

Correlative Study On The Distribution Of Major Chemical Elements And Traces Of The Minerals Of Petroleum Source Rocks Of Donga And Yogou Formations Of Termit Sedimentary Basin (Eastern Niger): The Implications Of The Depositional Environment

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Abstract:

Background: The coexistence of chemical éléments within a mineral or mineral assemblage is the result of certain affinities between these éléments. In the case of petroleum-bearing sedimentary rocks such as Donga and Yogou, these affinities often reflect the environmental conditions in which the rocks were deposited.

Materials and methods: The statistical study of the chemical éléments present in the minerals of the Donga and Yogou drill cuttings is based on the integration of elemental mineral geochemistry data obtained with an RFX.

Results: This study revealed the presence of 23 chemical éléments, of which Rb, Ba, Ni, V, Co, K, Fe, Al, Ti and Zr are derived from clay, detrital and heavy minerals, while the chemical éléments Cl, Mo, Pb, Zn, Cu, Cr, Si, S and Mn are linked to organic matter and are characteristic of an anoxic environment, with the exception of Si, which is derived from quartz in the Donga formation. The éléments Sr, Ca and Mg are largely derived from carbonates and P locally from phosphates. For the Yogou formation, the éléments Sr, Al, Fe, Ca, S and Mn come from clay minerals, pyrite and carbonates and are characteristic of suboxic to anoxic environments. The chemical éléments Ni, V, Ti, Zn, Cu and Ba are concentrated in detrital minerals of this formation, while the éléments Rb, Pb, Mg, K, Co and Cr are found preferentially in clay minerals, and the éléments Zr and Si in zircon and quartz respectively. The éléments P, Cl and Mo are linked to the salts present in these environments.

Key Word: Major elements, trace elements, source rocks, Donga formation, Yogou formation, Termit basin and depositional environments.

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I. Introduction

The concept of chemical elements (major, minor and trace elements) used in geochemistry results from quantitative considerations of elements within a mineral or an assemblage mineral (rocks). The study of the chemical element in minerals and rocks has shown that the ideal composition of these materials is often mostly theoretical, and that certain chemical elements can appear in small quantities as well as in large quantities within the minerals. Thus, independently of the study carried out on these elements, works have been carried out in order to consider them as a significant anomaly of the conditions of genesis of the mineral or the assemblage of minerals containing them [1]. While other works reveal that the coexistence of these chemical elements in the mineral or in the assemblage of minerals results from certain affinities between these elements [1], [2]. Therefore, they are often used for the interpretation of sediment deposit environments [3]–[6], the preservation process of the organic matter [7]–[12]; and the thermal degradation process of organic matter and hydrocarbon generation [13]–[18].

This study aims at characterizing the deposit environments of the Donga and Yogou formations from the elemental mineral geochemistry. The interest of this study is to contribute to the improvement of oil prospecting activities in the Termit sedimentary basin.

II. Material And Methods

Analyzed samples

Drill cuttings from the Donga and Yogou formations formed the samples set for this study. These samples 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.

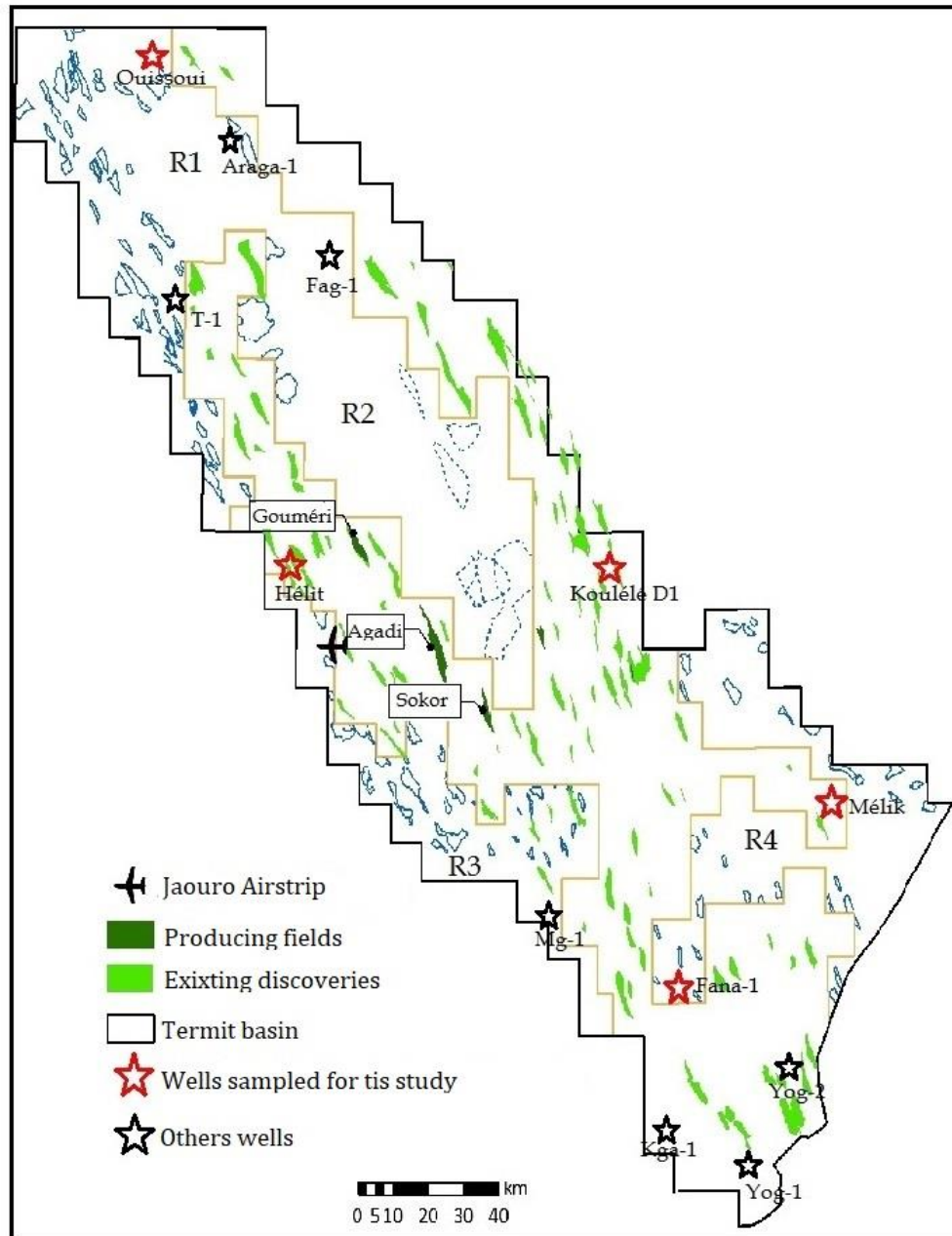


Figure 1: Termit sedimentary basin map with the locations of sampled wells (modified from [19])

X-ray fluorescence (XRF) analysis

The sample size was estimated on the basis of a single proportion design. The target population from which we Rock cuttings samples were washed to remove drilling mud. X-ray fluorescence (XRF) analysis has been applied to determine the composition of chemical elements (major and trace) in these samples. FRX has

been performed using a portable Niton XL3t® FRX spectrometer, coupled with a computer to ensure data transfer after the 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. Thus, this enabled the major chemical element composition of total rock samples to be determined.

Statistical analysis of trace chemical elements

Statistical analyses of chemical elements have been carried out using R software. These analyses concern multiple correlations and Principal Component Analysis.

Multiple correlations enable us to understand the various relationships between quantitative variables, in this case, the chemical elements (major and trace) present in the samples studied. To establish these relationships, Pearson's correlation has been applied. The measure is normalized and is defined between $-1 \leq r \leq +1$. The closer the correlation is to 1 or -1, the stronger is the link, and the closer it is to 0, the weaker or null it becomes. As the value of r has no intrinsic significance for the interpretation of the relationship, then its square, called the coefficient of determination, has been used. It is interpreted as the proportion of variance of a variable linearly explained by the other variable and vice versa. Proportions of at least 50% (equivalent to $|r| > 0.7$) have been retained.

Principal Component Analysis (PCA) makes variables return to a reduced-dimensional space distorting the reality in the least possible way. It is a multivariate data analysis method that enables the information contained in a table of quantitative variables to be summarized and visualized in order to establish the affinities between them.

III. Results and discussions

Chemical composition of the donga formation

The chemical elements present in the Donga formation are presented in Table no 1. They are composed of silicon, aluminum, iron, calcium, potassium, sulfur, titanium, magnesium, manganese and barium.

Table no 1: Elemental composition of chemical elements in the Donga formation

Samples	PM.Dg	PH.Dg	PK.Dg _2	PK.D g_2	PF.D g_1	PF.Dg _2	PO.Dg
Si	47.85	51.88	56.77	47.96	47.55	47.7	46.72
K	3.7	6.03	3.74	3.88	3.85	3.35	3.36
Ti	1.34	2.21	0.77	2.37	3.48	2.57	1.72
Mg	0	0.18	0.17	0.4	0.1	0.22	1.81
Mn	0,37	0,12	0,54	0,32	0,27	0,25	0,3
Ba	0,21	0,28	0,08	0,15	0,23	0,08	0,11
Fe	18,7	17,53	12,26	19,85	20,09	18,05	15,65
Ca	4,28	1,57	7,9	2,18	4,31	3,55	13,82
Zr	0,033	0,065	0,018	0,061	0,067	0,064	0,043
Sr	0,028	0,027	0,032	0,037	0,027	0,023	0,046
S	4,92	2	2,27	2,99	2,26	2,1	2
Rb	0,012	0,015	0,009	0,009	0,006	0,006	0,008
Pb	0,004	0,002	0,003	0,004	0,003	0	0,003
Zn	0,022	0,007	0,02	0,014	0,011	0,007	0,005
Cu	0,028	0,008	0,017	0,015	0,011	0,007	0,008
Ni	0,028	0,03	0,013	0,014	0,025	0,018	0,019
Cr	0,016	0,017	0,014	0,019	0,008	0,016	0,016
V	0,053	0,05	0,034	0,044	0,052	0,04	0,043
Co	0,0039	0,006	0,0022	0,0031	0,004	0,002	0,0025

Trace elements in this rock have concentrations below 5000 ppm. They include zirconium, chlorine, strontium, chromium, rubidium, nickel, phosphorus, copper, zinc, lead, vanadium, cobalt and molybdenum.

Principal component analysis of chemical elements in donga rocks

The chemical elements present in the Donga samples have been represented on the first two axes (DIM 1 and DIM 2) of the principal component analysis (PCA) with a percentage of 57.2% (Figure 2). This is sufficient for the data interpretation. The results of the PCA and multiple correlations enabled us to establish relationships between these elements by grouping them into four classes: class 1, class 2, class 3 and class 4 (Figure 2).

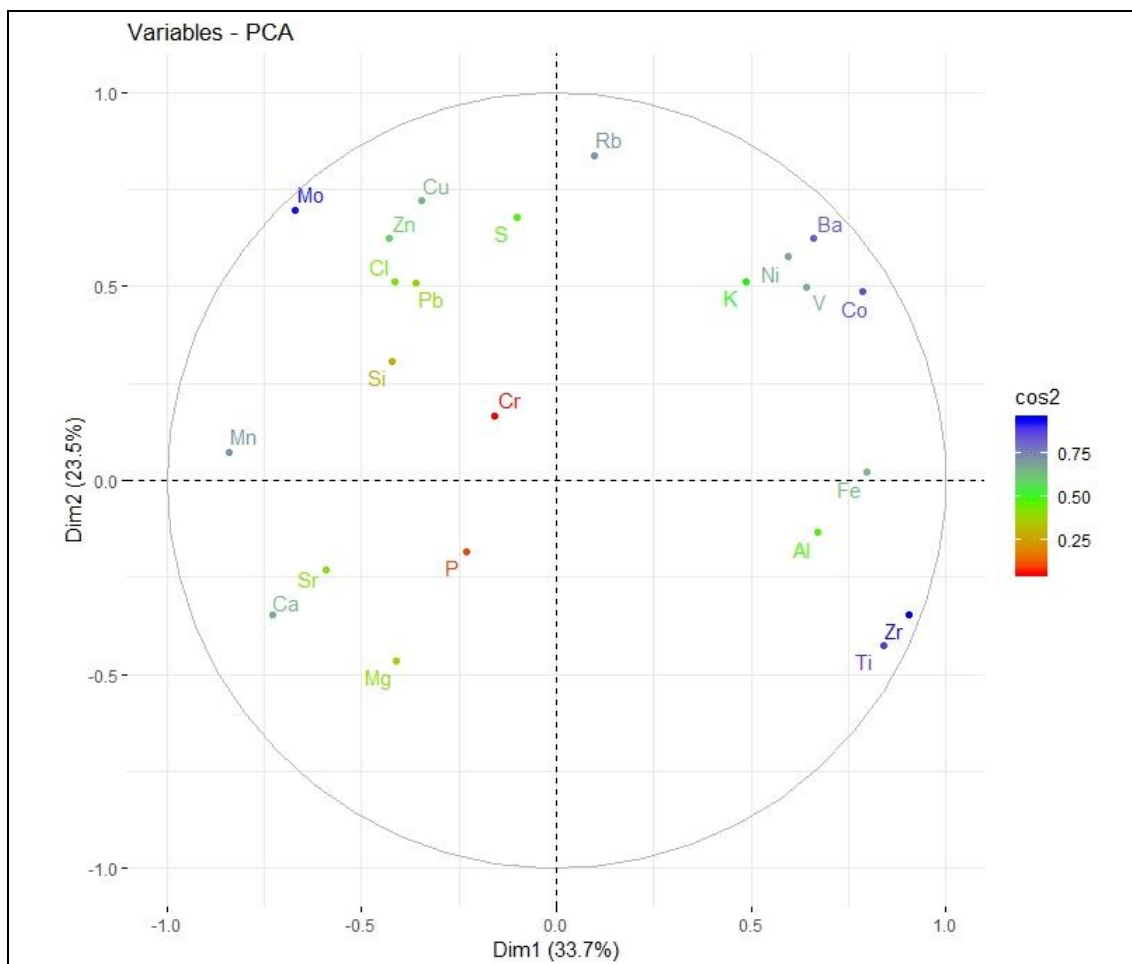


Figure 2: PCA of chemical elements in the Dongga formation

Multiple correlations of chemical elements in the dongga formation

Class 1 is made up of Rb, Ba, Ni, V, Co and K (Table no 2). This class is influenced by the positive zones of the Dim1 and Dim2 axes. The element Rb is rather explained only by the positive side of the Dim2 axis. These elements form weak (V_K and Rb_V), medium (Rb_Ni, Rb_Co, Ni_K and Rb_Ba) and strong (Rb_K, Ni_V, Ni_Co, Ni_Ba, V_Co, V_Ba, Co_K and K_Ba) or even very strong (Co_Ba) positive correlations. The weak and medium correlations have r values < 0.7. In these correlations, the variance of one element affects the other at 36%. These elements, therefore, come from several minerals. On the other hand, strong correlations (0.7 < r < 0.9) and very strong correlations (0.9 < r < 1) show strong links between chemical elements. The variance of one element influences the variance of the other by more than 50%. It can be as high as 95 (Co_Ba); so, both elements come from the same mineral. Chemical elements with high correlations suggest that they are found in at least one and the same mineral with the presence of one which conditions the presence of the other in the samples studied. Class 1 includes chemical elements from clay minerals, detrital minerals and heavy minerals present in the Dongga samples.

Table no 2: Positive correlation of Class 1 elements

	Rb	Ni	V	Co	K	Ba
Rb	1	0.563	0.367	0.575	0.794	0.615
Ni	0.563	1	0.867	0.862	0.581	0.868
V	0.367	0.867	1	0.776	0.369	0.878
Co	0.575	0.862	0.776	1	0.825	0.952
K	0.794	0.581	0.369	0.825	1	0.742
Ba	0.615	0.868	0.878	0.952	0.742	1

Class 2 contains more chemical elements (Table no 3): Cl, Mo, Pb, Zn, Cu, Cr, Si, S and Mn. These elements have positive or negative correlations that range from very weak to very strong. The most significant correlations in ascending order are Zn_S, Zn_Mn, Cl_Mo, Cu_S and Zn_Cu. These elements influence each other by more than 54%. The last two correlations reach over 86%. Some of these elements originate from the same mineral or deposit environment. According to [1], these elements come from an anoxic (oxygen-poor) environment. They are, therefore, linked to organic matter, hence the presence of sulfur in the environment. In this class, we note the presence of silicon, whose correlation with the other elements is very weak. This suggests an influence of quartz during FRX analysis, with some of the silicon in the other minerals being weakly expressed.

Table no 3: Correlation of Class 2 elements

	Cl	Mo	Pb	Zn	Cu	Cr	Si	S	Mn
Cl	1	0.806	0.317	0.021	0.199	0.376	0.171	0.177	-0.006
Mo	0.806	1	0.488	0.566	0.602	0.317	0.53	0.424	0.492
Pb	0.317	0.488	1	0.589	0.662	0.01	-0.006	0.56	0.416
Zn	0.021	0.566	0.589	1	0.928	-0.038	0.394	0.738	0.746
Cu	0.199	0.602	0.662	0.928	1	0.074	0.111	0.925	0.574
Cr	0.376	0.317	0.01	-0.038	0.074	1	-0.016	0.192	-0.112
Si	0.171	0.53	-0.006	0.394	0.111	-0.016	1	-0.219	0.476
S	0.177	0.424	0.56	0.738	0.925	0.192	-0.219	1	0.285
Mn	-0.006	0.492	0.416	0.746	0.574	-0.112	0.476	0.285	1

Class 3 includes the following minerals (Table no 4): P, Sr, Ca and Mg. They are explained by the negative sides of the Dim1 and Dim2 axes. The correlations between the elements Ca, Mg and Sr are strongly positive. They influence each other by 55% (Ca_Sr), 68% (Ca_Mg) and 75% (Mg_Sr). These elements largely derived from carbonates. Phosphorus correlates moderately with the other three elements (Sr, Ca and Mg), whose influence remains below 47%. It does not come from the same mineral like the other elements, but from the same deposit environment, which is here in situ. It could come from phosphates.

Table no 4: Positive correlations of class 3 elements

	P	Sr	Ca	Mg
P	1	0.684	0.67	0.676
Sr	0.684	1	0.742	0.87
Ca	0.67	0.742	1	0.828
Mg	0.676	0.87	0.828	1

Class 4 is composed of the elements Fe, Al, Ti and Zr (Table no 5). The Correlations between these elements are positive. Only the positive side of the Dim1 axis better explains these elements. In the Table no 5, Ti_Zr (r = 0.915) are very strongly correlated; the variance of one explains by 84% the variance of the other. Considering the presence of anatase reported in the work of [20], we can assume that Ti comes almost exclusively from this mineral. In view of its strong correlation with Zr, these two elements originate from the same mineral (anatase). The other correlations, which are strong (Fe_Ti and Zr_Fe) and medium (Al_Fe, Al_Zr and Al_Ti), influence each other between 58% and 60%; and between 26% and 38% respectively. Iron is strongly correlated with Zr and Ti, and is thought to originate partly from anatase, but also from other detrital elements such as goethite. The weak influence of Al on the other elements shows that it largely derives from different minerals. It was, therefore, the aluminum in clay minerals that expressed itself the more.

Table no 5: Positive correlations of class 4 elements

	Zr	Al	Fe	Ti
Zr	1	0.62	0.76	0.915
Al	0.62	1	0.632	0.507
Fe	0.76	0.632	1	0.773
Ti	0.915	0.507	0.773	1

There is also a relationship between the different classes. Class 1 and class 4 are positively correlated, with Zr_Co, Fe_V and Fe_Co being the most notable. The influence between the variances of these elements

remains below 32%, except the Fe_V relationship, where the influence is 50%. Classes 1 and 2 derive from the clay minerals, detrital minerals (anatase, muscovite, goethite and garnet) and heavy minerals present in the samples from the Donga formation. These elements are inherited from the weathering of continental rocks.

There is no significant correlation between classes 2 and 3. Nevertheless, the elements in these classes originate from the same anoxic environment except silicon, which comes from quartz.

Negative correlations exist between classes 1 and 3 on the one hand, and between classes 2 and 4 on the other (Table no 6). These correlations mean that there are substitutions between the elements in these different classes. In classes 2 and 4, they are medium (Cl_Al, Cl_Ti, Mo_Al, Mo_Fe, Zr_Zn, Zr_Cu, Zr_Si, Zn_Ti, Cu_Ti, Si_Fe, Si_Ti, Fe_Mn and Ti_Mn), strong (Mo_Zr and Zr_Mn) and very strong (Mo_Ti). In the medium correlations, the variances influence each other by less than 50%. Mo and Mn tend to replace Zr in minerals. The variance is even greater between Mo and Ti, approaching 84%. Mo gradually replaces Ti in anatase. In classes 1 and 3, negative correlations are averages whose variances influence each other only slightly (< 25%).

Table no 6: Negative correlations between classes 2 and 4

	Cl	Mo	Zr	Zn	Cu	Si	Al	Fe	Ti	Mn
Cl	1	0.806	-0.475	0.021	0.199	0.171	-0.664	-0.436	-0.641	-0.006
Mo	0.806	1	-0.833	0.566	0.602	0.53	-0.614	-0.615	-0.913	0.492
Zr	-0.475	-0.833	1	-0.675	-0.607	-0.542	0.62	0.76	0.915	-0.857
Zn	0.021	0.566	-0.675	1	0.928	0.394	-0.097	-0.161	-0.543	0.746
Cu	0.199	0.602	-0.607	0.928	1	0.111	-0.091	0.021	-0.513	0.574
Si	0.171	0.53	-0.542	0.394	0.111	1	-0.316	-0.751	-0.576	0.476
Al	-0.664	-0.614	0.62	-0.097	-0.091	-0.316	1	0.632	0.507	-0.404
Fe	-0.436	-0.615	0.76	-0.161	0.021	-0.751	0.632	1	0.773	-0.588
Ti	-0.641	-0.913	0.915	-0.543	-0.513	-0.576	0.507	-0.773	1	-0.663
Mn	-0.006	0.492	-0.857	0.746	0.574	0.476	-0.404	-0.588	-0.663	1

Composition of the chemical elements of the Yogou formation

The major chemical elements present in the Yogou formation are listed in Table no 7. They include silicon, aluminum, iron, calcium, potassium, sulfur, titanium, magnesium, manganese and barium.

Table no 7: Elemental composition of chemical elements in the Yogou formations

Samples	PK.Yg_1	PH.Yg	PM.Yg_1	PF.Yg_1	PM.Yg_2	PF.Yg_2	PK.Yg_2
Si	53.66	61.61	55.77	62.49	54.81	63.29	52.73
P	0.09	0.2	0.14	0.1	0.16	0.18	0.12
Al	16.27	15.27	16.8	15.28	15.49	16.32	17.52
K	2.85	5.02	3.34	3.31	3.63	2.97	3.84
Ti	1.96	1.89	3.14	2.6	2.91	2.31	2.11
Mg	1.31	0.5	0.44	1.33	0.29	0.22	0.33
Mn	0.32	0.09	0.12	0.05	0.14	0.11	0.39
Ba	0.04	0.19	0.02	0.13	0.16	0.19	0.22
Cl	0.03	0.13	0.17	0.11	0.21	0.13	0.03
Mo	0	0.002	0.002	0	0.002	0.001	0.001
Fe	18.08	13.3	16.26	12.04	18.32	11.69	19.29
Ca	2.3	1.31	1.98	1.15	2.16	1.41	2.46
Zr	0.049	0.083	0.094	0.109	0.084	0.098	0.051
Sr	0.029	0.022	0.022	0.014	0.02	0.014	0.031
S	2.96	0.91	1.73	1.08	1.65	1.09	3.22
Rb	0.008	0.012	0.009	0.008	0.008	0.007	0.009
Pb	0.005	0.005	0.004	0.005	0.002	0	0.002
Zn	0.008	0.006	0.004	0.008	0.003	0.016	0.012
Cu	0.009	0.007	0.005	0.009	0.006	0.005	0.011
Ni	0.012	0.011	0.027	0.017	0.015	0.012	0.017
Cr	0.02	0.019	0.019	0.016	0.009	0.01	0.013
V	0.041	0.039	0.07	0.046	0.052	0.045	0.053
Co	0.0023	0.0054	0.0023	0.0033	0.002	0.0023	0.004

The trace elements in this rock also include zirconium, chlorine, strontium, chromium, rubidium, nickel, phosphorus, copper, zinc, lead, vanadium, cobalt and molybdenum. These are also elements with concentrations below 5000 ppm.

Principal component analysis of chemical elements in Yogou rocks

The first two axes (Dim1 and Dim2) explain the chemical elements present in the Yogou samples. The percentage is 56.9% (Figure 3). The results of the PCA and multiple correlations also reveal four classes: class 1, class 2, class 3 and class 4.

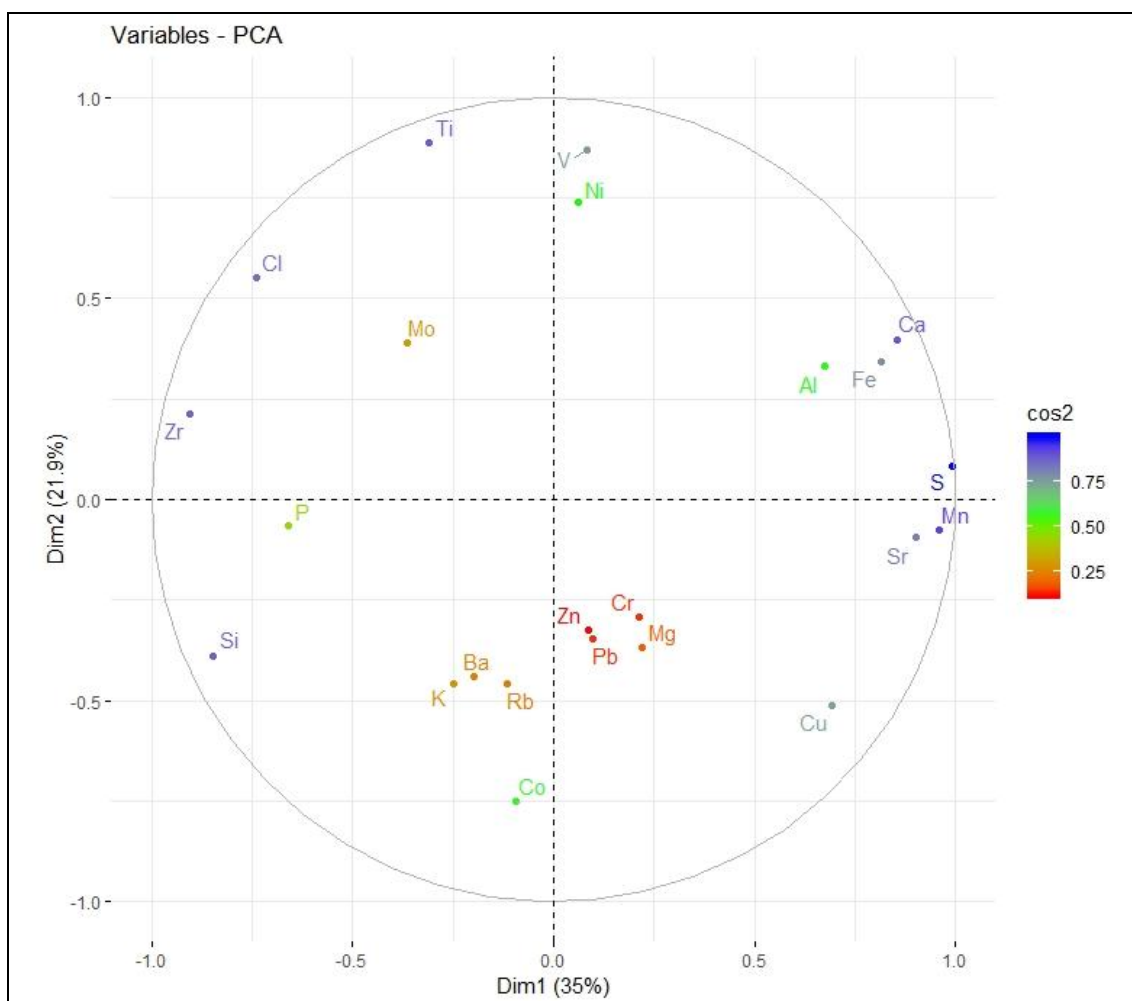


Figure 4: PCA of chemical elements in the Yogou Formation

Multiple correlations of chemical elements in the Yogou formation

In class 1, most of the correlations are strong and positive, except the correlations between Fe_Ca and S_Mn where they are very strong (Table no 8). The variances range from 52% to 80% for strong correlations and 94% for very strong correlations. These correlations show that the chemical elements come from at least the same minerals (clays, pyrite and carbonates). Here, the proportion of iron comes largely from pyrite, given its affinity with sulfur contrarily to the Donga formation, where the presence of sulfur is largely due to detrital minerals (goethite, anatase, etc.). According to the works of [1], [21], Class 1 elements are characteristic from suboxic to anoxic environments. There are average correlations in this class, namely Sr_Al and Al_Fe; these elements do not originate from the same mineral. Class 1 is influenced by the Dim1 axis (positive side).

Table no 8: Positive correlations of Class 1 elements

	Sr	Al	Fe	Ca	S	Mn
Sr	1	0.598	0.831	0.821	0.885	0.894
Al	0.598	1	0.521	0.665	0.724	0.724
Fe	0.831	0.521	1	0.97	0.846	0.782
Ca	0.821	0.665	0.97	1	0.896	0.842
S	0.885	0.724	0.846	0.896	1	0.97
Mn	0.894	0.724	0.782	0.842	0.97	1

As for class 2 (Table no 9

Table no), only the Dim2 axis (positive side) explains the elements in this class. Correlations between elements are positive and strong (Ni_Ti and V_Ti) to very strong (Ni_V). Nickel's variance explains 60% of Titanium's variance and 95% of Vanadium's variance. These elements derive from the same minerals. Ti, here, does not come from anatase, but probably from heavy minerals. This class forms no significant correlation with class 1.

Table no 9: Positive correlations of class 2 elements

	Ni	V	Ti
Ni	1	0.952	0.771
V	0.952	1	0.804
Ti	0.771	0.804	1

Class 3 is explained by the negative sides of the Dim1 and Dim2 axes (Table no 10). Significant correlations are P_Mo, Cl_Mo, Zr_Si. P, Mo and Cl probably originate from salts present in the environment, which is also suboxic to anoxic, as in class 1. Zr and Si, which individually form weak positive correlations with the other elements derive from heavy minerals and quartz respectively. The strong correlation between Si and Zr might be due to zircon inclusions in the grains of quartz of the Yogou formation. There is no correlation between Class 3 elements and those of Classes 1 and 2. Class 3 elements are from the same environment as Class 1 elements.

Table no 10: Positive correlations of class 3 elements

	P	Cl	Mo	Zr	Si
P	1	0.579	0.762	0.342	0.458
Cl	0.579	1	0.703	0.693	0.277
Mo	0.762	0.703	1	0.176	-0.071
Zr	0.342	0.693	0.176	1	0.771
Si	0.458	0.277	-0.071	0.771	1

In the last class, only the Dim2 axis (negative side) explains the elements except for Cu, where the Dim1 axis (negative side) is also expressed (Table no 11). The chemical elements concerned are: Rb, Pb, Zn, Cu, Cr, Co, K, Mg and Ba. The correlations are mostly positive, except between certain elements where they are negative (Pb_Zn, Rb_Zn, Pb_Ba, Cr_Ba). Negative correlations show that these elements do not share the same source. However, substitutions occur between elements in the current deposit environment. The remarkable positive correlations ($0.7 < r < 1$) are: Rb_Co, Rb_K, Pb_Mg, Pb_Cr, Co_K. These elements originate, in part, from the same minerals, in occurrence clay minerals. Other positive correlations reflect the presence of detrital minerals. This class shows no remarkable correlation with the other classes.

Table no 11: Positive and negative correlations of class 4 elements

	Rb	Pb	Zn	Cu	Cr	Co	K	Mg	Ba
Rb	1	0.503	-0.38	0.08	0.512	0.851	0.923	-0.13	0.176
Pb	0.503	1	-0.58	0.3	0.871	0.355	0.254	0.735	-0.52
Zn	-0.38	-0.58	1	0.2	-0.34	0.039	-0.3	-0.13	0.473
Cu	0.084	0.299	0.2	1	0.185	0.393	0.073	0.468	0.217
Cr	0.512	0.871	-0.34	0.19	1	0.326	0.158	0.577	-0.62
Co	0.851	0.355	0.039	0.39	0.326	1	0.866	-0.03	0.516
K	0.923	0.254	-0.3	0.07	0.158	0.866	1	-0.32	0.494
Mg	-0.13	0.735	-0.13	0.47	0.577	-0.03	-0.32	1	-0.49
Ba	0.176	-0.52	0.473	0.22	-0.62	0.516	0.494	-0.49	1

IV. Summary of correlations

Correlations between chemical elements are highly dependent on the minerals present in the studied sample. Two chemical elements may be strongly correlated in one sample and not in another. In this case, the two elements are not in the same mineral in the second sample. This is the case for iron, which is bound to sulfur in the Yogou samples, whereas it is bound to titanium and weakly bound to sulfur (correlation coefficient 0.26) in the Donga samples. In the first case, the iron comes from pyrite, and in the second case, a significant proportion of the iron comes from anatase and detrital minerals. Silicon is also strongly bound to zirconium in

the Yogou samples, but it is not bound to any chemical element in the Donga samples. This is due to the inclusion of zircon in quartz in the Yogou samples, since almost all the silicon derives from quartz in both the Donga and Yogou formations.

V. Conclusion

Based on the results of the PCR analysis of the chemical elements present in the Donga and Yogou formations, it can be stated that the correlations between the chemical elements are highly dependent on the minerals present in the sample under study. This is the case of iron and silicon. The former is linked to sulfur in the Yogou samples, whereas it is linked to titanium and weakly linked to sulfur in the Donga samples, although silicon is not linked to any chemical element. This study reveals that the chemism of the deposit environments of the Donga and Yogou formations is different. Thus, the Donga formation is deposited in anoxic environments, whereas the Yogou formation is deposited from suboxic to anoxic environments.

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