

Assessment of Vanadium in Stream Sediments from River Mbete, Loum Area (Pan-African Fold Belt, Cameroon): Implications for Vanadium Exploration

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Abstract:- The Loum area is located in the southwestern part of the central domain of the Pan-African Fold Belt in Cameroon. The assessment of vanadium in this area is carried out through stream sediments survey in River Mbete. Collected samples were analyzed by AR-ICP-MS method. Analyses show Fe₂O₃ and MgO enrichment and mostly negative trend of major oxides with vanadium. V (av. = 926.7 ppm) and Mn (av. = 613.8 ppm) are highly concentrated in stream sediments while Ba, Ga and Sr have low contents, and the presence of Ba and Sr suggests their association with feldspar. Histogramic distributions show that trace elements are positively skewed. Strongly positive correlation coefficients and the close association between V and some elements indicates a common source. The antithetic relationship between vanadium and Co, Cr, Mn, Ni implies an empirical inverse distribution of Co, Cr, Mn, Ni, V in the V-formation. The correlation of Zn with Co, Cr, Mo, Mn, Ni, V, Sc is a reflection of their transition metals relationship, while the presence of Th and La reflects their mutual association as light ion Lithophile elements. Trace element concentrations were of geogenic origins and the high vanadium contents in the concentrates could be link to the volcanic emission. A four-factor model cumulatively accounting for 85.488% of the total variance data is recorded: factor 1 (Co- Cr- Mn- Ni- Sc) accounts for 43.516% of the total variance. The high loading of trace elements in factor 1 suggests their high mobility within the environment and the 43.516% of total variance suggests the significance of the elements in stream sediments, and Ni is associated with V. Factor 2 (Cr- Mn- zn- Ti) represents 18.496% of total variance and reflects an environment for the enrichment of Cr and Mn association. Factor 3 (Ba- Sc- Sr) accounts for 16.044% reflecting a lithological controlled formation. Factor 4 (Hg- Pb) contributes about 7.432% and suggests their association with chalcophile elements. Principal component analysis results in four components that explain 85.488% of the total variance. The first component (Co, Cr, Cu, Mn, Ni, Sc, Zn)

accounts for 53.882% of the variance is highly correlated and reflects the association of V with transition metals. The second component (Cu, Pb, Sb) accounting for 16.180% is correlated with chalcophile elements. The third component accounting for 8.612% of the variance is very weakly loaded. The fourth component (Pb, Hg) accounting for 6.814%. The resulting component plot shows the placement of elements in three major principal components, in which elements scattering in the rotated space displaying their mutual association. Cluster analysis gave rise to four clusters: cluster 1 (Ba, Ga, Th, Co, La) exhibits a strong correlation between Ba and Ga. Cluster 2 (Cr, Zn, Pb, Cu, Ni) shows a clear close geochemical relationship between the elements in this group. Cluster 3 (Mo, Sc, Sr) displays a strong correlation between Mo and Sc. Cluster 4 (Mn, V, Hg, Sb) illustrates a close association between Mn and V. The majority of trace elements fall within the background values, except Mn, Ni, Pb, V that contents exceed the upper background threshold values and therefore refer to anomalous, but these anomalous elements are not viable enough to be exploited. The median value of Loum vanadium is higher than the median values of vanadium recorded in Fongo-Tongo (Cameroon), in the world: Canada, Foregs samples, Upper continental crust, soil, and smaller than the one obtained in Ngaoundal (Cameroon). In the boxplot, patterns in V distribution between all solid sample media and laterite are broadly similar and different to the one reported from Loum V that shows higher. The results of this work serve as guide for vanadium exploration in the Loum area.

Keywords:- Loum Area; Pan-African Fold Belt; Vanadium; River Mbete; V-Formation; Geogenic Origins; Upper Background Threshold.

I. INTRODUCTION

Vanadium with chemical symbol V is a d-block transition metal, silver in color, appearing in the first long period of the periodic table between titanium and chromium, and belongs to group 5, along with Nb and Ta. It has an atomic number of 23, an atomic mass of 51 and is the 20th most abundant element in the earth's crust; approximately 138 ppm in the total continental crust [1]. It is, however, more dispersed in the crust than either of those elements, and concentrated mineral deposits are consequently rare. Vanadium has several oxidation forms (between +2 and +5) and two stable isotopes: ⁵⁰V (that is radioactive with a half-life of 1.5×10^{17} years) and ⁵¹V, with atomic abundance of 0.25% and 99.75%, respectively. In the lithosphere, vanadium displays three main oxidation states (+3, +4, +5), it occurs as reducing V(III) form, whereas in oxidizing conditions V prevails under V(IV) form. Vanadium (II) is particularly unstable in the environment. Vanadium (III) is more stable than V(II), but it is also gradually oxidized by the air or dissolved oxygen. Vanadium (V) is expected to be the prevailing form in waters exposed to atmospheric oxygen, whereas V(IV) may be present in reducing environments [2].

Vanadium is a lithophile metallic element at low pressure, but may be siderophile at the elevated pressures suggested for core formation in the Earth [3]. It is incompatible in most silicate minerals, although it may be moderately compatible in some pyroxenes [4]. Widely and sparsely distributed, V is not found as the free metal in nature. It originates from primary sources such as ores (iron oxide deposits), metallurgical slags (processing of U and Ti ores), and petroleum residues. Other sources include vanadiferous sandstones, bauxite, coals, or oil shales [2]. Vanadium is widely distributed in igneous and sedimentary rocks and minerals. Magnetite (Fe,V)₃O₄, carnotite [K₂(UO₂)₂(VO₄)₂·3H₂O], roscoelite [KV³⁺₂(Si₃Al)O₁₀(OH)₂], vanadinite [Pb₅(VO₄)₃Cl], mottramite [PbCu(VO₄)(OH)] and patrónite (VS₄) are the most important V-carriers. It is also present in some crude oils as organic complexes and also present as a trace element in mica, apatite, pyroxene and amphibole [3]. The vast majority of the world vanadium are derived from mineral concentrates (typically vanadium rich and titanium rich magnetite) separated from mined ore or as a by-product of steel making slags. It can also be obtained by heating crushed ore in the presence of carbon and chlorine to produce vanadium tri-chloride, which is then heated with magnesium in an argon atmosphere.

Vanadium is a rare, medium hard, ductile, steel blue metal, which is quite valuable in manufacturing industry due to its malleable, ductile and corrosion-resistant qualities [5], [6] and stability against alkalis and sulfuric and hydrochloric acids [7]. Vanadium is biologically active and is an essential nutrient for many animals. Its precise biochemical function is still in some doubt [8], but [9] suggest a role in peroxidase enzymes. An intake of over 10mg V per day can be toxic for adults, but this greatly depends on its speciation and oxidation state; the source is

usually airborne anthropogenic V [8]. In severe cases, toxic levels of V causes the inhibition of certain enzymes with animals, which has several neurological effects, and can cause breathing disorders, paralyzes and negative effects on the liver and kidneys. Little are known about vanadium in Cameroon. Preliminary investigations began in 1964 by Le Fur who indicated the concentration of vanadium in two ferruginous laterite nodules as follows: 1.26% V₂O₅ with 0.71% V and 1.12% V₂O₅ with 0.63% V respectively. These nodules were collected by Limasset in 1962 in Nkomakak situated at 3 km from Akom II in South Cameroon. Also multi-element analyses have been done in the processes of bauxitization of basaltic rocks in the Adamaoua Region [10]. The vanadium contents of certain basalts and bauxites from Fongo-Tongo (Ouest Cameroon) range between 12-320 ppm in the laterites (basalts alteration), 250 ppm in basalts and 60-438 ppm in bauxite from Fongo-Tongo [11]. Furthermore, [12] recorded the vanadium contents in Ngaoundal (Adamaoua Region) varying between 0.25-0.33% V₂O₅ in the basalt samples and 0.37-1.18% V₂O₅ in the laterite profiles. Vanadium deposits in Cameroon occur in the mafic rocks (doleritic gabbro, peridotite and amphibolites), their alteration products (Adamaoua bauxites, Fongo-Tongo bauxites, Bamboutos bauxites), also in bauxites and often riche in titanium [12]. The reserves of vanadium in the bauxites of Cameroon represent 7 tones and their contents vary from 0.47-1.12%. These contents and reserves are susceptible to constitute rentable deposits. The purpose of this work is to study the distribution and the origin of vanadium in stream sediment samples collected in river Mbete, Loum area in Cameroon.

II. GEOLOGIC SETTING

The study area is located in the southwestern part of the central domain of the Pan-African Fold Belt (PAFB) in Cameroon (Fig. 1). The PAFB or Central African Orogen is a major Neoproterozoic Orogen linked to the Trans-Saharan Belt of western Africa and to the Brasiliano Orogen of NE Brazil [13] and [14]. In Cameroon, three main domains were distinguished in the PAFB [15] - [21]. These are from south to north (Fig. 1): (1) the southern domain, which corresponds to the northern edge of the Congo Craton, formed by Neoproterozoic metasediments deposited in a passive margin environment and metamorphosed under high pressure conditions at 616 Ma; (2) the northern domain consisting of subordinate 830 Ma old metavolcanic rocks of tholeiitic and alkaline affinities; (3) the central domain, which contains the present study area, is situated between the Sanaga shear zone (SSZ) and the Betaré-Oya shear zone (BOSZ; [22] to the south, and the Tibati-Banyo fault (TBSZ) to the north [23]. Lithologically, the central Cameroon domain is dominated by a NE-SW elongated regional-scale plutonic complex intrusive into a Palaeoproterozoic basement and locally covered by Cretaceous deposits (Mbéré and Djérem basins) and by Cenozoic volcanic rocks of the Cameroon Volcanic Line (CVL).

The study area is located between latitude 4°43'-4°45' Nord and between longitude 9°40'-9°44' East and belongs to the southwest sector of the Tombel graben and constitute a sequence of the Tombel Shear Zone (TSZ) which is a segment of the Central Cameroon Shear Zone (CCSZ). The Tombel graben is a plutonic volcanic horst linked with metamorphic basement marked by two major tectonic events [24] intercalated between the strato-volcanoes of Mount Cameroon and Manengouba. The graben has the same N30°E elongation axis of the Cameroon Volcanic Line and is 44 Km long and 10-20 km wide defining a rectangle. Its surface is about 800 km² with a gradual increase in altitude from 100 km in the South to more than 500m in the North [24].

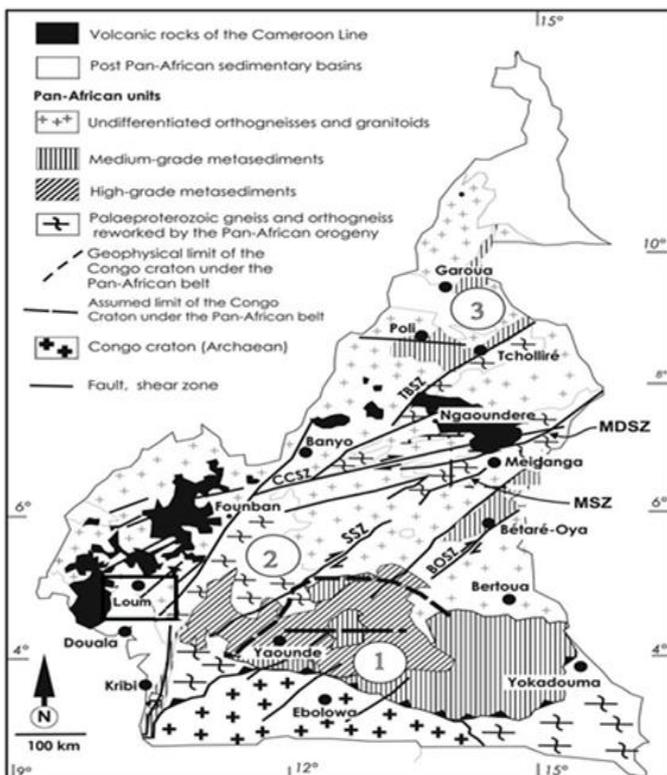


Fig 1:- Geologic map of Cameroon (modified from [16], [20], [22], [26], [27]) showing major lithotectonic units and shear zones: (1) southern domain; (2) central domain; (3) northern domain; CCSZ, Central Cameroon shear zone; TBSZ, Tcholliré-Banyo shear zone; SSZ, Sanaga shear zone; BOSZ, Betaré- Oya shear zone. The location of the study area Loum is marked by a box.

III. METHODS OF INVESTIGATION

A total of nineteen (19) active stream sediment samples were collected through panning from River Mbété in Loum with sample spacing of 150m. Global positioning system (GPS) instrument was used to locate the northings (latitudes) and eastings (longitudes). Sediments were collected about 50 cm deep to avoid high Fe-Mn oxide content and humus. Concentrates obtained then packaged in polythene bags, sealed and labeled. The samples were then air dried, weighed and packed in labeled sacks. Thirteen (13) samples were subsequently sent to Activation

Laboratories (ACTLABS) in Canada for geochemical analysis using the Aqua Regia - Inductively Coupled Plasma-Mass Spectrometry (AR-ICP-MS) method. The analysis provided data on the major and trace elements from which the elements had been used for this work. The concentrates were subjected to pre-analysis preparation by drying (60°C) and sieved (177 µm). 0.5g of the dried, sieved samples is then digested in aqua regia (combination of HCl and nitric acid to leach sulphides, some oxides and silicates) at 90°C in a micro-processor controlled digestion block from 2 hours. Details of the ICP-MS methods are given in [28]. Statistical method involving use of correlation analysis is done to explain and interpret the data in order to specify the elemental relationships. The factor analysis singles out variable elements that are mutually related into principal associations (factors) on the basis of their mutual correlation coefficient. These associations may now be interpreted to relate to lithology or mineralization or environmental issues. In the factor analysis, only elements with positive loadings greater than 0.40 are considered significant. The upper background threshold (UBT) formula below was adopted in the calculations and determination of elemental anomalies.

$UBTq = Md + 0.5 [3/q(Q3-Md)]^{1/2}$, where $q = 0.05$; $Md =$ Median; $Q =$ quartile.

The UBT can also be determined by using the proposal of [29] by taking into account the percentile of 98p, 95p along the cumulative curve distribution of the element concentrations. However, in most determinations, the UBT is calculated by using the formula stated above in the interpretation of elemental anomalies.

IV. RESULTS AND DISCUSSION

A. Major Elements

The major elements chemistry of stream sediments from River Mbete as presented in Table 1 show that the stream sediments host the following elements, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, and SO₃ at varying percentage. The chemical composition show that Fe₂O₃ varies between 18.2 to 29.4 wt% with an average of 23.82 followed by MgO (0.93 to 6.48 wt %) with an average of 2.74wt%. Al₂O₃ and TiO₂ range between 0.45-0.55.44 wt% and 0.31-0.45wt% respectively. The concentration of the others major elements falls above their respective detection limit, except SO₃ (< 1) that is uniform and its concentration falls below the detection limit. Major element variations are shown on selected graphs in Fig. 2. The overall major elements show negative trend with vanadium. Concentrations of Al₂O₃ and Fe₂O₃ increase monotonously with increasing amount of V while K₂O contents are scattered on variation diagrams (Fig. 2).

B. Trace Elements

Trace elements distribution (Table 1) shows that the study area hosts the following elements V, Ba, Sr, Cr, Co and Ni, Cu, Zn as trace metals, all at varying concentrations in parts per million. V (599 to > 1000 ppm; average = 926.7 ppm = 926.7 mg/kg according to the relation 1 ppm = g/t)

and Mn (459-942 ppm; average = 613.8 ppm) display higher contents while Cr (110-158 ppm) and Ni (85.4-331 ppm) show moderate values. The average content of vanadium (926.7 ppm; Table 1, 2) in the study area is very higher compared with the average V contents of CI

chondrites (54.6 ppm to 56.5 ppm), silicate Earth (86 ppm), bulk Earth (105 ppm), metallic core (150 ppm), bulk continental crust (96 ppm to 230 ppm; recommended average = 138 ppm [1].

AS ¹	LM1	LM2	LM3	LM4	LM5	LM6	LM7	LM11	LM12	LM13	LM15	LM16	LM19	DL ²
TiO ₂ (%)	0.305	0.37	0.311	0.453	0.354	0.445	0.406	0.4	0.344	0.34	0.362	0.389	0.377	0.001
Al ₂ O ₃	0.45	0.46	0.45	0.45	0.47	0.51	0.47	0.55	0.48	0.48	0.49	0.49	0.51	0.01
Fe ₂ O ₃	25	24.5	21.2	23	19.4	22.2	18.2	26.5	25.9	27	24.5	29.4	22.9	0.01
MgO	1.6	1.2	3.39	3.46	5.12	3.32	6.48	2.83	1.58	1.56	1.94	0.93	2.19	0.01
CaO	0.14	0.13	0.22	0.17	0.21	0.17	0.26	0.25	0.15	0.13	0.16	0.1	0.16	0.01
Na ₂ O	0.018	0.015	0.018	0.022	0.028	0.022	0.038	0.02	0.016	0.02	0.02	0.018	0.016	0.001
K ₂ O	0.02	0.02	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01
P ₂ O ₅	0.047	0.043	0.073	0.043	0.057	0.044	0.059	0.079	0.046	0.05	0.052	0.032	0.054	0.001
SO ₃	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1
Ag (ppm)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
As	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.5
Au	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.5
B	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	20
Ba	26.8	25.2	25.9	24.2	26.9	27.6	31.7	28.6	28.5	28	29.9	27.8	25.1	0.5
Bi	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
Cd	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
Co	38.3	35.6	47.8	54	61	49.8	72.9	47.1	40.7	41.2	42	37.1	41.7	0.1
Cr	110	115	121	148	137	136	158	130	116	113	122	118	120	1
Cu	41.9	5.6	9.1	99.6	100	114	29.4	7.6	6.2	6	6	6.1	62.9	0.2
Ga	24	24	19	19	16	20	14	24	26	26	24	28	21	1
Hg	0.02	0.04	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.01
Mn	459	510	580	721	770	664	942	618	564	542	544	524	542	1
Mo	4.7	5.3	4.3	4	3.3	3.7	2.9	5.1	5.8	5.5	5.4	5.5	4.6	0.1
Ni	117	99.7	221	213	280	196	331	184	139	134	153	85.4	165	0.1
Pb	408	4.3	10	125	64.3	135	40.7	3.2	1.2	4.7	1.5	1	1.6	0.1
Sb	0.4	< 0.1	1.2	1.6	0.3	1.9	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
Sc	2	2.1	2.3	2.4	2.7	2.5	3.2	2.8	2.4	2.3	2.4	2.4	2.4	0.1
Se	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.8	< 0.5	< 0.5	< 0.5	< 0.5	0.5
Sr	8	8	9	8	10	8	11	12	10	9	9	7	7	1
Te	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.2
Th	64.2	113	49.1	31	30.5	67.1	50.3	57.5	77.3	61.2	88.8	134	52.9	0.1
Tl	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
V	>1000	>1000	868	880	756	944	599	>1000	>1000	>1000	>1000	>1000	>1000	2
W	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
Zn	140	134	130	150	146	150	157	141	143	135	133	140	126	1
La	37	42	32	20	25	33	17	34	28	31	42	33	33	1

¹⁾ Analyte symbol; ²⁾ Detection limit

Table 1:- Chemical Analyses of Stream Sediments from River Mbete

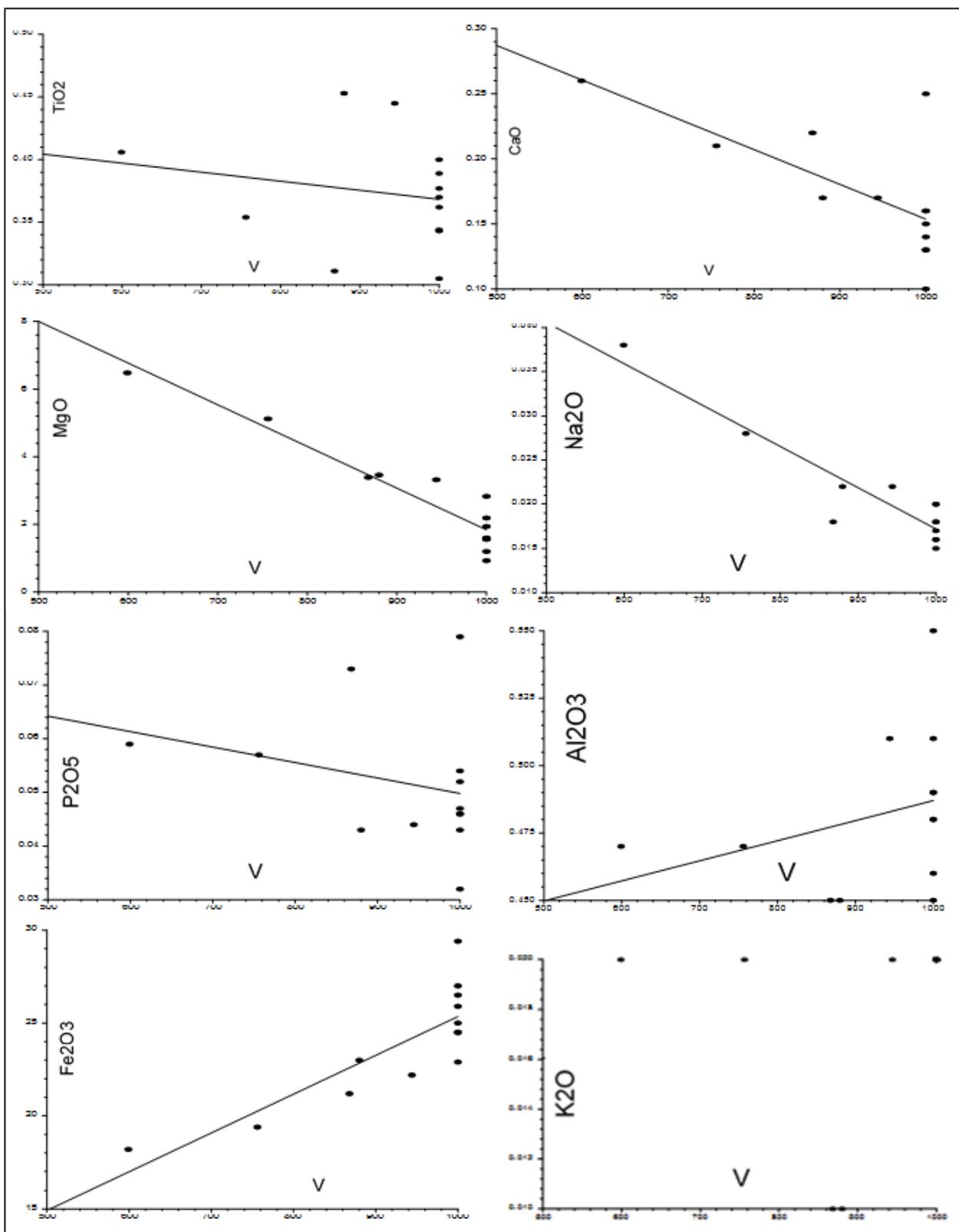


Fig 2:- Binary Plots of Major Elements against Vanadium

However, these values of V have been further reviewed by [30] - [32]. Ba and Ga contents are low and vary from 24.2 to 31.7 and 14 to 28 ppm respectively. Sr (7-12 ppm) is low and the presence suggests its association with feldspar. The concentrations of CaO and Zn in Table 1 show that their values range between 0.1 and 0.26 ppm and

from 126 to 157 ppm respectively. Pb (1-408 ppm; average = 61.6 ppm) and Th (30.5-134 ppm; average = 67.45 ppm) are present in the stream sediments, the source of Pb is doubtful but its high mobility potential is suggestive of extraneous input of material in the environment [33]. The elements such as Co, Cu and La show relative high

contents and the other trace elements like Ag, Au, B, Bi, Cd, Sb and Se yield below their respective detection limit.

B. Multivariate Statistic Analysis (MSA)

The MSA techniques is hitherto applied to examine the inter element associations using correlation, models and analysis. The analysis factors related variables into principal associations on the basis of their mutual correlation coefficients [34].

➤ Chemical Parameters

Table 2 presents the descriptive statistics of elements in stream sediments. The arithmetic mean, standard deviation, skewness, kurtosis, range and the upper background threshold (UBT) are summarized. Amongst the trace elements V, Mn, Ni, Zn, and Cr have values that range between 599 to >1000 ppm, 459-942 ppm, 85.4-331 ppm, 126 to 157 ppm, 110-158 ppm with their mean values as 926.69 ppm, 613.85 ppm, 178.32 ppm, 140.38 ppm and 126.46 ppm respectively. Ba (24.2 to 31.7 ppm) and Sr (7 to 12 ppm) are incompatible elements and they are weakly enriched in the samples. The presence of Th (30.5 to 134 ppm) and Pb (1 to 408 ppm) in the samples establishes their mutual relationship as radioactive elements [33]. The histogram distribution of Ga, Co, Pb, Th, Zn, Ni, Mn, V elements by skewness and kurtosis elements have been drawn and the frequency graphs for these elements are given in Fig. 3. The cumulative curves of the content distribution of elements show that they are positively skewed, an indication of their concentrative abundance as shown also in Table 2.

➤ Pearson Correlation Coefficient Factor

Some of the trace elements data in Table 1 are lognormally transformed into Table 3 before the performance of the factor analysis models as proposed by [35]. Orthogonal transformation of the factor matrix has been carried out in line with [36] method. The correlation coefficient values of the elements, using Pearson method, for the studied stream sediment samples is given in Table 3 in which the high correlation coefficient values ($r = 0.50-0.59$) are in green, strong correlation coefficient values ($r = 0.60-0.79$) are in yellow and very strong correlation coefficient values ($r = 0.80-0.99$) are in red. All of this suggests a common source for the elements.

Accordingly, there is a very strong positive correlation between V and Ga ($r = 0.88$) and between V and Mo ($r = 0.86$). An antithetic relationship exists between vanadium and Co, Cr, Mn, Ni (Fig. 4) which is reflected in the very strong negative correlation ($r = -0.81$ to -0.95) between the five components and in the empirical inverse

distribution of Co, Cr, Mn, Ni and vanadium in the V-formation. The strong correlation is observed between V and La, V and Sc, and V displays a high correlation coefficient with Th (Table 3; Fig. 4). The close association between V and these elements indicates a common source. Zn correlates with Co, Cr, Mn, Ni, Sc and negatively with La, Mo and V. The correlation of Zn with Co, Cr, Mo, Mn, Ni, V and Sc (Table 3) is a reflection of their transition metals relationship. Th correlates easily with both the transition metals (Cr, Cu, Mn, Mo, Co, Ni) and the rare earth element (La) as well as with Ga. The presence of Th and La in the samples reflects their mutual association as light ion Lithophile elements (LILE) that are usually mobile. Trace element concentrations in stream sediments were of geogenic origins and not influenced by anthropogenic sources. The generally high vanadium contents in all the stream sediment samples could be link to the volcanic emission, with relation to basaltic rocks of Mount Kupe, one of the volcanoes of the Cameroon Volcanic Line, situated around the study area and lying in the Tombel Graben. Therefore, the results of this work serve as guide for vanadium exploration in the Loum area.

➤ Factor Analysis

Table 4 presents a four-factor model cumulatively accounting for 85.488% of the total data variance. Factor 1 (Co- Cr- Mn- Ni- Sc) is heavily loaded with respect to Co, Mn and Ni. Other elements that have contributed to the loading significantly are Cu, Hg, Sr, Zn, Ga, Mo, Sb and Fe. The elements Ga (-0.961%) and Mo (-0.888%) display a negatively high loading implying that the samples are depleted in Ga and Mo. The factor accounts for 43.516% of the total variance of the 4-factor model. The high loading of the trace elements suggests their high mobility within the environment. The 43.516% of total variance suggests the significance of the elements in stream sediments and Ni is associated with vanadium. Factor 2 (Cr- Mn- zn- Ti) accounts for almost 18.496% of total data variance. This element grouping reflects an environment for the enrichment of two associated minerals Cr and Mn. Factor 3 (Ba- Sc- Sr) accounts for 16.044% of total data variance with Ba and Sr elements contributing more loading and reflecting a lithological controlled formation. The association of Ba and Sr in this factor is an implication of their relationship to feldspar. Furthermore, the strong loading of Ba (0.865%) may be due to the formation of (BaCO_3), white mineral. Factor 4 (Hg) contributes about 7.432% of the total data variance and suggest his association with the chalcophile elements together with Pb (-0.802%) that also contribute a bit to the loading of this factor.

	Mean	Median	Mode	Std. Deviation	Variance	Skewness	Kurtosis	Range	Min	Max	UBT	25 P ³	50 P	75 P
AS														
Ba	27.4	27.6	24.2 ^a	2.07	4.27	0.44	0.21	7.5	24.2	31.7	28.86	25.55	27.6	28.55
Co	46.86	42	35.6 ^a	10.62	112.84	1.41	1.88	37.3	35.6	72.9	42.39	39.5	42	51.9
Cr	126.46	121	110 ^a	14.52	210.77	1.05	0.32	48	110	158	121.31	115.5	121	136.5
Cu	38.03	9.1	6	41.84	1750.81	0.95	-0.79	108.4	5.6	114	9.13	6.05	9.1	81.25
Ga	21.92	24	24	4.15	17.24	-0.51	-0.53	14	14	28	25.22	19	24	25
La	31.31	33	33	7.42	55.06	-0.48	0.04	25	17	42	33.77	26.5	33	35.5
Mn	613.85	564	542	131.58	17312.47	1.46	2.13	483	459	942	564.11	533	564	692.5
Mo	4.62	4.7	5.50	0.93	0.86	-0.57	-0.83	2.9	2.9	5.8	6.11	3.85	4.7	5.45
Ni	178.32	165	85.4 ^a	70.67	4993.61	0.85	0.43	245.6	85.4	331	165.17	125.5	165	217
Pb	61.58	4.7	1 ^a	114.37	13080.89	2.67	7.79	407	1	408	4.83	1.55	4.7	94.65
Sb	0.48	0.1	0.1	0.64	0.42	1.56	0.97	1.8	0.1	1.9	1.56	0.1	0.1	0.8
Sc	2.45	2.4	2.4	0.31	0.09	1.11	2.07	1.2	2	3.2	5.14	2.3	2.4	2.6
Sr	8.92	9	8	1.5	2.24	0.68	-0.06	5	7	12	10.22	8	9	10
Th	67.45	61.2	30.5 ^a	29.92	895.15	1.05	0.89	103.5	30.5	134	61.46	50	61	83.05
V	926.69	1000	1000	124.31	15452.9	-1.91	3.36	401	599	1000	1000.27	874	1000	1000
Zn	140.38	140	140 ^a	8.85	78.26	0.23	-0.45	31	126	157	140.43	133.5	140	148
Ti	3737.69	3700	3050	450.61	203052.56	0.30	-0.37	1480	3050	4530	3700.07	3435	3700	4030
Fe	238230.77	245000	245000	31252.08	976692307.69	-0.17	-0.20	112000	182000	294000	245000.01	217000	245000	262000

³⁾ Percentile

Table 2:- Descriptive Statistic of Elements

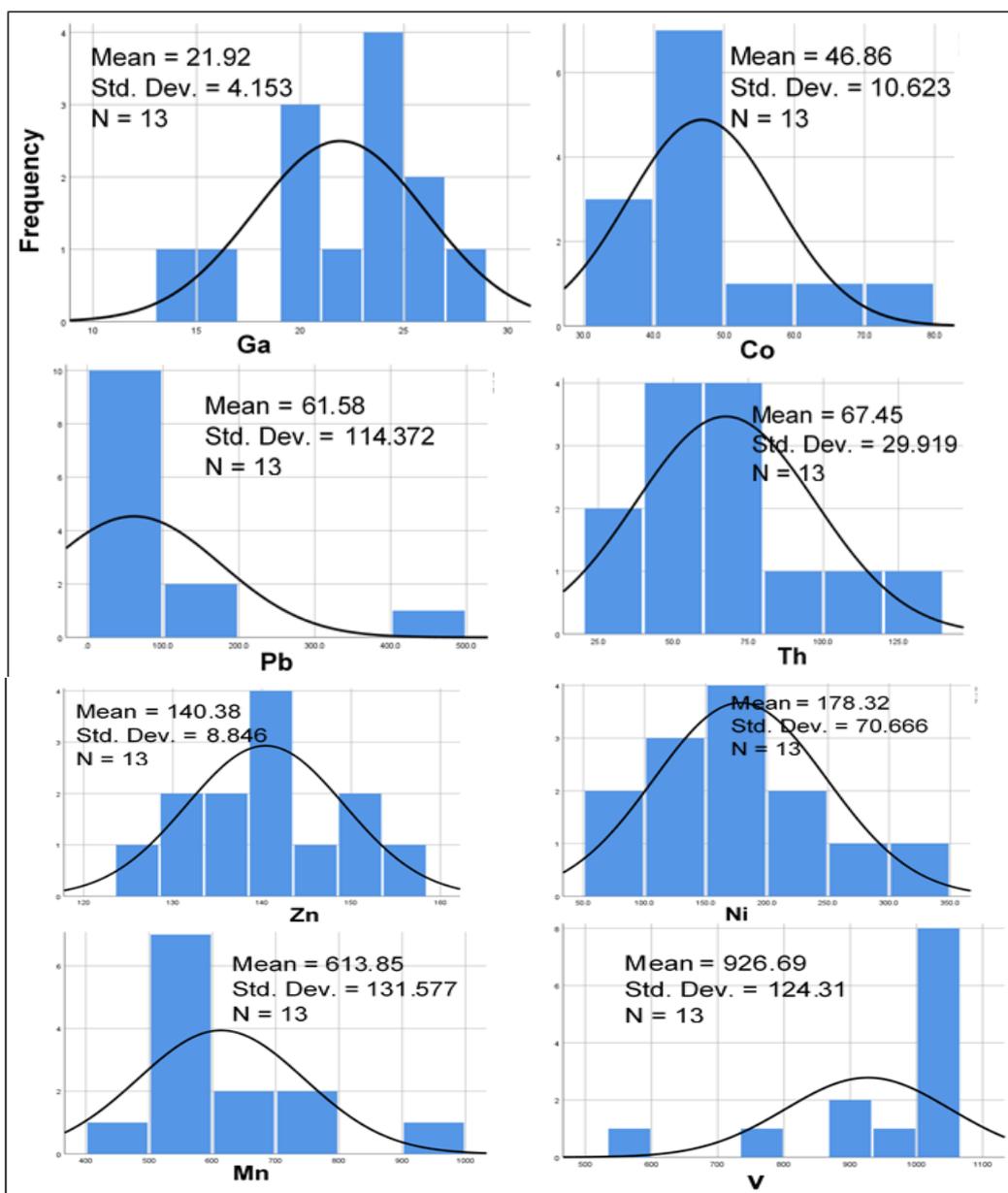


Fig 3:- Cumulative Frequency of Selected Elements

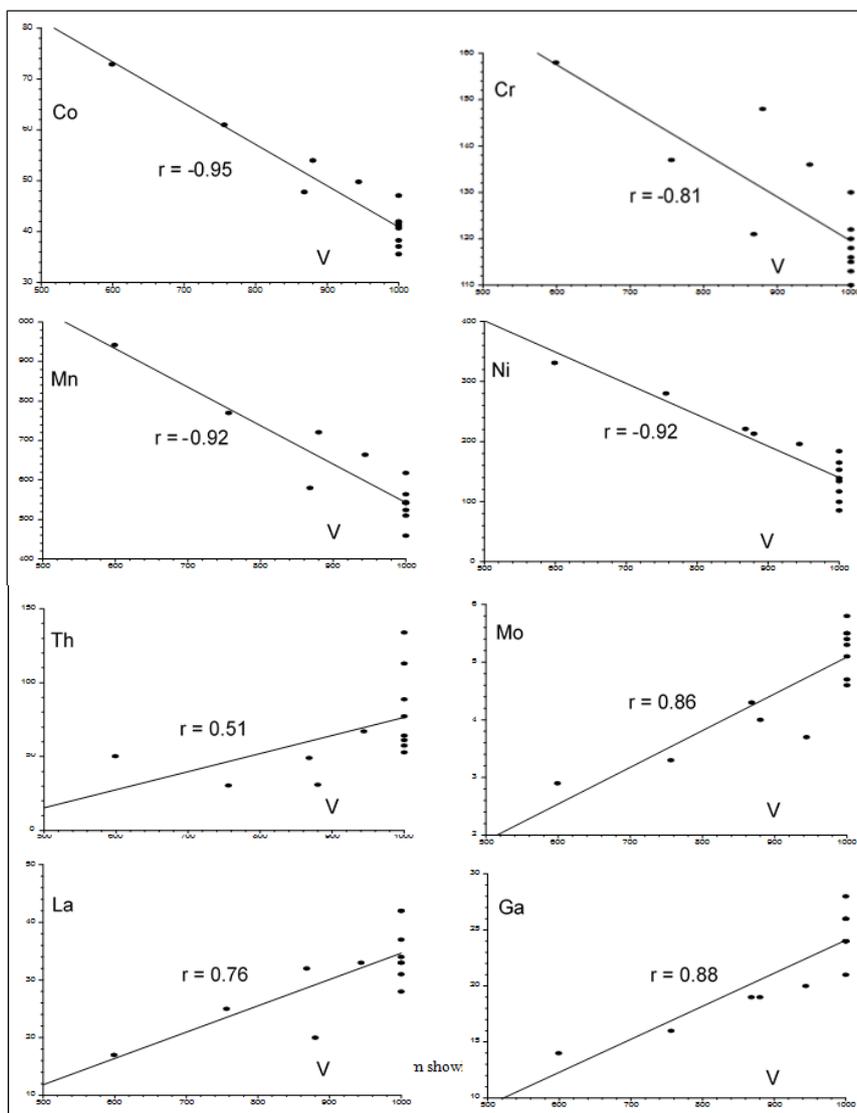


Fig 4:- Binary plots of trace elements against vanadium showing negative and positive correlation

	Ba	Co	Cr	Cu	Ga	Hg	La	Mn	Mo	Ni	Pb	Sb	Sc	Se	Sr	Th	V	Zn
Ba	1																	
Co	0.37	1																
Cr	0.25	0.92	1															
Cu	-0.36	0.44	0.52	1														
Ga	-0.04	-0.89	-0.80	-0.58	1													
Hg	-0.25	0.27	0.30	0.20	-0.41	1												
La	-0.15	-0.8	-0.77	-0.40	0.63	-0.20	1											
Mn	0.38	0.98	0.95	0.43	-0.84	0.34	-0.82	1										
Mo	-0.05	-0.88	-0.81	-0.69	0.95	-0.33	0.64	-0.83	1									
Ni	0.29	0.97	0.85	0.44	-0.94	0.28	-0.74	0.92	-0.88	1								
Pb	-0.17	-0.02	-0.05	0.39	-0.08	-0.12	0.02	-0.12	-0.25	-0.06	1							
Sb	-0.40	0.21	0.36	0.65	-0.36	0.31	-0.22	0.20	-0.45	0.24	0.31	1						
Sc	0.63	0.84	0.80	0.15	-0.59	0.03	-0.64	0.87	-0.58	0.79	-0.34	-0.11	1					
Se	0.16	-0.17	-0.22	-0.23	0.29	0.18	-0.13	-0.11	0.38	-0.17	-0.16	-0.18	-0.05	1				
Sr	0.60	0.53	0.39	-0.23	-0.28	0.05	-0.33	0.51	-0.18	0.54	-0.22	-0.26	0.68	0.22	1			
Th	0.13	-0.64	-0.52	-0.56	0.71	-0.04	0.60	-0.54	0.65	-0.73	-0.22	-0.36	-0.35	0.01	-0.37	1		
V	-0.33	-0.95	-0.81	-0.31	0.88	-0.38	0.76	-0.92	0.86	-0.92	0.02	-0.12	-0.73	0.18	-0.42	0.51	1	
Zn	0.39	0.71	0.76	0.45	-0.48	0.30	-0.70	0.77	-0.60	0.57	0.26	0.31	0.61	0.09	0.38	-0.27	-0.63	1

Table 3:- Person Correlation Matrix

AS	Factor 1	Factor 2	Factor 3	Factor 4
Ba	0.079	0.209	0.865	-0.053
Co	0.873	0.411	0.248	0.028
Cr	0.693	0.681	0.099	0.092
Cu	0.471	0.448	-0.582	-0.292
Ga	-0.961	-0.181	0.102	-0.068
Hg	0.374	0.095	-0.384	0.632
La	-0.650	-0.479	-0.143	0.036
Mn	0.788	0.536	0.251	0.141
Mo	-0.888	-0.330	0.150	0.100
Ni	0.936	0.254	0.195	0.052
Pb	0.110	-0.020	-0.337	-0.802
Sb	0.257	0.399	-0.684	-0.133
Sc	0.552	0.499	0.601	0.152
Sr	0.402	0.052	0.721	0.060
Th	-0.787	0.000	0.096	0.327
V	-0.881	-0.252	-0.221	-0.127
Zn	0.423	0.762	0.159	-0.152
Ti	0.044	0.921	-0.166	0.166
Fe	-0.951	-0.026	0.122	-0.117
Value	8.268	3.514	3.048	1.412
% of Var.	43.516	18.496	16.044	7.432
Cum. %	43.516	62.012	78.057	85.488

Table 4:- Varimax Rotated Factor Analysis with Kaiser (1958) Normalization

➤ *Principal Component Analysis (PCA)*

Principal component analysis is usually used as a complementary method to better determine and interpret the relationships between the soil variables. This method is based on the correlation matrix among the variables [37]. It can explain much information about the basic structure of the data, and also, the possible relationships among the data [38]. PCA results in four components that explain 85.488% of the total variance for the studied samples is presented in (Table 5). This table provides the factor loadings of the original variables studied here and the four components generated by PCA that helps in interpreting these components. The first component that accounted for 53.882% of the variance was highly correlated with Co (0.985%), Cr (0.939%), Cu (0.545%), Mn (0.973%), Ni (0.962%), Sc (0.784%), Zn (0.739%), reflecting the association of vanadium with transition metals (Table 5). The second component accounting for 16.180% of the

variance is correlated with chalcophile elements: Cu (0.699%), Pb (0.525%) and Sb (0.0737%). The third component accounting for 8.612% of the variance is very weakly loaded. The fourth component accounting for 6.814% of the variance is correlated with Pb (0.680%) and a minor contribution of Hg (-0.709%). The component plot (Fig. 5) obtained after component analysis shows the placement of elements in three major principal components, in which elements scattering in the rotated space displaying their mutual association.

AS	Principal Components			
	PC 1	PC 2	PC 3	PC 4
Ba	0.254	-0.804	-0.107	0.279
Co	0.985	-0.143	0.053	0.031
Cr	0.939	-0.017	-0.281	-0.016
Cu	0.554	0.699	-0.148	0.173
Ga	-0.920	-0.182	-0.276	0.128
Hg	0.354	0.261	-0.016	-0.709
La	-0.808	0.043	0.104	-0.092
Mn	0.973	-0.174	-0.112	-0.054
Mo	-0.914	-0.269	-0.136	-0.047
Ni	0.962	-0.099	0.214	-0.031
Pb	0.026	0.525	0.177	0.680
Sb	0.337	0.737	-0.232	0.004
Sc	0.784	-0.538	-0.179	0.029
Sr	0.453	-0.669	0.158	0.094
Th	-0.670	-0.244	-0.412	-0.240
V	-0.918	0.148	-0.180	0.093
Zn	0.739	-0.038	-0.439	0.261
Ti	0.458	0.173	-0.813	-0.075
Fe	-0.837	-0.181	-0.399	0.200
Eigen value	10.238	3.074	1.636	1.295
% of Var.	53.882	16.180	8.612	6.814
Cum. %	53.882	70.062	78.674	85.488

Table 5:- Factor Loadings of the Stream Sediments Variables

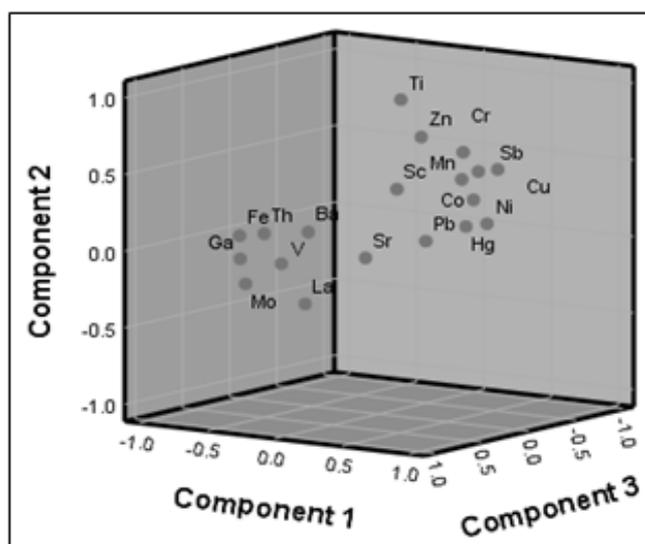


Fig 5:- Component plot in the rotated space for three PCA components

➤ Cluster Analysis

Cluster analysis as a technique in multivariate statistical analysis helps in finding the real groups and reduces the data density. This type of analysis was carried out for the normalized data as follows Fig. 6. There are four important paragenetic groups or clusters based on the cluster analyses (dendrograms) of the geochemical data obtained in Loum. The first group contains Ba and Ga associated with minor amounts of Th, Co and La. In this group, there is a strong correlation between Ba and Ga. These elements show rather weak correlations with La, Co and Th. The second group comprises Cr and Zn associated with Pb, Cu and Ni. Within this group, there is a strong correlation between Cr and Zn. There is a clear close geochemical relationship between these elements in this group. There is a strong correlation between Mo and Sc with amount of Sr in the third group. The fourth group comprises Mn and V associated with minor amounts of Hg and Sb which have a strong correlation between Mn and V (Fig. 6).

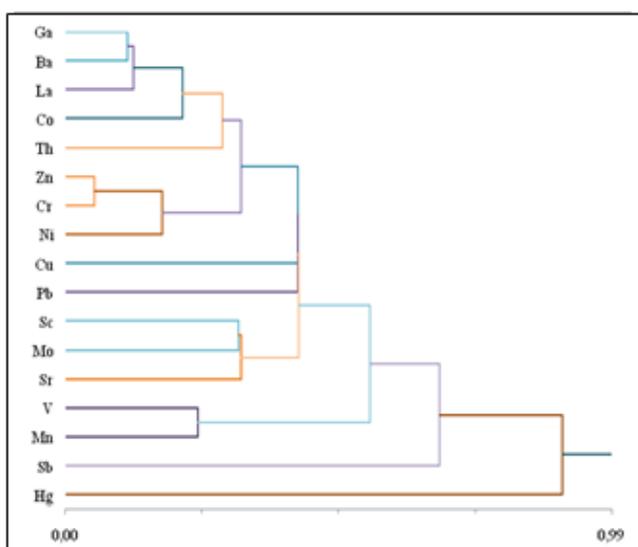


Fig 6:- Cluster Analysis Plot

➤ Upperbackground Threshold (UBT)

The upper background threshold (UBT) values are calculated for the trace elements and the values are presented in Tables 2. The UBT is the upper limit of element concentration above which the element is considered anomalous. Most of the trace elements calculated fall within the background values (Table 1, 2) except Mn and Ni in samples LM3 to LM11, Pb (samples LM1, LM3 to LM7). V (samples LM1, LM2, LM11 to LM19) whose contents exceed the UBT [Mn (564.11 ppm),

Ni (165.17 ppm), Pb (4.83 ppm), V (1000.27 ppm)] respectively and are therefore anomalous. However, these anomalous elements are not viable enough to be exploited.

C. Comparison of Loum Vanadium with some Reference Datasets

The Loum V is compared with other known deposits in the world in term of median concentration (Table 6). The median value of vanadium (1000 ppm = 1000 mg/kg) in stream sediments of River Mbete is greater than the median values for the total vanadium (Table 6) recorded in stream sediments in Canada (38 mg/kg, Aqua regia ICP-AES method [39], in the Foregs samples [3]: 62 mg/kg (Total XRF analysis), with a range from < 2 to 407 mg/kg, and 29 mg/kg (Aqua regia ICP-AES method). High V values in stream sediment (> 89 mg/kg) are located mainly in southern Finland, northern Fennoscandia (iron ores), central Norway (Caledonian layered mafic intrusions such as Sulitjelma), and the Caledonides of Norway generally [3]. The values of vanadium (ICP-MS analysis) are a bit higher in subsoil (63 mg/kg) and topsoil (60 mg/kg), with a range from 1.28 to 325 mg/kg in subsoils and 2.71 to 537 mg/kg in topsoils [3], in the Upper continental crust (97 mg/kg; [1], in soil (90 mg/kg; [40], but they are still more smaller compared with the median of the studied vanadium. Also total V values in stream sediments from River Mbete is largely greater than V from floodplain sediment determined by XRF, vary from < 2 to 266 mg/kg, with a median of 56 mg/kg, and the aqua regia extractable from 3 to 140 mg/kg vanadium, with a median of 29 mg/kg [3]. The median value of vanadium of laterite materials resulted from the bauxitization processes of hawaite in Adamaoua at Ngaoundal (Cameroon) is 0.56% and 0.29% in basalts [12]. These concentrations of vanadium correspond to 0.56% V₂O₅ and 0.29% V₂O₅ respectively. They are also respectively equivalent to 5600 ppm = 5600 mg/kg and 2900 ppm = 2900 mg/kg following the relation 1% = 10⁴ ppm. In the laterites, V concentrations range from 0.37 to 1.18% (= 3700 to 11800 ppm or 3700 to 11800 mg/kg), and this vanadium is exploitable. The median concentration of Loum V is also greater than the one recorded by [11] in bauxites from Fongo-Tongo (64 ppm).

In a boxplot comparing V variation of Loum with sample media (subsoil, topsoil, stream sediment, floodplain sediment [3] and laterite [11]) presented in Fig. 7, patterns in V distribution between all solid sample media and laterite are broadly similar. These patterns are different to the one seen of stream sediment reported in Loum that shows higher than in other sample media and laterites.

Vanadium (V)	Origin-source	Number of samples	Size fraction (mm)	Extraction	Median (mg/kg)	References
Crust	Upper continental	n.a.	n.a.	Total	97	[1]
Subsoil	FOREGS	790	<2	Total (ICP-MS)	62.8	[3]
Subsoil	FOREGS	784	<2	Aqua regia (ICP-MS)	33	
Topsoil	FOREGS	843	<2	Total (ICP-MS)	60.4	
Topsoil	FOREGS	837	<2	Aqua regia (ICP-MS)	33	
Soil	World	n.a.	n.a.	Total	90	
Soil, C-horizon	Barents region	1357	<2	Aqua regia (ICP-AES)	24.2	[41]
Water	FOREGS	807	Filtered <0.45 µm		0.46 µg/l	[3]
Water	World	n.a.	n.a.		1 µg/l	[42]
Stream sediment	FOREGS	852	<0.15	Total (XRF)	62	[3]
Stream sediment	FOREGS	845	<0.15	Aqua regia (ICP-AES)	29	
Floodplain sediment	FOREGS	747	<2	Total (XRF)	56	
Floodplain sediment	FOREGS	747	<2	Aqua regia (ICP-AES)	29	
Stream sediment	Canada	49938	<0.18	Aqua regia (ICP-AES)	38	
Laterite	Ngaoundal (Cameroon)	38	n.a.		0.56% V ₂ O ₅ = 5600 ppm = 5600 mg/kg	[12]
Basalt		2			0.29% V ₂ O ₅	[11]
Laterite basalt	Ouest Cameroon	5			64 ppm	
Bauxite	Fongo-Tongo (Ouest Cameroon)	2			249	
Ferruginous nodule	Akom II (South Cameroon)	2			1.19% V ₂ O ₅ ; 0.67% V	Le Fur, in 1964
Stream sediment	Loum (Cameroon)	13	n.a.	Aqua regia (ICP-MS)	1000 ppm = 1000 mg/kg	This study

Table 6:- Comparison of Loum V in Stream Sediments with Some Reference Datasets

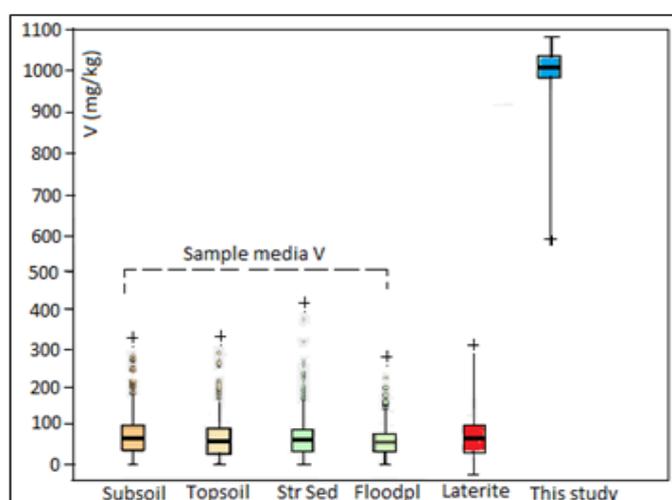


Fig 7:- Boxplot comparison of V variation of Loum with sample media V [3] and laterite V [11].

V. CONCLUSION

Stream sediments geochemical survey carried out in River Mbete, Loum area within the Pan-African Fold Belt in Cameroon has revealed Fe₂O₃ (av. = 23.82%) and MgO (av. = 2.74%) enrichment with mostly negative trend of major oxides with vanadium. V (av. = 926.7 ppm) and Mn (av. = 613.8 ppm) are highly concentrated in stream sediments while Ni, Zn and Cr exhibit moderated concentrations. The average content of vanadium in Loum is very higher compared with the average V contents of CI chondrites, silicate Earth, bulk Earth, metallic core and bulk continental crust. Ba, Ga and Sr have low contents and the presence of Ba and Sr suggests their association with feldspar. The histogrammic distributions show that trace elements are positively skewed.

Strongly positive correlation coefficients (r = 0.50-0.99) and the close association between V and some elements indicates a common source. The antithetic relationship between vanadium and Co, Cr, Mn, Ni underlined by a very strong negative correlation (r = -0.81

to -0.95) implies an empirical inverse distribution of Co, Cr, Mn, Ni and vanadium in the V-formation. The correlation of Zn with Co, Cr, Mo, Mn, Ni, V and Sc is a reflection of their transition metals relationship, while the presence of Th and La reflects their mutual association as light ion Lithophile elements (LILE) that are usually mobile. Trace element concentrations were of geogenic origins and not influenced by anthropogenic sources. The generally high vanadium contents in stream sediments could be link to the volcanic emission, with relation to basaltic rocks of Mount Kupe, one of the volcanoes of the Cameroon Volcanic Line, situated around the study area and lying in the Tombel Graben. Therefore, the results of this work serve as guide for vanadium exploration in the Loum area.

A four-factor model cumulatively accounting for 85.488% of the total variance data is recorded: factor 1 (Co- Cr- Mn- Ni- Sc) accounts for 43.516% of the total variance of the 4-factor model, the high loading of trace elements suggests their high mobility within the environment and the 43.516% of total variance suggests the significance of the elements in stream sediments, and Ni is associated with vanadium. Factor 2 (Cr- Mn- zn- Ti) represents 18.496% of total variance and reflects an environment for the enrichment of two associated minerals, Cr and Mn. Factor 3 (Ba- Sc- Sr) accounts for 16.044% of total variance reflecting a lithological controlled formation. Factor 4 (Hg- Pb) contributes about 7.432% of the total data variance and suggest their association with chalcophile elements.

Principal component analysis results in four components that explain 85.488% of the total variance. The first component (Co, Cr, Cu, Mn, Ni, Sc, Zn) accounts for 53.882% of the variance is highly correlated and reflects the association of vanadium with transition metals. The second component (Cu, Pb, Sb) accounting for 16.180% is correlated with chalcophile elements. The third component accounting for 8.612% of the variance is very weakly loaded. The fourth component (Pb, Hg) accounting for 6.814%. The resulting component plot shows the placement of elements in three major principal components, in which elements scattering in the rotated space displaying their mutual association.

Cluster analysis gave rise to four clusters: (i) cluster 1 (Ba, Ga, Th, Co, La) exhibits a strong correlation between Ba and Ga, and weak correlations with La, Co, Th; (ii) cluster 2 (Cr, Zn, Pb, Cu, Ni) shows a clear close geochemical relationship between the elements in this group; (iii) cluster 3 (Mo, Sc, Sr) displays a strong correlation between Mo and Sc; (iv) cluster 4 (Mn, V, Hg, Sb) illustrates a close association between Mn and V. Majority of the trace elements fall within the background values except Mn, Ni, Pb and V that contents exceed the UBT values and therefore refer to anomalous. However, these anomalous elements are not viable enough to be exploited.

The median value of Loum vanadium (1000 ppm = 1000 mg/kg) is largely higher than the median values of vanadium recorded in Fongo-Tongo (Cameroon), in the world: Canada, Foregs samples (subsoils, topsoils, foodplain, stream sediment), Upper continental crust, soil, and smaller than the one obtained in Adamaoua Region in Cameroon. In the boxplot, patterns in V distribution between all solid sample media and laterite are broadly similar and different to the one reported from Loum V that shows higher.

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