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Preliminary Study of Chemical Elements Distribution in Petroleum Source Rocks Donga and Yogou Formations of the Termit Sedimentary Basin (Est-Niger)

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Abstract

XRF and EDX analyses were carried out on 18 batches of representative raw samples to determine the distribution of major chemical elements in the petroleum source rocks of Donga and Yogou formations of Termit sedimentary basin. The chemical composition of these formations is dominated by silicon (Si), aluminum (Al) and iron (Fe). This is consistent with the oxide composition, which is also dominated by silicon oxide (SiO_2), aluminum oxide (Al_2O_3) and iron monoxide (FeO). No less important chemical elements are calcium (Ca), potassium (K), sulfur (S), titanium (Ti), magnesium (Mg), manganese (Mn) and barium (Ba), as well as some of their oxides. All these major chemical elements are carried by silicate detrital minerals associated with pyrite and goethite and/or clay minerals such as kaolinite and interstratified illite, smectite and chlorite. This trend is illustrated by the values of the Si/Al and SiO_2/Al_2O_3 ratios.

Keywords

Distribution, Major Elements, Source Rocks, Donga Formation, Yogou Formation, Termit Basin

1. Introduction

The distribution of chemical elements in the lithosphere is linked to the geological processes (magmatism, metamorphism, hydrothermalism and sedimentary processes) that led to the formation of the rocks and minerals that are their essential constituents. The combined effects of these geological processes govern the systematic distribution in various geological environments or natural systems [1]. Thus, the relative abundance of chemical elements proposed by chemists and mineralogists, in particular [1] [2], reflects the geochemical processes occurring within or at the earth's surface. These geochemical processes allow chemical elements to be a useful geochemical tracer [2] [3] [4] [5] [6]. The coexistence of these chemical elements in terrestrial materials (rocks and minerals) results from certain affinities between these elements [7] [8]. In the case of petroleum sedimentary rocks such as those of Donga and Yogou (Termit Basin, Niger), these affinities often reflect the conditions under which the rocks were formed: transport, deposition and diagenesis [9] [10] [11] [12] [13]. Petroleum source rocks in the Donga and Yogou formations have been subjected to a summary mineralogical characterization [14], but without addressing the way in which chemical elements are distributed.

2. Materials and Methods

2.1. Samples Analyzed

The samples analyzed were those of petroleum source rocks from the Donga and Yogou formations of the Termit sedimentary basin (**Figure 1**). They were collected in collaboration with the Centre de Documentation et d'Archives Pétrolières du Niger (CDP). They include cuttings from the Koulélé-1D, Fana-1, Helit-1, Melek-1 and Ounissoui-E1 wells (**Figure 1**).

Sampling was carried out with a 10-meter sampling step.

2.2. Methods

Rock cuttings samples were washed to remove drilling mud. X-ray fluorescence (XRF) analysis and scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS) were applied to determine the composition of major chemical elements in these samples.

XRF was performed using a portable Niton XL3t® XRF spectrometer, coupled with a computer to ensure data transfer after analysis using Niton Data Transfer (NDT) software. Measurements in All-Geo mode were carried out on an accessory fitted with a Radio Frequency Identification (RFID) chip, enabling the analyzer to detect it automatically and convert it into a benchtop analyzer. Scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS) were used to study the crystalline form of minerals using digital images, and to determine the major chemical elements and oxide composition of the samples analyzed.

The tool used is a D.C.A.R. Variable Pressure SEM/EDS (MEB FEG Supra 40 VP Zeiss), equipped with an X-ray detector (OXFORD Instruments X-Max 20) connected to an EDS microanalyzer platform (Inca Dry Cool, without liquid nitrogen).

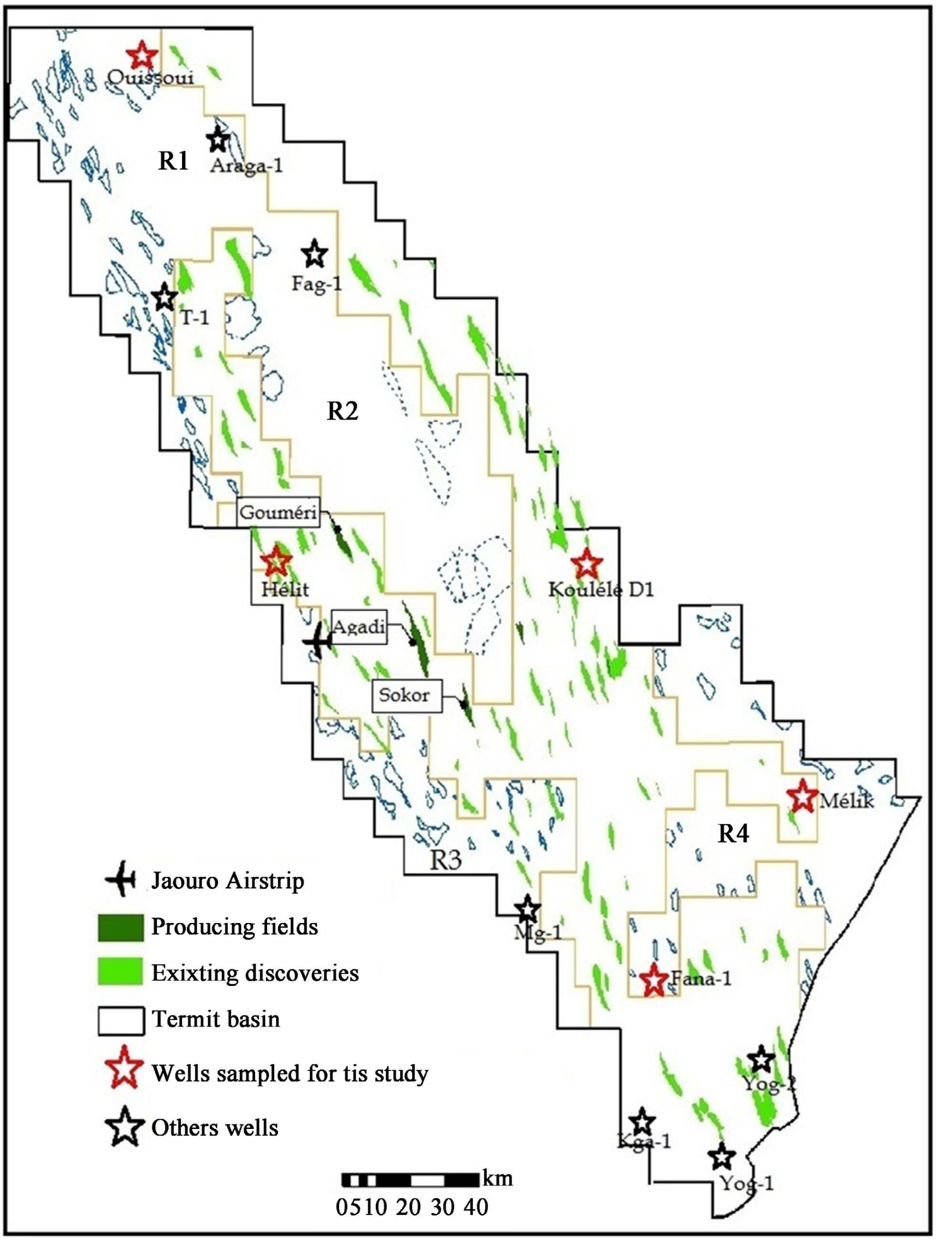


Figure 1. Map location of sampled wells in Termit basin (modified from [15]).

3. Results

3.1. Chemical Composition of the Donga Formation

The results of the distribution of major chemical elements in the Donga formation are shown in Table 1. They include silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), potassium (K), sulfur (S), titanium (Ti), magnesium (Mg), manganese (Mn) and barium (Ba).

Elements Mg, Mn and Ba have very low proportions, averaging no more than 0.5% (Table 1). The elements K, S and Ti have low average proportions of 3.99%, 2.65% and 2.07% respectively. Ca has a relatively low average value of 5.37%, with the highest value in sample PO.E2.Dg (13.82%).

Table 1. Elemental composition of major chemical elements in the Donga formation.

Samples \ Elements	Si	Al	Fe	Ca	K	S	Ti	Mg	Mn	Ba	Si/Al
PM.E6.Dg	47.85	17.96	18.7	4.28	3.7	4.92	1.34	0	0.37	0.21	2.66
PH.E7.Dg	51.88	18.06	17.53	1.57	6.03	2	2.21	0.18	0.12	0.28	2.87
PK.E22.Dg	56.77	15.12	12.26	7.9	3.74	2.27	0.77	0.17	0.54	0.08	3.76
PF.E20.Dg	47.55	17.69	20.09	4.31	3.85	2.26	3.48	0.1	0.27	0.23	2.69
PK.E20.Dg	47.96	19.81	19.85	2.18	3.88	2.99	2.37	0.4	0.32	0.15	2.42
PF.E21.Dg	47.7	22.03	18.05	3.55	3.35	2.1	2.57	0.22	0.25	0.08	2.16
PO.E2.Dg	46.72	13.87	15.65	13.82	3.36	2	1.72	1.81	0.3	0.11	3.37
Average Dg	49.49	17.79	17.45	5.37	3.99	2.65	2.07	0.41	0.31	0.16	2.85

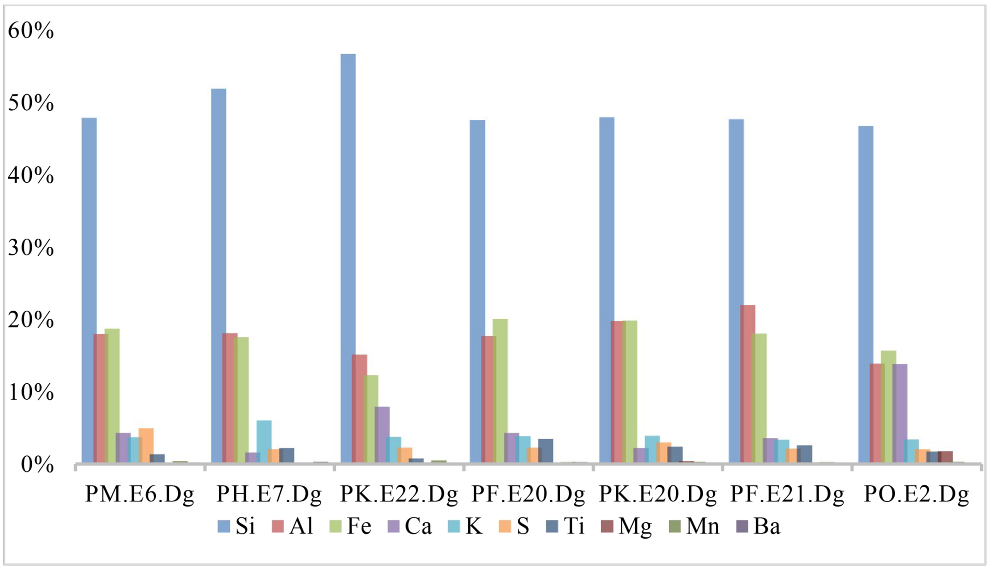


Figure 2. Proportions of major chemical elements in Donga Formation rocks.

Figure 2 shows the histogram of the different proportions of major chemical elements in the Donga formation. The Donga formation is relatively rich in silicon, aluminum and iron (Figure 2), with average proportions of 49.49%, 17.79% and 17.45% respectively. The highest proportions of these elements are found in samples PK.E22.Dg (56.77%), PF.E21.Dg (22.03%) and PF.E20.Dg (20.09%) respectively.

3.2. Chemical Composition of the Yogou Formation

The major chemical elements present in the Yogou formation are listed in Table 2. They are composed of silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), potassium (K), sulfur (S), titanium (Ti), magnesium (Mg), manganese (Mn) and barium (Ba).

The elements Si, Al and Fe (Table 2) are the most abundant in the Yogou formation. Their average proportions are 57.77%, 16.17% and 15.57% respectively. The highest proportions of these chemical elements are found in samples PF.E11.Yg (63.29%), PK.E26.Yg (17.52%) and PK.E26.Yg (19.29%) respectively.

Elements Ca, K, S and Ti have low proportions, averaging 1.82%, 3.57%, 1.81% and 2.42% respectively. The element K has the highest value in sample PH.E42.Yg (5.02%). The other three chemical elements, Mg, Mn and Ba, are in very low proportions, averaging no more than 0.7% (Table 2).

Figure 3 shows the histogram of the different proportions of major elements in the Yogou formation. Figure 3 shows that silicon is the most abundant chemical element in the Yogou formation.

3.3. Si/Al Chemical Element Ratios in the Donga and Yogou Formations

The Si/Al ratios presented in Table 1 and Table 2 range from 2.16 to 3.76, with an average of 2.80 for the Donga samples, and from 3.01 to 4.09, with an average

Table 2. Elemental composition of major chemical elements in the Yogou formation.

Elements / Samples	Si	Al	Fe	Ca	K	S	Ti	Mg	Mn	Ba	Si/Al
PK.E25.Yg	53.66	16.27	18.08	2.3	2.85	2.96	1.96	1.31	0.32	0.04	3.3
PH.E42.Yg	61.31	15.27	13.3	1.31	5.02	0.91	1.89	0.5	0.09	0.19	4.03
PM.E1.Yg	55.77	16.8	16.26	1.98	3.34	1.73	3.14	0.44	0.12	0.02	3.32
PF.E11.Yg	62.49	15.28	12.04	1.15	3.31	1.08	2.6	1.33	0.05	0.13	4.09
PM.E2.Yg	54.81	15.49	18.32	2.16	3.63	1.65	2.91	0.29	0.14	0.16	3.54
PF.E10.Yg	63.29	16.32	11.69	1.41	2.97	1.09	2.31	0.22	0.11	0.19	3.88
PK.E26.Yg	52.73	17.52	16.87	2.46	3.84	3.22	2.11	0.33	0.39	0.22	3.01
Average Yg	57.29	16.14	15.57	1.82	3.57	1.81	2.42	0.63	0.17	0.14	3.60

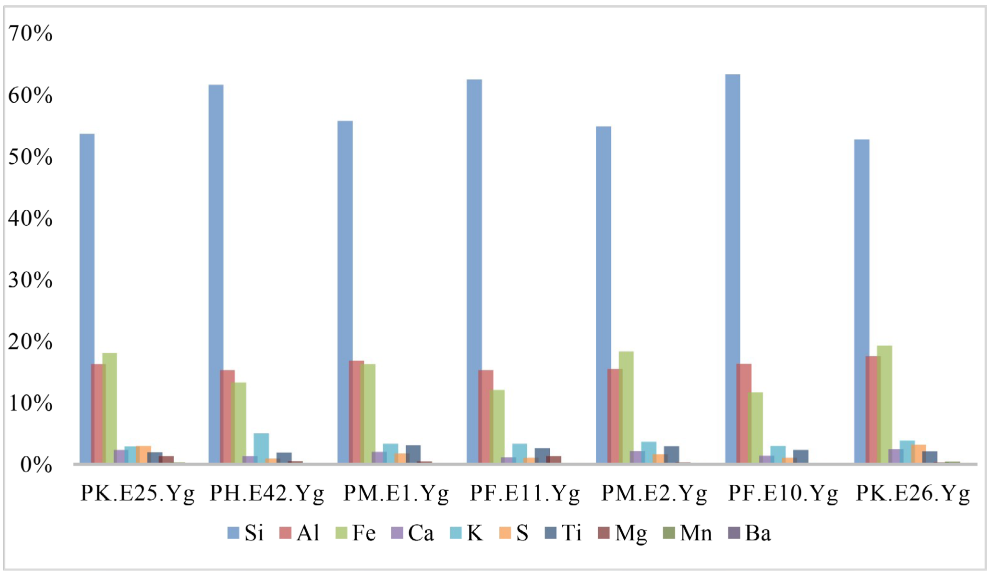


Figure 3. Proportions of major chemical elements in rocks of the Yogou formation.

of 3.60 for the Yogou samples (**Figure 4**).

Figure 4 shows the histogram of Si/Al atomic ratios of major chemical elements for the Donga formation in green and the Yogou formation in orange.

3.4. Identifying the Major Element and Oxide Composition of Donga and Yogou

Images and corresponding energy dispersive spectra of samples from the Donga and Yogou formations are shown in **Figures 5-8**.

The majority of element peaks in the EDS spectra, such as silicon (Si), aluminum (Al), magnesium (Mg), iron (Fe), sodium (Na), potassium (K), calcium (Ca), titanium (Ti) and sulfur (S), are common elements observed with XRF.

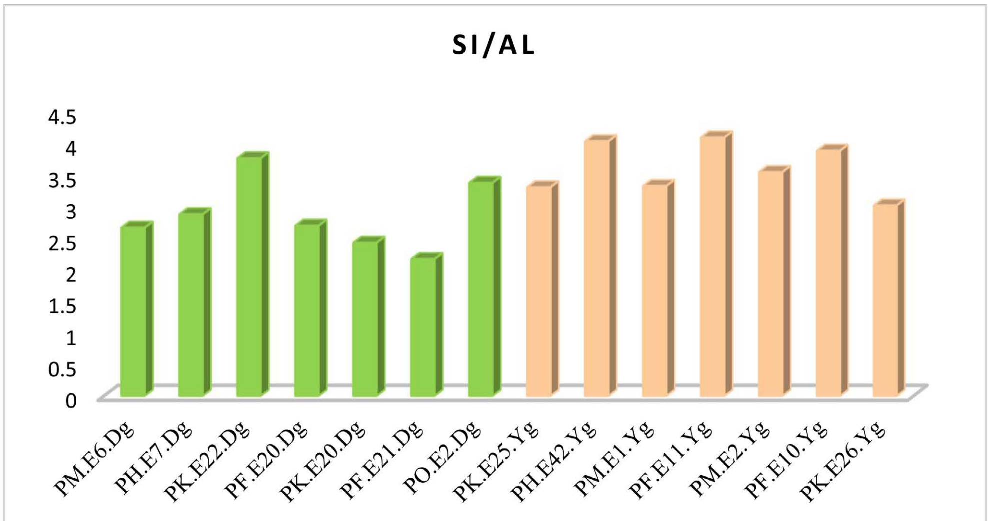
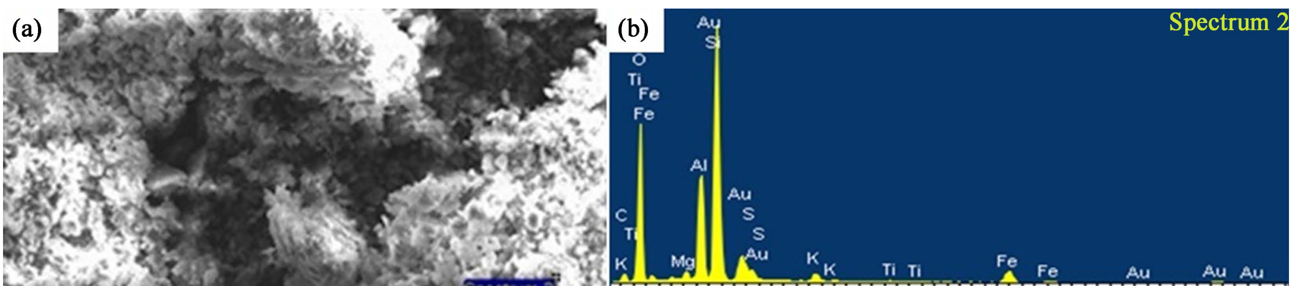
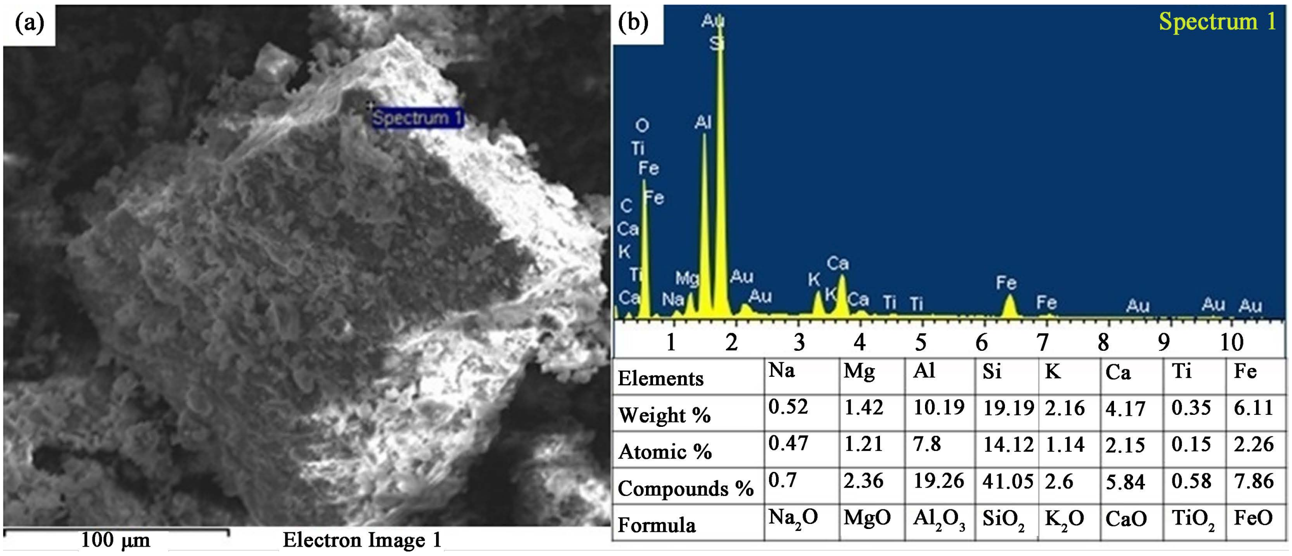


Figure 4. Atomic ratio (Si/Al) of the major chemical elements Si and Al in rocks from the Donga (green) and Yogou (orange) formations.



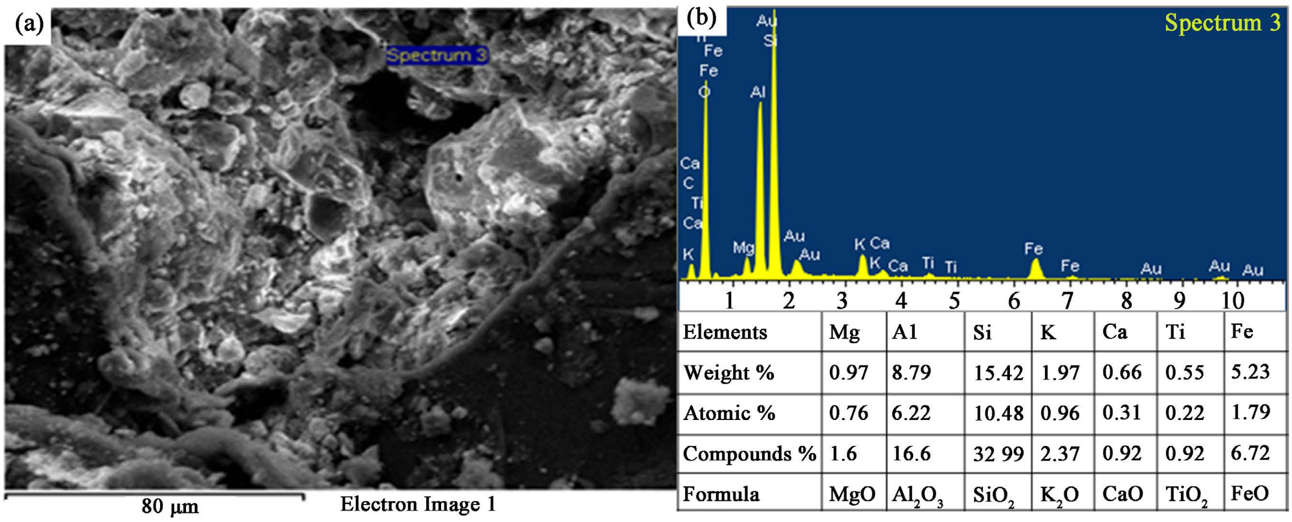
Elements	Mg	Al	Si	S	K	Ti	Fe
Weight %	0.52	7.01	18.97	1.06	0.91	0.23	3.93
Atomic %	0.43	5.22	13.57	0.67	0.46	0.10	1.41
Compounds %	0.87	13.24	40.59	2.65	1.09	0.39	5.05
Formula	MgO	Al_2O_3	SiO	SO_3	K_2O	TiO_2	FeO

Figure 5. SEM and EDS images: (a) SEM micrographs showing the irregular crystalline form of the minerals and (b) EDS spectra of sample PK.E20.Dg from the Donga formation (spectrum 2) showing the major chemical elements with their compositions (by weight, atomic and %¨).



Elements	Na	Mg	Al	Si	K	Ca	Ti	Fe
Weight %	0.52	1.42	10.19	19.19	2.16	4.17	0.35	6.11
Atomic %	0.47	1.21	7.8	14.12	1.14	2.15	0.15	2.26
Compounds %	0.7	2.36	19.26	41.05	2.6	5.84	0.58	7.86
Formula	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO

Figure 6. SEM and EDS images: (a) SEM micrographs showing the irregular crystalline form of la minerals and (b) EDS spectra of Donga Formation rock sample PK.E21.Dg (spectrum 1) showing the major chemical elements with their compositions (by weight, atomic and %¨).



Elements	Mg	A1	Si	K	Ca	Ti	Fe
Weight %	0.97	8.79	15.42	1.97	0.66	0.55	5.23
Atomic %	0.76	6.22	10.48	0.96	0.31	0.22	1.79
Compounds %	1.6	16.6	32 99	2.37	0.92	0.92	6.72
Formula	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO

Figure 7. SEM and EDS images: (a) SEM micrographs showing the irregular crystalline form of the minerals and (b) EDS spectra of rock sample PK.E26.Yg from the Yogou formation (spectrum 3) showing the major chemical elements with their compositions (by weight, atomic and %¨).

The elements gold (Au) and carbon (C) are taken from the sample support grid during analysis. The main chemical elements identified using energy dispersive spectrometry are shown in Table 4 and Figure 9, and the oxides in Figure 10.

3.4.1 Major Chemical Elements

Table 3 shows the proportions of major chemical elements in the EDS analysis of the Donga and Yogou samples.

Magnesium (Mg The chemical elements Si, Al and Fe are the most abundant, with average proportions of 19.08%, 11.10% and 5.02% respectively in the Donga

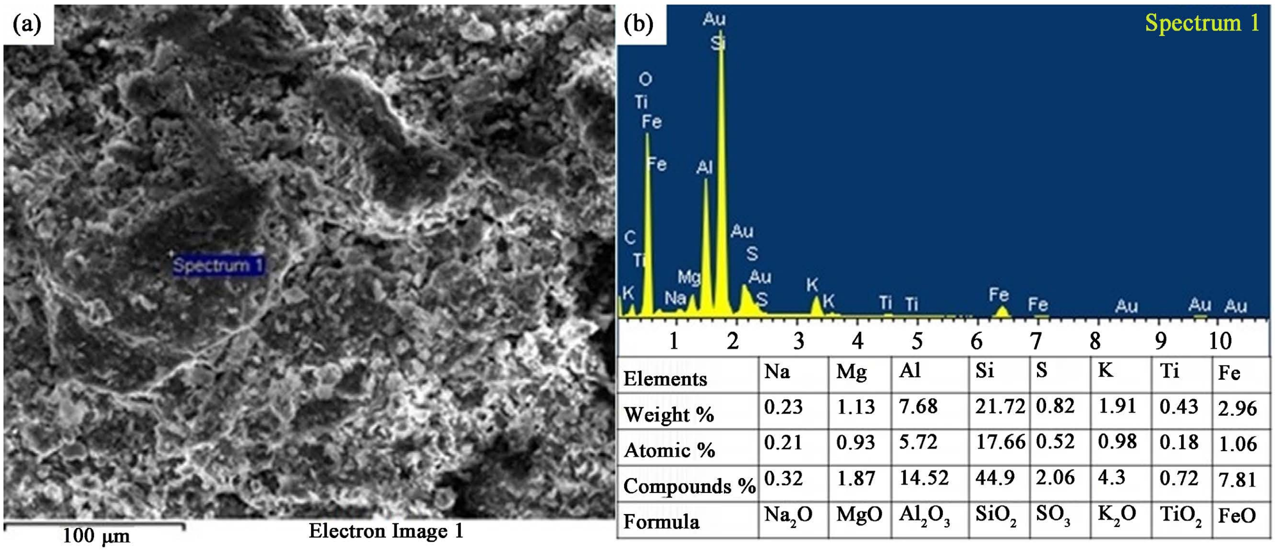


Figure 8. SEM and EDS images: (a) SEM micrographs showing the irregular crystalline form of the minerals and (b) EDS spectrm of rock sample PM.E1.Yg from the Yogou formation (spectrum 1) showing the major chemical elements with their compositions (by weight, atomic and %¨).

Table 3. Major chemical elements in EDS analysis.

Samples \ Elements	Al	Si	Fe	K	Ti	Ca	Mg	Na	S	Si/Al
Échant.	Weight %									Ratio
PK.E20.Dg	12.01	18.97	3.93	0.91	0.23	0	0.52	0	1.76	1.58
PK.E21.Dg	10.19	19.19	6.11	2.16	0.35	4.17	1.42	0.52	0	1.88
PK.E26.Yg	8.79	20.42	5.23	1.97	0.55	0.66	0.97	0	0	2.32
PM.E1.Yg	7.68	21.72	2.96	1.91	0.43	0	1.13	0.23	0.82	2.83
Average Dg	11.10	19.08	5.02	1.54	0.29	2.09	0.97	0.26	0.88	1.73
Average Yg	8.24	21.07	4.10	1.94	0.49	0.33	1.05	0.12	0.41	2.58

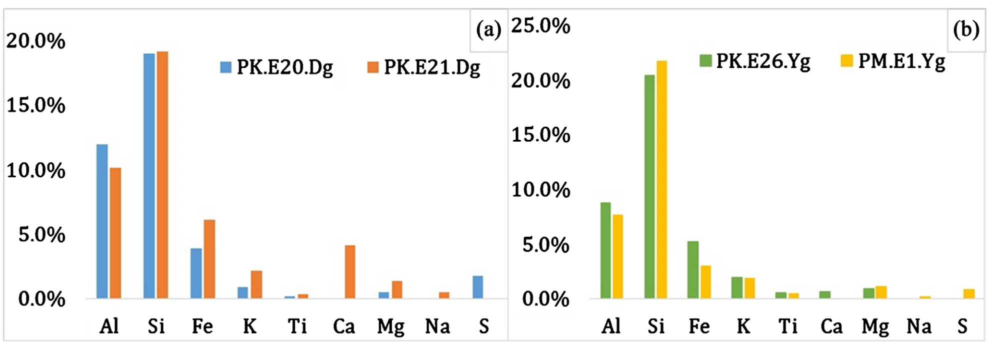


Figure 9. Major chemical elements from EDS analysis of samples from the Donga (a) and Yogou (b) formations.

formation, and 21.07%, 8.24% and 4.1% in the Yogou formation. They are followed by Ca with 2.09% and K with 1.54% for Donga. In the Yogou formation, these chemical elements have 1.05% and 1.94% respectively. The chemical elements Ti, Mg, S and Na are in very low proportions, averaging no more than 1% (Table 3). Si/Al ratios are 1.58 and 1.88 for the Donga formation and 2.32 and 2.83 for the Yogou formation (Table 3).

Figure 9 shows the histogram of the different proportions of major chemical elements obtained by EDS analysis in the Donga and Yogou formations.

This figure shows the abundance of the elements Si, Al and Fe in both formations.

3.4.2. Oxides in the Donga and Yogou Formations

The proportion of oxides contained in rocks from the Donga and Yogou formations is shown in Table 4. These oxides include silicon oxide (SiO_2), aluminum (Al_2O_3), iron (FeO), potassium (K_2O), titanium (TiO_2), calcium (CaO), magnesium (MgO), sodium (Na_2O) and sulfur (SO_3).

Analysis of this table shows that SiO_2 is the most abundant oxide, with an average proportion of 40.82% for Donga and 46.45% for Yogou (Figure 10). It is followed by Al_2O_3. The average proportion of this element is 19.25% for Donga and 15.06% for Yogou. It is therefore less abundant in the latter formation (Figure 10). FeO oxide is also moderately abundant in these formations. These average proportions are 6.46% and 7.27% respectively in the Donga and Yogou formations. The proportions of other oxides are, in order of abundance, K_2O (2.85% and 3.34%), MgO (1.62% and 1.74%), SO_3 (2.65% and 1.03%), Ti_2O (0.49% and 0.82%) and Na_2O (0.35% and 0.16) in the Donga and Yogou formations.

Figure 10 shows the histogram of oxide proportions obtained by EDS analysis on samples from the Donga (Figure 10(a)) and Yogou (Figure 10(b)) formations. Analysis of this figure also shows the abundant proportions of the following oxides: SiO_2, Al_2O_3 and FeO in both formations. These results are in agreement with the proportions of major elements obtained by XRF and EDS analyses.

Figure 11 shows the histogram of the different values of the ratio of major chemical elements and oxides obtained by EDS analysis of samples from the Donga and Yogou formations.

Table 4. Oxides from EDS analysis of Donga and Yogou samples.

Elements / Samples	Al_2O_3	SiO_2	FeO	K_2O	TiO_2	CaO	MgO	Na_2O	SO_3	SiO_2/Al_2O_3
	Weight %									Ratio
PK.E20.Dg	19.24	40.59	5.05	3.09	0.39	0	0.87	0	2.65	2.11
PK.E21.Dg	19.26	41.05	7.86	2.6	0.58	5.84	2.36	0.7	0	2.13
PK.E26.Yg	15.6	47.99	6.72	2.37	0.92	0.92	1.6	0	0	3.08
PM.E1.Yg	14.52	44.9	7.81	4.3	0.72	0	1.87	0.32	2.06	3.09
Average Dg	19.25	40.82	6.46	2.85	0.49	2.92	1.62	0.35	2.65	2.12
Average Yg	15.06	46.45	7.27	3.34	0.82	0.46	1.74	0.16	1.03	3.08

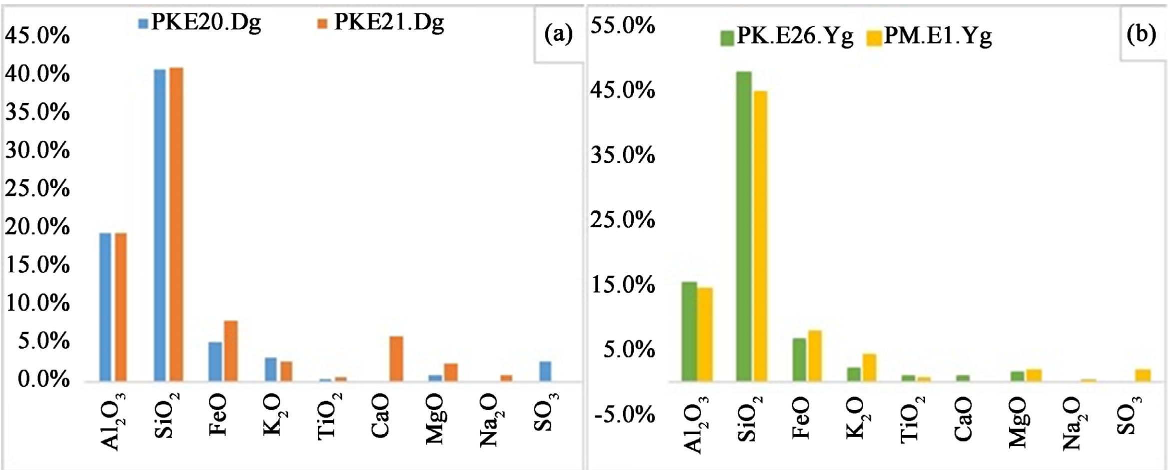


Figure 10. Oxides in samples from the Donga (a) and Yogou (b) formations.

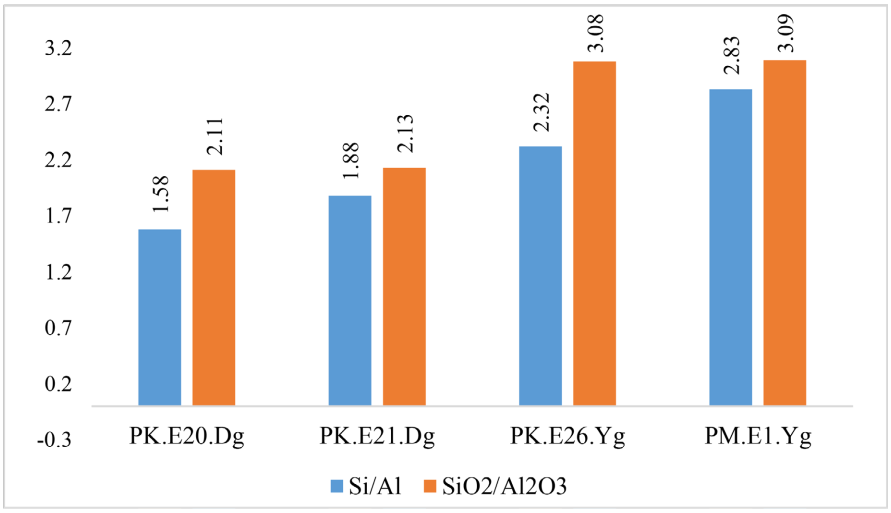


Figure 11. Si/Al and SiO_2/Al_2O_3 ratios of major chemical elements from EDS analysis of samples from the Donga and Yogou formations.

4. Discussion

4.1. Major Chemical Elements in the Donga and Yogou Formations

The abundance of major elements such as silicon, aluminum and iron in the samples from Donga and Yogou formations revealed by XRF analysis is attributable to the presence of detrital minerals in these samples. Furthermore, the high proportion of Fe in these formations is either due to the presence of pyrite and goethite, or to substitutions in the octahedral and tetrahedral structures of Al^{3+} by Fe^{2+} and Si^{4+} by Al^{3+} or Fe^{3+} respectively in the clay material. These observations concerning the presence of non-silicates minerals iron-rich, notably pyrite and goethite, are in line with the work of [14]. Also, the presence of relatively high levels of the elements K and Ca is probably due to these substitutions. This could result in a slight charge deficit in the structure, which can be compensated for by these modifier cations (interfoliar) in the tetrahedral and octahedral sites as described by [16]. In addition, the uniform distribution of Fe and

Mg elements on clay particles can be interpreted as the result of substitution of these elements in the clay crystal lattice and during the deposition of nanocrystalline grains of associated minerals such as pyrite, goethite as revealed by [14].

Also, the average Ti, K and K_2O contents, with an average of 3.99% and 3.57% by weight for Ti, 2.07% and 2.42% by weight for K and 2.85% and 3.34% by weight for K_2O respectively for the Donga and Yogou formations, are relatively high. This suggests that the presence of titanium (Ti) in these formations is either linked to the crystalline networks of the clay minerals, or originates from detrital materials [16] [17] and confirmed by the work of [14] on the mineralogical characterization of the Donga and Yogou formations.

4.2. Oxides in the Donga and Yogou Formations

The works of [18] [19] has shown that Al_2O_3 and SiO_2 contents are respectively proportional to the presence of clays and silicate detrital materials such as quartz. In this study, SiO_2 is abundant in the Yogou formation, while Al_2O_3 is abundant in the Donga formation. This distribution characterizes a predominance of clay minerals in the Donga formation and is probably explained by the presence of sandy lenses in the Yogou formation, constituting Upper Cretaceous reservoirs in the Termit sedimentary basin, as described in the works of [20] [21] [22] [23] in the same Termit sedimentary basin.

Iron oxide (FeO) is also an important component in the Donga and Yogou formations, averaging 6.46% and 7.27% by weight respectively. This iron oxide (FeO) has known preferential associations with iron sulfides such as pyrite and marcasite. Mineralogical examination by [14] confirmed that the extent of iron concentration generally coincides with the presence of pyrite in these formations.

4.3. Influence of Si/Al and SiO_2/Al_2O_3 Ratios and Donga and Yogou Oxides

The Al/Si ratios, which vary from 0.27 to 0.46 with an average of 0.35 for the Donga formation and from 0.2 to 0.33 with an average of 0.28 for the Yogou formation, are respectively low (**Table 2** and **Table 3**), suggesting according to [18] that Si in most sediments is associated with silicates and clay minerals. According to previous work [14] [24], the SiO_2/Al_2O_3 ratio values in the Donga and Yogou formations belong to the range of SiO_2/Al_2O_3 ratio values for 2:1 type clays (2Si and 1Al which is 2 to 4) [25] [26]. These ratios are significantly higher than those of standard kaolinite (ranging from 1.73 to 1.8) [25] [26]. This may be due to the presence of siliceous minerals, particularly quartz, in the rocks of the Donga and Yogou formations, as shown by [14].

The abundance of silicon and aluminum on the one hand, and the relatively high Si/Al ratios on the other, provided by X-ray fluorescence spectrometry, confirm a clay, quartz and muscovite enrichment of the rocks in these formations, as noted by [14]. The high iron content is linked to the presence of pyrite in samples from the Donga and Yogou formations. Then, the relatively high contents of chemical elements such as S, Ti, Mg, Mn, and also Fe, Ca, and K is due to the presence of accessory minerals such as garnet, siderite, goethite and anatase in the Donga formation and sericite, anatase and goethite in the Yogou formation and pyrite and muscovite in these two formations [14].

In addition to the high Si/Al ratios, the K and Ca element contents are probably due to substitutions in the octahedral and tetrahedral structures of Al^{3+} by Fe^{2+} and Si^{4+} by Al^{3+} or Fe^{3+} respectively. The results of mineralogical analysis of clay fractions from the Donga and Yogou formations obtained by [14] reveal the presence of interstratified clay minerals such that illite, smectite and chlorite type. Si/Al ratio values between 1 and 3, obtained by EDS analysis, indicate the predominance of kaolinite, 2:1 clays such as smectite and illite and siliceous minerals as described by [14].

5. Conclusions

The distribution of chemical elements in petroleum source rocks of Donga and Yogou formations of the Termit sedimentary basin (Niger), shows that Fe, Si and Al are the most abundant elements. The major chemical element compositions of the samples analyzed are controlled mainly by clay minerals rather than by non-clay silicate minerals. This trend is illustrated by the values of the Si/Al ratios, although the proportion of silicate minerals is not negligible. The main oxides (SiO_2, Al_2O_3 and FeO) identified by this study are unevenly distributed throughout the formations. The predominance of SiO_2 and Al_2O_3 confirms the presence of quartz and clay minerals, as does the XRF analysis.

The major chemical elements identified in the Donga and Yogou formations are borne by minerals such as pyrite, goethite, clays, quartz, muscovite, siderite, anatase and garnet.

Finally, the Donga and Yogou formations are dominated by clays and contain silicate minerals associated with pyrite and goethite, while the clay fractions of these rocks are dominated by kaolinite and interbedded minerals such as illite, smectite and chlorite types.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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