.6	1.6	1.8	0.1	0.003	0.4	25.3
DG 10	615	3.8	0.8	0.1	0.6	0.8	1.3	0.1	0.025	2.4	31.4
DG 11	1059.9	4.6	0.8	0.03	0.2	0.6	0.8	0.0	0.015	0.8	40.4
DG 12	849	4.9	0.8	0.02	0.3	1.7	1.3	0.1	0.018	1.5	43.8
DG 13	834.3	3.3	0.8	0.04	0.2	0.3	1.6	0.1	0.017	0.6	41.3
DG 14	902.5	2.4	0.7	0.01	0.2	0.3	1.3	0.1	0.008	0.5	44.8
DG 15	1096.8	5.5	0.8	0.01	0.6	0.2	1.3	0.1	0.016	3.4	31.5
GB 01	1154.9	7.8	0.9	0.04	0.5	4.9	1.3	0.1	0.021	4.2	46.1
GB 02	1415.7	2.3	0.7	0.02	0.4	1.3	1.3	0.1	0.005	0.8	41.2
GB 03	1138.2	0.9	0.5	0.03	0.8	0.5	1.5	0.1	0.002	0.7	29.4
GB 04	1281.7	1.5	0.6	0.02	0.6	1.1	0.1	0.1	0.004	0.9	55.2
GB 05	1078.4	10.4	0.9	0.03	0.8	9.6	1.3	0.1	0.035	8.4	62.9
GB 06	943.4	3.7	0.8	0.04	0.7	6.6	1.4	0.1	0.015	2.6	55.6
GB 07	996.2	4.2	0.8	0.1	0.6	7.8	1.1	0.1	0.016	2.6	60.8
GB 08	1059.2	3.5	0.8	0.01	0.6	0.5	1.0	0.0	0.010	2.0	30.8
GB 09	609.6	3.8	0.8	0.1	0.2	0.1	0.7	0.0	0.029	0.7	34.2
GB 10	824.8	4.1	0.8	0.1	0.1	0.1	0.3	0.0	0.015	0.6	41.1
GB 11	680.6	3.8	0.8	0.02	0.2	0.2	1.5	0.1	0.022	0.8	41.6
GB 12	739.7	3.9	0.8	0.04	0.3	1.2	1.3	0.1	0.019	1.0	45.7
GB 13	744	2.2	0.7	0.1	0.6	3.3	1.2	0.1	0.011	1.4	49.4
GB 14	940.4	2.9	0.7	0.03	0.9	2.4	0.9	0.0	0.013	2.6	40.6
GB 15	769.3	3.4	0.8	0.02	0.9	0.5	0.9	0.1	0.017	3.1	38.3

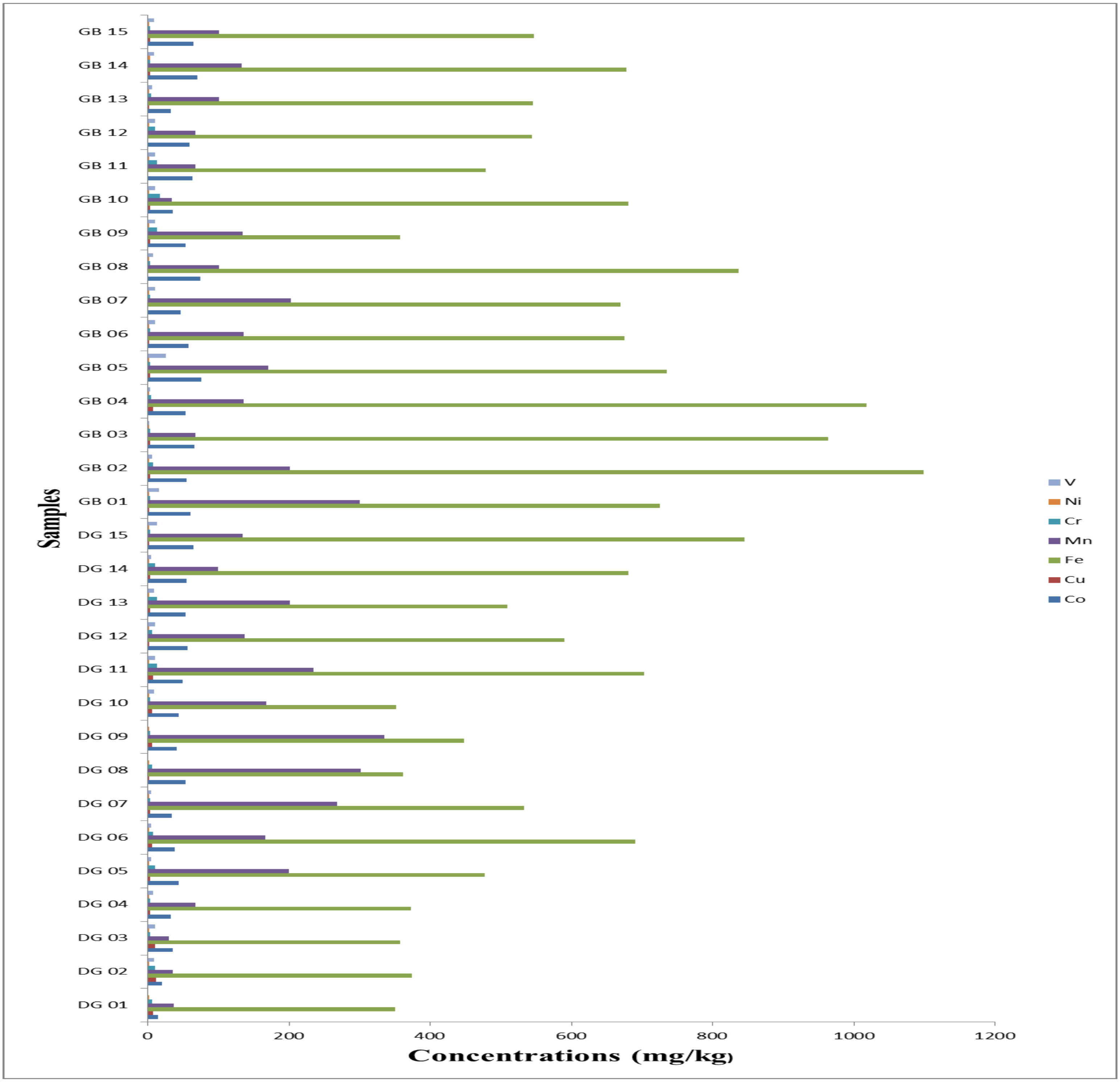


Fig. 4: A plot of the concentrations of the trace metals versus samples

Origin of organic matter

The origin of the shale samples was assessed through the utilization of various parameters computed from the trace and rare earth element values (Table 2). The TTM present in the shales ranged from 479.9–1415.7 mg/kg (Table 2). Typically, the contents of trace elements are relatively elevated, which is indicative of shales primarily formed from marine organic matter [45-46]. Several investigations [39,43,46-48] have indicated that source rocks containing sapropelic organic matter typically exhibit a greater abundance of V and Ni than those comprising humic or humic/sapropelic content. Oils of marine origin frequently possess a V/Ni ratio greater than 1, while those of terrestrial origin have a V/Ni ratio less than 1. In the current study, the V/Ni values ranged from 0.6 to 10.9 (Table 2), which suggests that the shales were formed through a mixed input of marine and terrigenous organic matter. Nevertheless, the high V/Ni values noted for the majority of the samples suggest a greater contribution from marine organic matter relative to terrestrial [39,43,45,47-48]. The cross plot of V vs Ni (Fig. 5) clearly illustrates that the shale samples were formed through a mixed origin and supports the notion that the shale samples were predominantly formed from marine organic matter with a low contribution from terrigenous organic matter [45]. The ternary plot of V, Ni, and Co also corroborates that the shale samples have received similar source facies (Fig. 6).

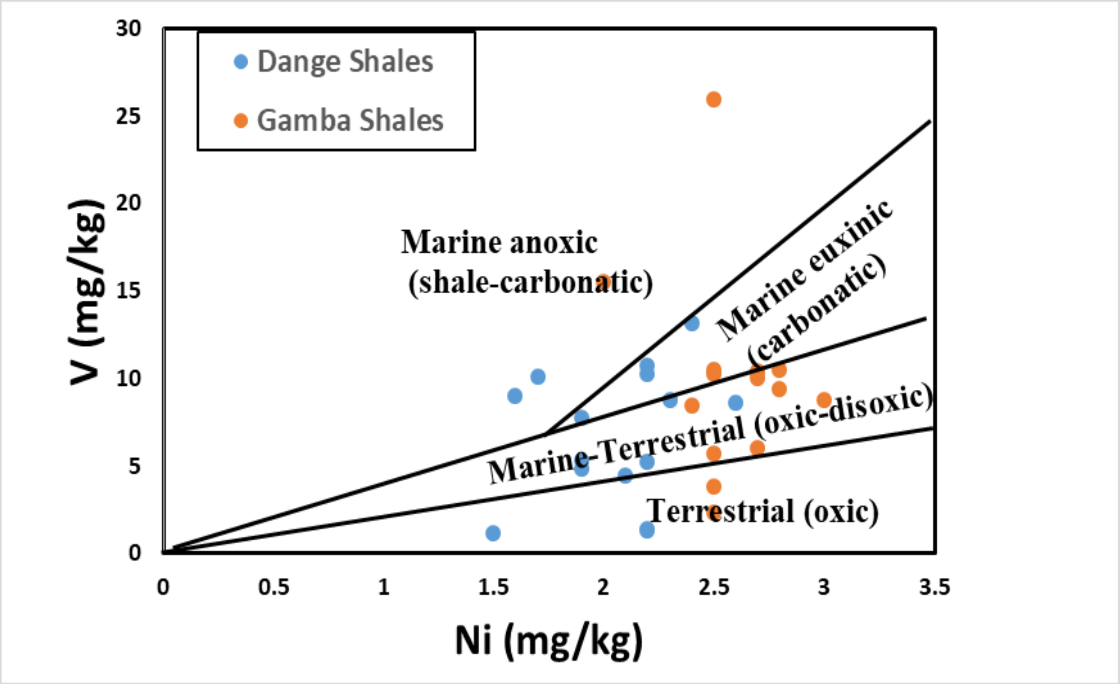


Fig. 5: Cross plots of V and Ni concentration values in the shale samples from Sokoto Basin (after Galarraga et al. [45]).

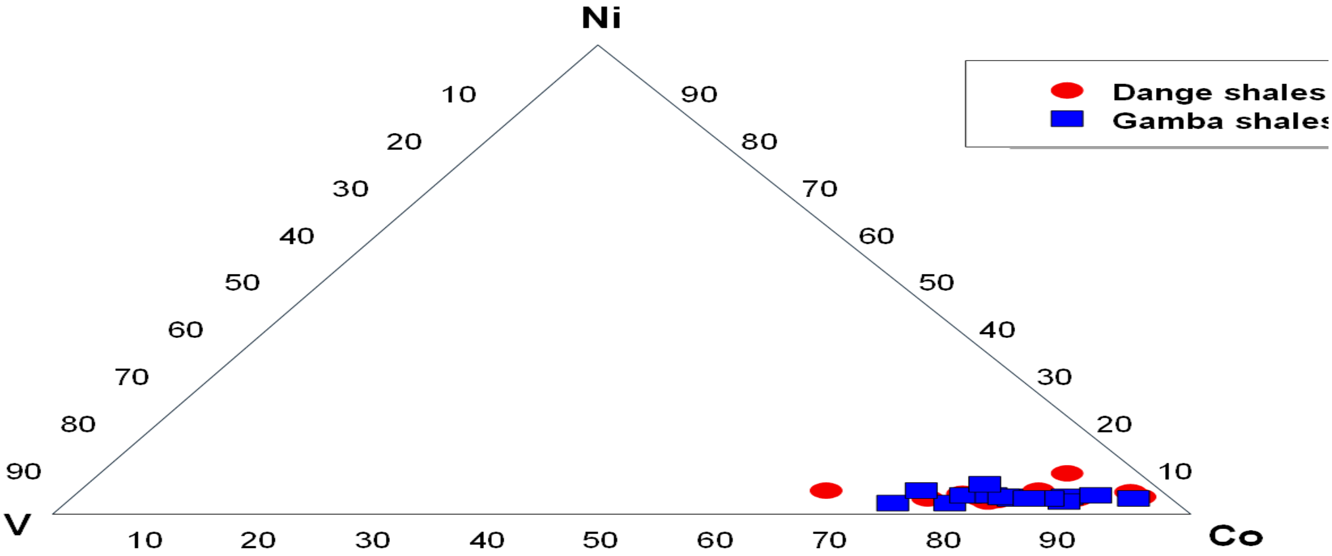


Fig. 6: Ternary plot of Ni, V, and Co in the shale samples from Sokoto Basin.

Depositional environments

The evaluation of depositional environments of shales is based on the distribution, abundance, and geochemical ratios calculated from the elements. The preferential preservation of Ni and V in organic matter is dependent on the specific depositional conditions of said organic matter. V contents exhibit higher values relative to Ni under anoxic conditions, while Ni predominates over V in oxic sedimentary conditions, as indicated by Galarraga et al. [45] and Akinyemi et al. [46].

In the present study, V prevails over Ni (Table 1), indicating the anoxic sedimentary condition of the organic matter from which the shales were derived. The redox sensitive elemental ratios that are generally considered for evaluation include V/Fe, V/Ni, V/(V + Ni), Ni/Co, and Ni/Mo [42,45,49-51]. The V/Ni and V/(V + Ni) ratios are widely used in hydrocarbon-source correlations as they exhibit significant variation between different sedimentary settings and are generally not influenced by reservoir mineralogy or fluid migration [49,52]. Prior research has shown that bitumen derived from source rocks deposited in reducing environments has a V/Ni ratio of > 3.0 [47,51,53-54]. Furthermore, the V/(V + Ni) ratio, as per Hatch and Leventhal [55], values > 0.84, 0.54–0.82, and 0.46–0.60, respectively, suggest euxinic, anoxic, and dysoxic conditions. In the present study, the V/Ni and V/(V + Ni) values vary from 0.6 to 10.9 mg/kg and 0.4 to 0.9 mg/kg, respectively, as presented in Table 2. Therefore, both parameters (i.e., V/Ni and V/(V + Ni)) indicate that the majority of the analyzed shales were formed under reducing conditions (euxinic to anoxic depositional environments; Table 2). Prior studies have suggested that a cross plot of Ni versus V concentrations (Fig. 5) could facilitate the determination of the paleo-depositional environment [45,47,50,51,53]. The bulk of the shales are positioned within the marine zones (Fig. 5), except for a few samples that fall in the terrestrial (oxic) zone. Consequently, the shales were primarily derived from marine organic matter that was deposited in an anoxic environment. The cross plot of V/(V + Ni) versus V/Fe (Fig. 7) shows a tendency of correlation, implying that V/Fe ratio can be utilized to infer depositional environments in Sokoto Basin.

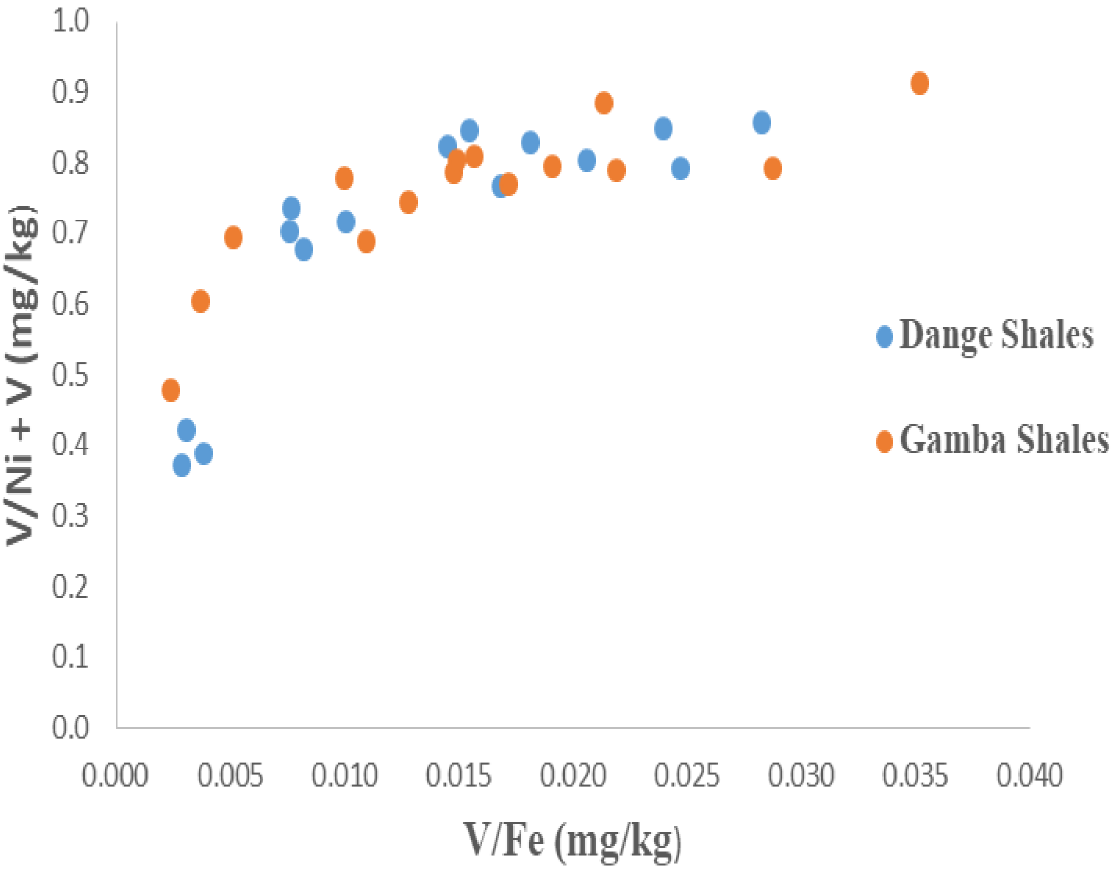
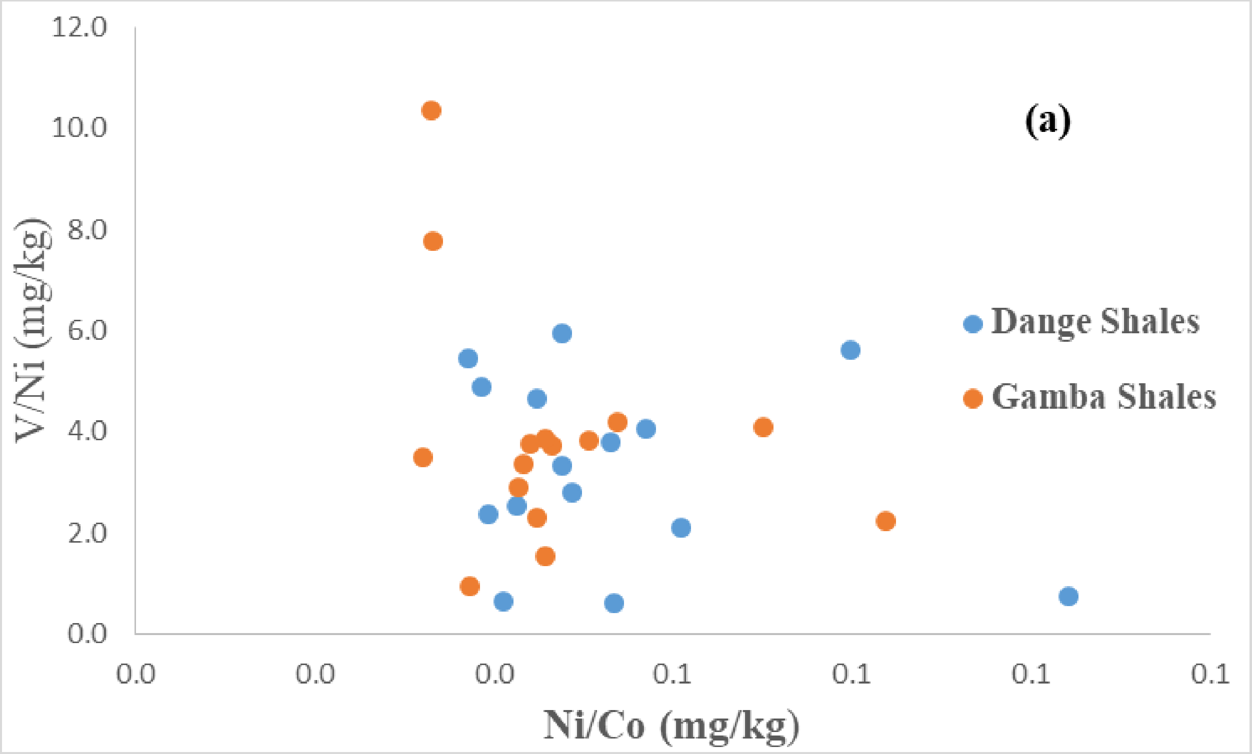


Fig. 7: Cross plot showing relationship between V/Ni+V and V/Fe in the shales from Sokoto Basin

The Ni/Co ratio of organic matter is a widely accepted indicator of the depositional environment of source rocks. To illustrate, Jones and Manning [56] and Shi et al. [51] conducted a comparison of Ni/Co ratios and the degree of pyritization (DOP) of shales, leading to the proposal that Ni/Co ratios of > 7.0, 5.0–7.0, and < 5.0 correspond to anoxic, dysoxic, and oxic environments, respectively. In the present study, the Ni/Co ratios of the shales ranged from 0.03 to 0.10, which is indicative of an oxic depositional environment, as demonstrated in Table 2. Additionally, the Ni/Mo ratio is a useful means of inferring the depositional environment of the source rocks. This is broadly consistent with the insights received from V/Ni and V/(V + Ni) ratios, which suggest that the shales received minimal contributions from the terrestrial organic matter. Akinlua et al. [50] have demonstrated that the smaller the Ni/Mo ratio, the greater the proportion of marine components in the organic matter. The Ni/Mo values in the present study ranged from 0.1 to 0.9 (Table 2), indicating a significant contribution of marine organic matter. This finding is generally consistent with the V/Ni and V/(V + Ni) ratios. Furthermore, the cross plots of Ni/Co versus V/Ni and Ni/Mo (Fig. 8) suggest that the shales have received comparable inputs of organic matter.

Provenance sensitive parameters

The evaluation of shale provenance was carried out by computing the ratios of some rare earth elements present in the shale samples. The chemical characteristics of the source rocks can be inferred from the Zr/Cr, La/Sc, and La/Co ratios, and these ratios are believed to be preserved in the expelled hydrocarbons. A Zr/Cr value exceeding 2.0 indicates that the source rock has a felsic origin, whereas a value less than 1.0 signifies that the source rock is of mafic origin [51,57]. Similarly, a La/Sc value ranging from 2.5 to 16.3 indicates a felsic source rock, while a value ranging from 0.43 to 0.86 indicates a mafic source rock [51,58]. The La/Co value can also be used to determine the origin of the source rocks, with values ranging from 1.8 to 13.8 indicating a felsic source rock and values ranging from 0.14 to 0.38 indicating a mafic source rock [51,58]. In the present study, the Zr/Cr, La/Sc, and La/Co values recorded in the shale samples were in the range of 0.1 to 9.6, 0.1 to 1.9, and 0.03 to 0.10, respectively (Table 2), indicating that the provenance of the shales is a mixture of felsic and mafic sources. This finding further confirms that the shale samples were formed from a mixed origin, with a significant contribution from marine organic matter in relation to terrestrial matter. The evidence presented in Figure 9 also supports the conclusion that the shale samples were formed from a mixed origin.



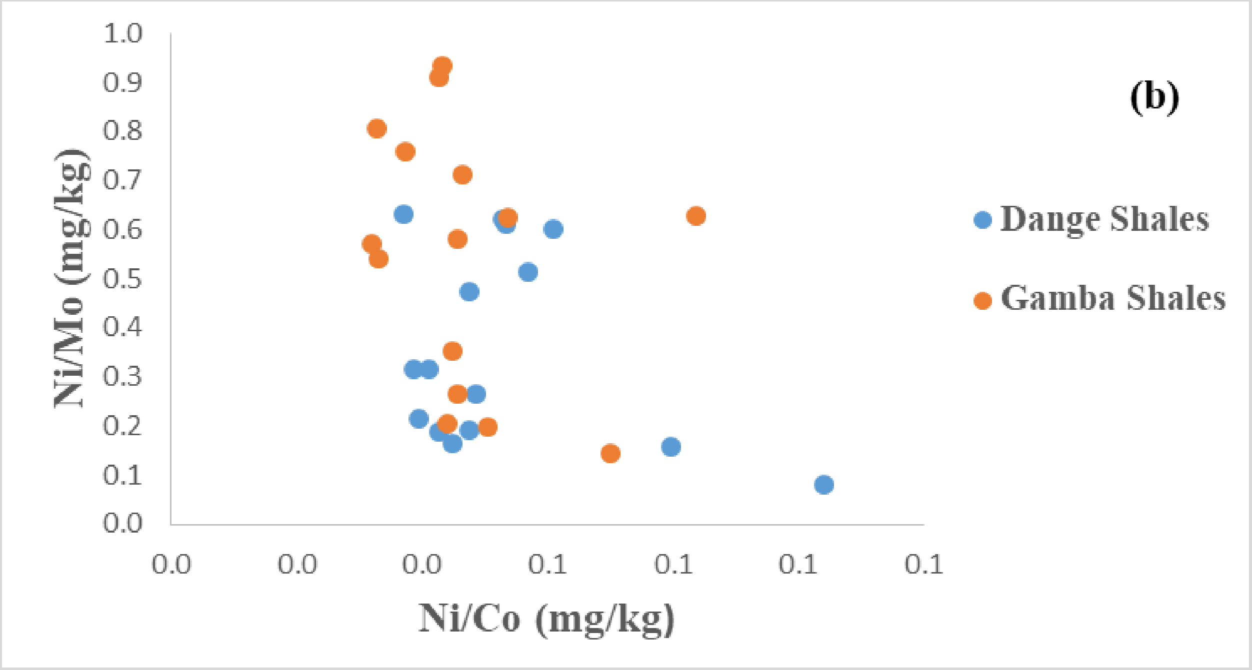


Fig. 8: Cross plots of Ni/Co versus (a) Ni/V and (b) Ni/Mo in the shales from Sokoto Basin.

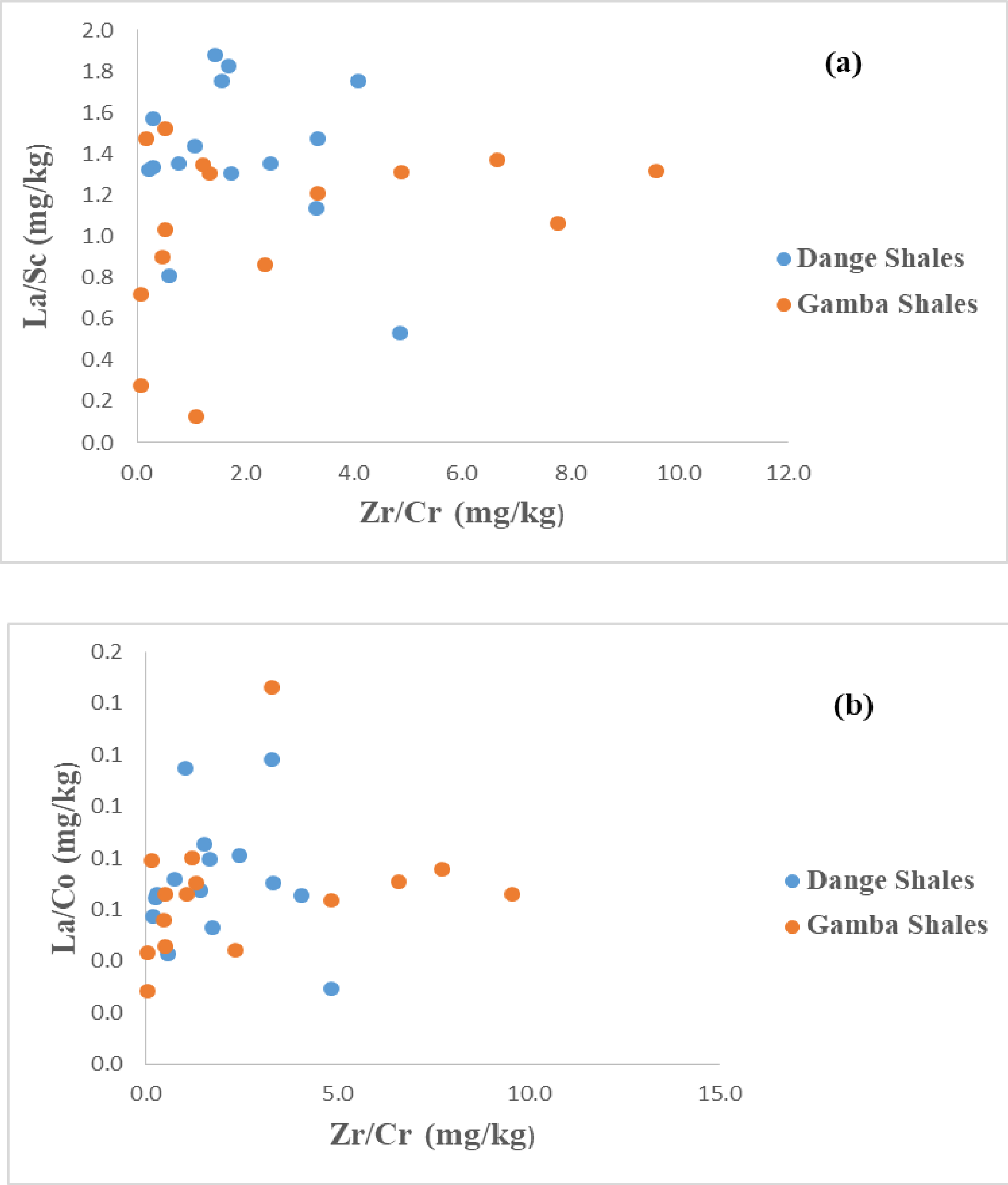


Fig. 9: Cross plots of Zr/Cr versus (a) La/Sc and (b) La/Co in the shales from Sokoto Basin.

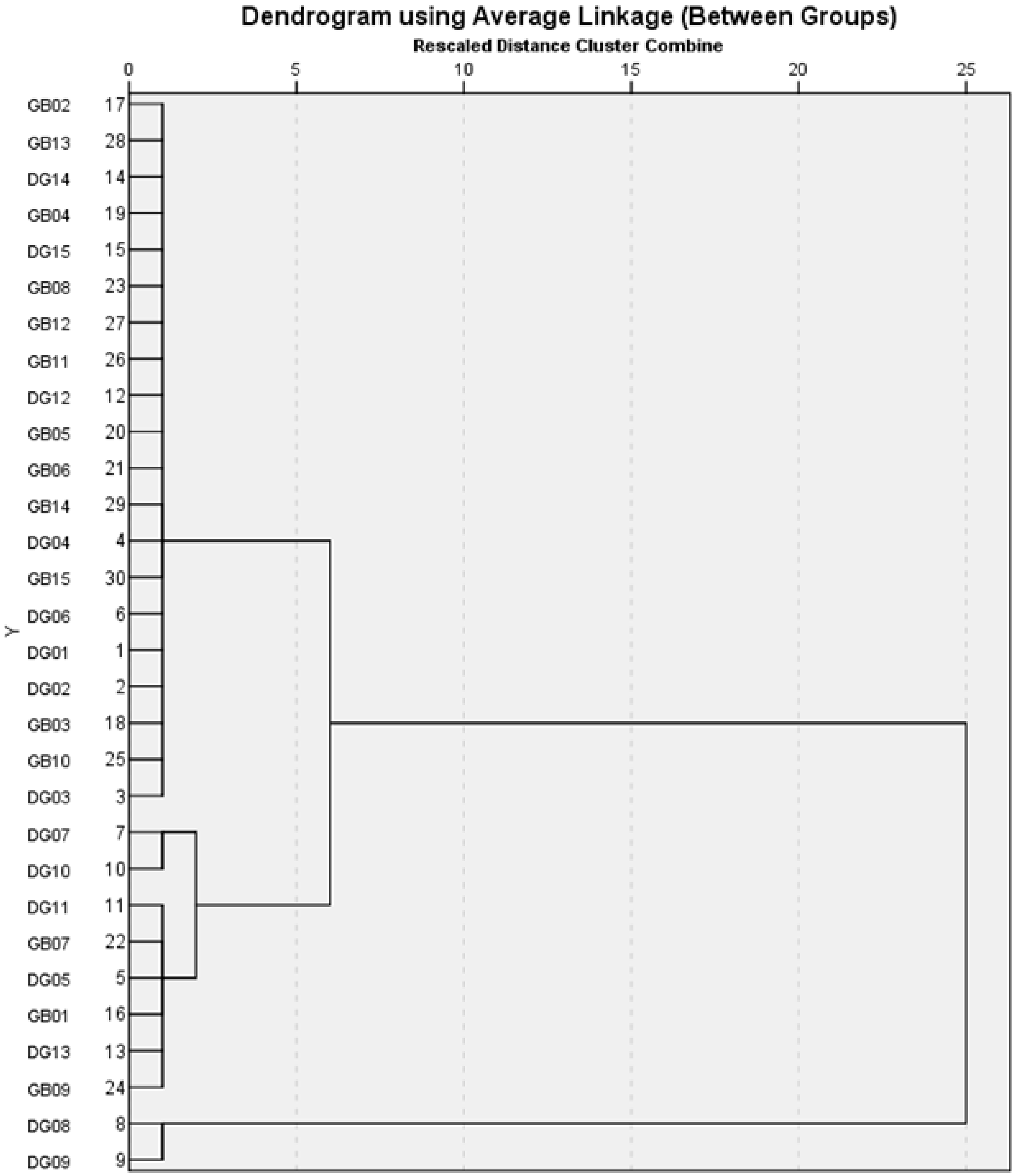


Fig. 10: Dendrogram cluster analysis of the shale samples from Sokoto Basin using biophile elements (Co, Ni, and V) as variables.

Hierarchical Cluster Analysis

A cluster analysis was performed on the trace and rare earth elements data in a statistical evaluation. When studying the origin of geological samples, cluster analysis of element abundances based on Pearson correlation is widely utilized [38,51]. The dendrogram cluster analysis of the shale samples utilizing the biogenic elements (i.e. elements of proven association with organic matter), Co, Ni and V as variables, indicated no significant variations among shale samples from Dange and Gamba Formations (Fig. 10). However, the dendrogram subtly indicates the existence of three classes of shales in Dange and Gamba Formations. Most samples clustered together in Class II, implying that the shale samples studied are almost derived from the same source. Class I consists of eleven (11) samples while Class III consists of five samples (5) samples. This inference supports the results obtained from the experimental data, which means the discrimination obtained from the cluster analysis was based on source facies.

CONCLUSION

The current study has examined the elemental geochemistry of the late Paleocene shales from Sokoto Basin, Nigeria, in relation to source facies, depositional conditions, and provenance. The samples were subjected to analysis using Inductively Coupled Plasma-Mass Spectrometry. The trace elements, including Co, Cr, Cu, Fe, Mn, Ni, and V, were determined, while the rare earth elements included Cs, Ga, La, Mo, Rb, Sb, Sc, and Zr. These samples indicated that Fe was the most abundant trace element, which is an indication of siliciclastic facies. Mn was the second most abundant element, followed by Co. Conversely, Ni was the least detected trace element in the shales. The trace elements contents were relatively high, an indication of shales that were predominantly formed from marine organic matter. Among the rare earth elements (REEs) detected, Mo, Sb, and Zr had relatively high concentrations compared to other REEs. The relatively high Mo, Sb, and Zr values were due to the fact that, in the ocean, Mo, Sb, and Zr were oxidized to form insoluble compounds and are preferentially precipitated. The precipitated Mo, Sb, and Zr were probably incorporated into the organic matter from which the shales were formed, especially during the processes that took place at the water–sediment interface. The concentrations of the elements were found to be influenced by source and depositional facies. Various geochemical parameters computed from the elements suggested that the shales were formed from the mixed input of marine and terrestrial organic matter with the major contribution from marine organic matter under anoxic to sub-oxic conditions. This results of this study have indicated that the variations in the abundance and distribution of elements were effective in determining the source facies, depositional conditions, and provenance of the shales from Sokoto Basin, NW Nigeria.

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