

Petrography, Sedimentology and Geochemistry of Rocks and Sediments from Three Key Localities from the South-East Region of the Yaoundé Group (Centre Region, Cameroon): **Implications for Rutile Exploration**

Jules Mbanga Nyobe1*, Louise Marie Ngo Bidjeck Bondje1, Dieudonné Charles Ilouga2, Elisé Sababa¹

¹Department of Earth Sciences, University of Yaoundé I, Yaoundé, Cameroon ²Higher Teachers Training College, University of Yaoundé I, Yaoundé, Cameroon Email: *julesnyobe@yahoo.com

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Abstract

The Otele, Matomb and Nguibassal localities correspond to the SW part of the Yaoundé Group. Field observations, rocks and stream sediments of the study area were examined using rock tin sections, granulometric, morphoscopic and X-ray fluorescence analysis to identify their distribution, the nature of the basement, provenance useful minerals and some weathering process that affect them to show the exploration significance of these outcomes. From these it appears that, three rocks types occur in the areas: gneisses, micaschists and amphibolite, respectively with the following minerals assemblage: (Fks + Bt + Qz + Ky + Pl + Msc + Grt + Op), (Bt + Qz + Msc + Fks + Op + Ky + Grt) and (Amp + Bt + Pl + Kfs + Qz + Px + Grt + Op). Sedimentological analyses reveal the dominance of unworn grains of rutile quartz and kyanite that suggest a short transport; while less abundant minor shiny dulls and sub-rounded grains suggest a long transport. Sediments collected are homometric, well sorted, well classified, with immature rutile due to their angular shapes. Silica is the most important major element ranging in concentration between 47.56 wt% SiO₂ in amphibolite to 61.21 wt% SiO₂ in gneiss. Stream sediments chemistry equally showed that silica and alumina are the remarkable elements with values of 53.92 wt% and 13.33 wt% respectively with important increase of TiO₂ ranging between 51.77 and 95.03 wt%. The TiO₂ percentage met in minerals of the global fraction and rutile concentrate come from the same minerals in the rock, and percentage increases when linked to heavy minerals observation suggested the Ti percentage to mainly come from rutile. Impurities present in the rutile lattice include: V, Nb, Ta, Cr and CaO. Rutile was found to come from the same area but with several source rocks (Felsic and mafic). High Nb contents (277 - 768.33 ppm) as compared to Cr (394 - 444.33 ppm) associated to the elevated ratio of LREE/HREE coupled to the negative Eu anomalies in rocks and sediments of the study area are indicative of felsic source material. Moreover, enrichment in Cr as compared to Nb at Nguibassal suggested rutile to originate from mafic rocks.

Keywords

Rutile, Global Fraction, SW Yaoundé Group, Unworn Grains, Impurities

1. Introduction

The SW part of the Yaoundé Group contained several key rutile host areas among which Otele, Nguibassal and Matomb. This Group is characterized by rocks containing kyanite and rutile [1]. Lithologic formations are constituted by a mixture of kyanite-titanite minerals containing variable part of cryptocrystalline to paracrystalline compounds [2] [3] associated to zircon [4]. Prospected zones in the Yaoundé Group are limited but geochemical characteristics are similar from one sector to another. The source of heavy metals in the listed key zones, particularly for rutile is subject to several hypotheses. Some works (e.g. [1] [5]) envisaged local deposits and indicated that sources were probably in the Yaoundé Group. However, according to [4], the minerals could have been issued from metamorphic formations, and their distribution being assured by the various nearby water courses. Moreover, [4] proposed a supply from local sources, because prospection in the watershed of Lobo, NW of the Yaoundé Group has revealed considerable concentration of rutile in alluviums and in nearby rocks. According to this author, a great part of the alluvial material of this sector has been probably furnished by the metamorphic rocks in place. They further suggest that, the rocks in place could have concentrated rutile at the time of their formation and dismantling.

Deciphering these assertions could be of great importance when it comes to rutile exploration in the Yaoundé Group. The validity of these proposed hypotheses can be tested by petrographic, sedimentologic and geochemical study of materials from these three key areas of the SW of Yaoundé Group. The aim of this study is to characterize rocks and mainly sediments in order to rutile exploration in the study area.

2. Geographical and Geological Setting

The Otele, Nguibassal and Matomb areas are located in the Center Region of Cameroon, in the Nyong and Kelle Division as well as a small part of the Mefou and Akono Division, in the central region of Cameroon. It lies between the parallels 3°36'15" to 4°2'56" North and meridians 11°2'10" to 11°17'37" East (**Figure 1**).



Figure 1. Location map of the study area in the central region of Cameroon [1].

According to the Eseka climatic data close to the study area, the climate is of equatorial type with four seasons and it belongs to the dense humid forest domain, characterized by a dominant step of raised trees and a lower floor or sub-wood formed of trees and of rare herbaceous plants [6]. The area belongs to two watersheds: the Sanaga at Lobo and the Nyong at Teba and Nyamakouba with a dendritic hydrographic network.

The study areas are included in the Yaoundé Group, which is an allochthonous unit emplaced onto the Congo Craton that constitutes a part of the Central African Mobile Zone (CAMZ) [1] [7] [8]. Two great geological formations underlie South Cameroon within the CAMZ. The basement constituted of metamorphic rocks (gneisses, quartzites and schists) and the Yaoundé Group that comprises the Mbalmayo-Bengbis-Ayos series and the Yaoundé series [9]. The occurrence of rutile and kyanite in the East and West of Yaoundé Group is known in gneisses and micaschists since the last century.

3. Methodology

3.1. Field Methods

Geological fieldwork mainly involved sampling, with a total of 36 samples representing the various lithologies of the study area collected in the field. In addition, 1.5 kg of stream sediment samples were collected in each sampling point of the three main locations, with four at Otele (Nyk1p, NykIIv, Nyk2, and SOP1) in the Nyamakouba watershed, two at Nguibassal (MBE, and MBA) in the Lobo watershed and three at Matomb (VRO1, VRO2, and MTC) in the Teba watershed, panned *in situ* during the river alluvial survey.

3.2. Laboratory Methods

A total of 16 samples from three locations were collected in the field, including 8 rock types among which: gneisses (KA1, NK2, GE2, and Ml), amphibolites (NKD1 and NKD2) and micaschists (RM, Li); alongside 8 stream sediments samples with the global fraction (SOP1, VSO1, and VSO2) and the concentrate (MBE, MBA, and MTC).

Representative rocks outcropping in the area devoid of any visible secondary alteration were selected, with thin sections done and investigated at the Institute of Mining and Geological Research of Nkolbisson (Cameroon).

The global fraction of stream sediments was collected and lager clasts removed with the sieve of mesh 5 mm. The sediment concentrates were also prepared after washing the sample in a pan and shaking it sideways. Thus, heavy minerals could be found at the bottom.

Scanning separation of pre-concentrated heavy minerals of stream sediments were done at Otele, in two localities (Mabando and Nkolmelen) on four points, at Nguibassal on two points and Matomb on three points (Figure 1). All the collected stream sediment samples were dried in an oven, and then split to obtain two samples of 750 g each. They were then subjected to sedimentological analysis, including: granulometric analysis (sieving with a standardized AFNOR sieve column using the methods of [10] and [11]. The limits of sorting used are those of [12], while the asymmetric coefficient was interpreted as per [13].

Heavy mineral separation was done using the fraction between 2 mm and 0.125 mm at Otele and 1 mm and 0.125 mm at Matomb and Nguibassal to determine the heavy minerals associated to rutile in the sediments, and morphoscopic analyses of rutile, quartz and kyanite minerals observation in the fraction between 2 mm and 0.125 mm were performed using a binocular microscope.

Eight representative rocks samples, the global fraction and the concentrate of sediment were chosen for whole-rock geochemical analyses. The bulk samples were initially reduced in a jaw crusher and then manually fine powdered in agate mortars to avoid any contamination.

Major oxides were analyzed using a Phillips MagiX PRO Model 2440 X-ray fluorescence (XRF) spectrometer provided with suitable software SUPER Q 3.0, at the CSIR-National Geophysical Research Institute Hyderabad. SUPER Q 3.0 is a software package integrated with other analytical instruments that makes the spectrometer accessible to administrators and routine operators with minimal training time. It generates optimized analysis programs for the elements to be measured. These programs allow the standardization of analysis methods within a company. Pressed pellets of the representative samples and geochemical reference materials were prepared separately and loaded into XRF for analysis. Pressed pellets preparation involved weighing two grams on finely powdered (200 mesh ASTM) sample/standard in collapsible aluminum cups filled at the bottom with 2.5 g of boric acid, later pressed under a hydraulic pressure of 25t to obtain the pellet. International rock reference materials from Japan, Canada, France and National Geophysical Research Institute (India) were used to calibrate the instrument and to check the accuracy of analytical data. The precision and accuracy of the analysis was <2 wt% RSD for almost all the major oxides.

For trace elements including rare earth elements (REE) and high field strength elements (HFSE), the homogenized sample powder was dissolved in reagent grade HF:HNO₃ acid mixture in Savillex screw top vessels. A test (0.05 g) of sample was added to 25 ml Savillex Teflon pressure decomposition vessels. To each sample, 10 ml of an acid mixture (containing 7:3:2 HF-HNO₃-HCl) was added. Subsequently, 5 ml of 1 ng/ml 103Rh solution was added as an internal standard to each Savillex vessel. After thorough swirling, the vessels were tightly closed and kept on a hot plate at $\sim 140^{\circ}$ C for 48 h. Following this, the vessels were opened and the contents were evaporated at 200°C to near dryness with, a few drops of HClO4 to ensure complete removal of HF and HCl from the mixture. The remaining residues were dissolved by adding 10 ml of 1.1 HNO₃ and the volume we made to 250 ml with Milli Q de-ionized water (18 M Ω) and the solution was stored finally in HDPE tolls. Matrixes matching certified reference materials JG-2, JG-3, JB-2 from geological survey of Japan and G-1A, G-2 from USGS along with couple of procedural banks were also prepared with the sample batch by adopting the same protocol described above to neglect errors due to reagent and handing. In the present investigation, very clear solutions were obtained for all the samples and calibration standard. Solutions were analyzed by PerkinElmer[®] Model ELAN DRCTM II ICP mass spectrometer (PerkinElmer, Inc, Shelton, CT, USA) at the CSIR-National Geophysical Research Institute (NGRI), Hyderabad, India. The sample introduction consisted of a standard Meinhard nebulizer with a cyclonic spray chamber. All quantitative measurements were performed using the instrument software (ELAN v. 3.1). This software uses knowledge-driven routines in combination with numerical calculations (quantitative was used as an internal standard and external drift was corrected by repeated analyses of 1.5000 solutions of JG-2, JG-3 and JB-2, which were also used as calibration standards accordingly. Instrument response was corroborated to two independent digestions of G-1 and G-2. Precision and accuracy are better than RSD 5% for the majority of trace elements.

4. Results

4.1. Petrography

Petrographic studies reveal that, the study area is made up of three distinct metamorphic rocks namely gneisses, micaschists and amphibolites. These rocks outcrop as blocks and as paved surfaces. The distribution and dispersion of the different lithological units are shown in (**Figure 2**). Detail observations were carried out by mapping and description are documented here.

4.1.1. Gneisses

They are the most wide-spread rocks of the study area. Gneisses crop out as blocks, boulders and slab. Their foliation is defined by alternating dark mafic and clear quartzo-feldspathic bands (Figure 2(A)). The dark mafic bands are composed



Figure 2. Macroscopic and microscopic view of gneisse, micaschists, and amphibolites of the study area (A) Gneisses showing alteration of dark mafic and white quartzofeldspatic band; (B) Photomicroph showing gneiss paragenesis; (C) Encounvered schistosity micaschist hand specimen; (D) Microphotographic showing micaschist paragenesis; (E) Field photo of amphibolites with abundant white quartz overprinting; (F) Microphotographs displaying amphibolite paragenesis.

of biotite, garnet, and opaque minerals, while the clear bands are composed of quartz and feldspars. Microscopic scale observation showed a granoblastic hete-rogranular texture and mineral assemblage constituted of quartz 40% - 50%, pla-gioclase 15% - 20%, alkaline feldspar 10% - 15%, biotite 5% - 10%, kyanite 1% - 7%, muscovite 3% - 5%, garnet <10%, rutile 1% - 5%, and the other opaque minerals less than 10% (**Figure 2(B)**). Abundant biotite flakes of up to 0.12 mm that are observed within the rock texture, with some showing the transformation into muscovite.

4.1.2. Micaschists

They mainly occur at Matomb and Otele, and are crosscut by quartz lode rich in kyanite. Some blocks of quartzite are also associated. In general, the rock is dark grey in colour and biotite exhibits a local schistosity (Figure 2(C)). Under microscope, the textures that characterize micaschists include granoblastic, lepidoblastic heterogranular. The main minerals are: quartz (35% - 40%), Biotite (25%), plagioclase (15% - 20%), Muscovite (10% - 15%), alkaline feldspar (7% - 10%), secondary minerals include opaque minerals (5%), and garnet (4%) and kyanite (4%) (Figure 2(D)). Kyanite forms sky-blue porphyroblast of bladed habit which lie parallel to the foliation. Garnet is ovoid with length that could be up to 1 mm.

4.1.3. Amphibolites

They are the least abundant rock types in the study area. They crop out at Otele area (**Figure 2**). They are greenish with abundant white quartz overprinting, and are composed of quartz, amphibole slate, feldspar, muscovite, garnet and pyrite (**Figure 2(E)**).

Microscopic observations show a granoblastic heterogranular texture and mineral composition with amphibole quartz (20% - 25%), biotite (20%), plagioclase (15%), alkaline feldspar (15%), pyroxene (10%), muscovite (7%), garnet (7%), and opaque minerals (4%) (**Figure 2(F)**).

4.2. Sedimentological Analysis

Macroscopic observation of sediments showed that they are mainly composed of quartz, rutile, kyanite, and opaque minerals. Cumulative curve plotted obtained from granulometric analysis showed a steep to medium slope in the S form that is slightly truncated at the bottom and in tiers (**Figure 3**). Quartiles Q1, Q2, Q3 respectively representing 25%, 50%, and 75% of the sediments obtained from this curve permit to calculate the Krumbein deviation Quartile (Qdphi = $(Q1 \times Q3)/2$), the Track sorting index (So = $(Q1/Q3)^{1/2}$), and the asymmetric coefficient (AS = $Q1 \times Q3/(Q2)^2$) (**Table 1**). These results showed that, the Krumbein coefficient is between 0.11 and 0.22; the sorting index from 0.44 to 1.54 and the asymmetric coefficient from 0.96 to 1.27 (**Table 1**).

Data obtained permit to conclude that, the sediments of the three locations of the Yaoundé Group are well sorted, well classified and composed of fine grains



Figure 3. Cumulative curves showing well sorted and classified grains at all site.

	Otelé	Matomb	Nguibassal
Q1	0.25	0.31	0.30
Q2	0.47	0.55	0.58
Q3	0.85	1.1	1.50
Qdphi	0.11	0.17	0.22
So	0.80	1.88	2.23
As	0.96	1.28	1.4

Table 1. Summary of the various granulometric parameters.

at Nguibassal, medium to coarse grains at Matomb and Otele. Therefore, these sediments are homometric, well sorted and well classified.

In general, heavy mineral assemblage encountered in the three locations studied included the following mineral association: kyanite, rutile, brookite, zircon, andalusite, muscovite, apatite, garnet and tourmaline, and opaque minerals. Their shape mainly showed angular to sub-angular shape and very few sub-round grains (**Figures 4(A)-(F)**). Minerals such as staurolite sillimanite of minor importance were observed at Otele area. Relative abundance of heavy minerals in both global fraction and concentrate showed kyanite and rutile as the most recurrent minerals. Zircon is highly observed at Nguibassal area.

4.3. Morphoscophic Analysis

Morphoscopic studies on 981 grains of quartz, rutile and kyanite grains showed that, the grains are unworn, sub-blunt and shiny blunt (**Figures 5(A)-(E)**). Statistical counting of these grains reveals that, about 634 are unworn (approximately 64.62%), 195 are sub-blunt (19.87%), while 80 are shiny blunted grains(8.15%)



Figure 4. Heavy minerals of the area of study (A, B) Otelé area, (C, D) Matomb area, (E, F) Nguibassal area.

and the less significant sub-round grains (0.10%), showing a significant conflict throughout their transport under the effect of dynamic forces from where a distant origin (**Table 2**). The unworn grains with their angular shape indicate immature sediment that result from short transportation in the three locations of the study area. The less abundant sub-blunt would come from a more or less long transport by fluvial waters. Shiny blunted grains are characteristic of long transport in continental aquatic environments (rivers). Representation of these three minerals in global fraction showed a dominance of unworn grains in sediments. The total population therefore exhibits angular to sub-angular with a dominance of angular forms.

Alluvial rutile study varies from very coarse sand to fine sand in the Wentworth 1922 clastic particles size classification (from 2 mm to 0.125 mm). At Otele and Matomb areas, the grains seize is generally above 0.5 mm while rutile at Nguibassal area is smaller. They are black greyish, opaque with metallic luster and form subhedral crystals. Their shape appears as tabular or elongated with angular



Figure 5. Sediments morphology in the study area (A, B, C, D and E) (A) Unwons grains of kyanite, quartz and rutile alongside some shiny blunt quartz grains; (B) Sub blunt grains of rutile and elongated and rhombohedral kyanite; (C, D, E) Rutile concentrate with angular and sub-angular form.

Table 2. Habit and shapes of grains in the statistical counting of global sediment concentrate.

	Habit and shapes of grains											
Locaton		Uı	1worm gra	ins	Su	b-blunt gra	lins	Shi	Rounds mat			
	Granulometric intervals	Rutile	Quartz	Kyante	Rutile	Quartz	Kyante	Rutile	Quartz	Kyante		
	1 - 0.5 mm	88	70	66	23	18	17	6	4	4	-	
Oélé	0.5 - 0.125 mm	72	57	54	20	16	15	5	4	3	-	
	1 - 0.5 mm	28	13	12	17	3	3	15	2	2	1	
Gubassal	0.5 - 0.125 mm	29	11	11	16	2	2	14	2	2	-	
	1 - 0.5 mm	24	7	6	14	2	2	13	1		-	
Matomb	0.5 - 0.125 mm	50	31	29	26	12	11	18	5	4	-	
TOTAL	_	291	189	178	116	53	50	71	18	15	1	

to sub-angular borders dominant and very few are sub-round with sub-blunt borders.

Granulometric interval investigation of rutile encountered in the three locations of the study area showed that: from the four sampling points of Otele, SOP display 48.72% of total rutile grains and 51.38% was obtained in the remaining three sampling points (Nyk1p, NykIIv, and Nyk2) with equal repartition of rutile grains in intervals. The two sampling points of Matomb exhibit equal amount of rutile in the two samples and intervals; Nguibassal showed abundant rutile grains in the fraction between 0.5 - 0.125 mm (Table 3).

4.4. Geochemical Characteristics

Gneisses (KA1, NK2, GE2, Ml), amphibolites (NKD1, NKD2) and micaschists (RM, Li); alongside 8 stream sediments with the global fraction (SOP1, VSO1, VSO2,) and rutile concentrate (MBE, and MBA MTC) were assessed for their major, trace and REE.

4.4.1. Major Elements

Major elements composition of the analyzed rocks and sediment samples are given in (**Table 3**). The rocks and sediments exhibit important variations in concentrations of major elements. They are basic to acid with low to high SiO₂.

In all the rock types, silica is by quantity the most important major element ranging between 47.56 wt% SiO₂ in amphibolites to 67.18 wt% SiO₂ in gneisses (**Table 4**), followed by Al_2O_3 which varies from one rock type to another according to the rock composition. Average Al_2O_3 is 14.98 wt% in micaschists, 13.53 wt% in amphibolite; and 16.88 wt% in gneisses. Fe₂O₃ in gneisses vary from 4.61 to 6.85 wt%, but are of importance in amphibolites with 10.67 wt% and 11.79 wt%; while in micaschists the percentage average is 8.10 wt%. MgO values are low in gneisses and micaschists compared to amphibolites with percentage that range between 4.03 to 4.98 wt% and 10.64 to 11.87 wt% respectively. K₂O is of importance in all the rock types compared to the other alkaline Na₂O with values that range from 4.53 to 11.15 wt% and 1.64 to 4.72 wt% respectively. Gneisses

Φ (mm) 1 - 0.125											
		Number o	of Particles	Weig	ght (g)						
Sites	Samples	Rutile	Kyanite	Rutile	Kyanite						
	SOP1	90.00	32.00	1.06	0.07						
Mambando	Nyk2	8.00	135.00	0.04	1.85						
	NykIIv	7.00	12.00	0.01	1.7						
Nkolmelen	Nyk1p	8.00	98.00	0.06	1.04						
	MBE	73	5	0.9	1						
Lobo	MBA	65	20	0.06	0.83						

	Rocks								Sediments					
Chemical		Gn	eiss		Amph	ibolite	Mica	chist	Bulk					Concentrate
	KA1	NK2	GE2	M1	NKD2	NKD1	RM	Li	SOP1	VSO1	VSO2	MBE	MBA	MTC
SiO ₂	61.21	58.48	67.18	63.84	51.53	47.56	55.55	62.53	53.92	79.27	76.65	21.86	26.36	0.48
Al_2O_3	17.44	18.57	14.68	16.83	13.11	13.95	14.11	15.85	13.33	7.32	7.94	3.29	2.00	0.26
Fe ₂ O ₃	4.61	5.62	6.85	6.08	11.79	10.67	8.78	7.42	5.83	8.22	9.22	10.59	14.41	1.05
MnO	0.03	0.02	0.11	0.08	0.11	0.11	0.13	0.09	0.03	0.23	0.25	0.18	0.22	<dl< td=""></dl<>
MgO	4.03	4.84	2.75	2.43	11.87	10.64	4.98	3.39	0.20	1.08	1.17	0.22	0.14	<dl< td=""></dl<>
CaO	1.44	1.41	1.56	0.97	0.01	0.01	2.79	1.71	0.67	0.98	1.05	0.19	0.04	0.02
Na ₂ O	4.45	3.64	2.05	1.64	1.28	1.90	4.72	1.92	0.47	0.18	0.15	0.04	0.03	0.06
K ₂ O	4.53	5.61	1.92	4.80	7.97	11.15	5.32	3.55	1.95	0.25	0.21	0.05	0.02	0.02
${\rm TiO}_2$	0.93	1.15	1.42	1.19	2.01	2.84	2.91	1.53	1.19	1.17	1.79	57.65	51.77	95.03
P_2O_5	0.16	0.16	0.06	0.17	0.29	0.37	0.50	0.28	0.21	0.07	0.08	0.05	0.04	0.01
LOI	0.63	0.79	1.17	1.37	1.41	1.03	1.03	1.70	22.56	1.34	0.40	<ld< td=""><td><ld< td=""><td>0.34</td></ld<></td></ld<>	<ld< td=""><td>0.34</td></ld<>	0.34
K ₂ O/Na ₂ O	1.02	1.54	0.94	2.93	6.23	5.87	1.13	1.85	4.15	1.39	1.40	1.25	0.70	0.28
Total	99.46	100.29	99.75	99.40	101.38	100.23	100.82	99.97	100.36	100.11	98.91	94.49	94.44	97.28

Table 4. Major element contents (wt%) of the parent rock and alluvial sediments from Otelé, Matomb and Nguibassal zone.

LOI: Loss on Ignition.

exhibit a percentage of less than 2 wt% CaO, while its value in micaschists average is 2.25 wt% and varies between 2.01 and 2.8 wt% in amphibolites. MnO, CaO and P_2O_5 are the less abundant elements among the major oxides, ranging between 0.01 and 1.71 wt% except in micaschists where the value of CaO is 2.79 wt%. Average LOI is less than 1 in gneisses and above in amphibolites and micaschists. Micaschists and amphibolites are characterized by the highest contents in TiO₂ (greater than 2 wt%) except sample Li.

The global fraction of stream sediments chemistry from Otele and Matomb (SOP1, VSO1, and VSO2) equally showed that silica, alumina and iron are the remarkable oxides with average values of 69.95 wt%, 9.53 wt% and 7.76 wt% respectively (Table 4). The concentrations of the other major oxides are very low (less than 1 wt%), except that of K_2O which is above in the SOP sample and TiO₂ which value range from 1.17 wt% to 1.76 wt%.

Sediment concentrate (MBE, MBA and MTC) exhibit a high concentration of TiO_2 with an average value of 68.13 wt%. At Nguibassal, the concentrations in SiO_2 , Al_2O_3 , and Fe_2O_3 are higher (with an average value of 24.11 wt%, 2.64 wt% and 12.5 wt% respectively) compared to the Matomb sample (MTC where they are all below 1.5 wt%). The other major elements are not of significance (**Table 4**).

4.4.2. Trace Elements

Trace elements of high content in rocks are Zn (75 - 425.63 ppm), Ba (369.10 - 1653.99 ppm), Zr (94.48 - 484.5 ppm), Sr (104.76 - 1419.65 ppm) and Rb (66.67 - 142.12 ppm), (**Table 5**). Chromium values are low, except in micaschists (sample

	Rocks									Sediments				
Chemical elements		Gn	eiss		Amph	ibolite	Mica	chist	Bulk					Concentrate
	KA1	NK2	GE2	M1	NKD2	NKD1	RM	Li	SOP1	VSO1	VSO2	MBE	MBA	MTC
Cr	36.43	47.87	192	131	211.09	99.18	83.46	65	144.84	65	76	394	396	444.33
V	72.70	89.23	223.2	185.4	173.45	232.32	167.50	91.4	189.24	68.7	85.5	370	370	901.33
Ni	38.24	28.39	101.3	76.7	56.29	35.74	30.59	29.2	21.44	6.3	6.1	5.5	5.7	2.13
Zn	104.57	425.63	132.6	125	184.99	185.49	158.47	75	126.34	41	43	326	88	7.00
Cu	49.59	66.91	28.2	63.4	46.28	48.01	52.44	19.5	49.64	5	4.8	15	58.7	1.40
Со	14.15	16.50	26.72	22.95	38.46	45.30	34.50	13.31	7.67	9.83	10.88	11	10.61	0.78
Sc	3.75	4.30	14.8	14.7	12.08	8.72	6.73	12.6	5.66	29.9	33.6	20.4	14.7	3.07
Ba	842.35	853.93	8839	1070.5	1653.99	1540.78	958.87	369.1	481.44	70.8	56.7	22.3	8.2	4.17
Zr	94.48	117.80	484.5	166	155.38	137.12	303.77	134	213.72	144	196	1450	1450	66.33
Sr	349.28	318.74	436	170	104.76	132.35	1419.65	112.6	31.82	19.9	16.7	7.3	5	1.13
Y	9.30	16.94	217.2	24.19	33.23	33.73	27.41	29.08	5.66	47.37	58.53	21.77	15.18	0.13
Ga	20.51	20.29	19.2	21.28	23.87	22.20	24.76	15.03	21.03	5.12	5.42	4.69	2.73	1.32
Pb	26.85	50.16	21.95	17	12.25	12.01	12.22	13.8	23.78	3.3	3.7	10.3	15	2.00
Rb	101.92	139.55	11.13	92.57	142.12	122.13	66.67	59.73	46.74	8.25	6.78	2.21	0.83	0.48
Nb	11.65	15.66	70.49	19.68	45.27	18.02	107.29	7.35	41.03	40.3	63.1	277	277	768.33
Hf	3.01	3.91	13.182	4.58	5.21	4.51	7.10	3.72	6.92	3.86	5.44	29	29	2.81
Th	19.63	20.12	10.39	7.8	5.63	8.95	9.44	7.83	13.74	12.41	27.01	53.7	37.82	0.24
U	1.29	2.55	1.92	1.3	1.01	0.91	2.05	1.37	2.60	2.23	4.39	14.97	11.12	7.45
Та	2.62	4.55	1.92	1.25	0.56	5.67	19.87	0.54	11.31	3.08	3.05	11.86	104.31	85.89
Cs	2.05	2.08	0.48	1.22	1.37	1.18	0.83	3.02	1.28	0.35	0.29	0.1	0.07	0.02

Table 5. Trace element composition (ppm) of the parent rock and alluvial sediments from Otelé, Matomb and Nguibassal zone.

NKD2) with a value of 211.09 ppm. Vanadium values are above 100 ppm, except in two gneiss samples (KA1 and NK2) and micaschists (Li). Niobium and Ta contents are significant in sample RM (micaschists) with 107.29 ppm and 19.87 ppm respectively compared to other rock types where their contents are low, 23.51 ppm and 2.44 ppm respectively. Other trace elements have low content.

The global fraction trace elements of high content in the area include: Zr (144 - 213.73 ppm), Nb (40.3 - 63.1 ppm), and V (68.7 - 189.24 ppm). Otele samples are more enriched in Cr, V, Zn and Ba with values of 144.84 ppm, 189.24 ppm, 126.34 ppm and 481.44 ppm respectively, compared to the average 70.5 ppm, 77.1 ppm, 42 ppm and 63.75 ppm at Matomb (**Table 5**).

Rutile concentrate exhibit a high concentration in Zr (1450 ppm) at Nguibassal while the value is low at Matomb (66.33 ppm). Chromium value is similar at both Matomb and Nguibassal areas ranging between 394 ppm to 444.33 ppm (**Table 5**). Zn and Th are of importance at Nguibassal (average 207 and 45.76 ppm respectively) compared to Matomb (with 7 ppm and 0.24 ppm). Vanadium and Nb are enriched at Matomb concentrated samples (with values of 901.33 ppm and 768.33 ppm) compared to Nguibassal (with 370 ppm and 277 ppm).

4.4.3. Rare Earth Elements

The total REE content is very low in all the rocks ranging from 107.12 to 358.36 ppm. They are also enriched in LREE (LREE/HREE 4.71 to 24.58 ppm) (**Table 6**). REE with high concentrations are La (25.01 to 79.48 ppm), Ce (53.20 to 134.76 ppm), and Nd (27.51 to 48.83 ppm) (**Table 6**). The chondrite-normalized [14] REE patterns exhibit a strong enrichment in several REE (**Table 6**, **Figure 6**) and reveal a negative Eu anomaly (Eu/Eu^{*} ranging between 0.47 to 0.96) and no Ce-anomalies in rocks (**Figure 6**).

The global fraction total REE varies between 164.34 to 372.26 ppm with an enriched LREE (LREE/HREE 5.09 to 21.30) (**Table 6**). REE of high concentrations are La (33.85 - 78.88 ppm), Ce (67.31 - 155.2 ppm), and Nd (28.06 - 68.69

Table 6. Rare earth element distribution (ppm) of the parent rock and alluvial sediments from Otelé, Matomb and Nguibassal areas.

	Rocks									Sediments				
Chemical elements		Gn	eiss		Amph	ibolite	Mica	schist	Bulk					Concentrate
elements	KA1	NK2	GE2	M1	NKD2	NKD1	RM	Li	SOP1	VRO1	VRO2	MBE	MBA	MTC
La	76.95	51.41	78.1	26.17	25.01	40.15	79.48	20.57	39.45	33.85	77.88	140.36	94.88	51.09
Ce	101.95	100.88	159.5	56.06	53.2	77.66	134.76	42.01	76.16	67.31	155.2	273.2	191.14	102.23
Pr	13.42	11.3	18.3	6.28	6.76	8.96	13.94	4.78	8.07	7.95	18.39	31.78	22.08	41.05
Nd	44.15	39.84	69.61	24.6	27.51	33.93	48.83	18.07	28.06	29.62	68.59	115.72	82.67	44.64
Sm	6.03	7.09	11.62	4.9	6.14	6.71	8.32	3.53	4.53	5.49	12.08	20.65	14.67	8.02
Eu	1.31	1.53	1.49	1.19	1.29	1.48	2.6	0.9	0.7	0.67	1.17	3.29	1.96	0.86
Gd	4.81	6.4	8	4.42	6.82	7.28	8.14	3.66	3.28	5.66	9.44	12.99	8.88	6.92
Tb	0.5	0.84	0.88	0.7	1.03	1.09	1.07	0.72	0.32	1.15	1.56	1.15	0.8	1.24
Dy	2.41	4.6	4.59	4.4	7.08	7.3	6.58	4.99	1.62	8.24	10.44	4.48	3.24	8.49
Но	0.34	0.65	0.85	0.87	1.28	1.31	1.06	1.04	0.26	1.76	2.21	0.79	0.56	1.80
Er	0.85	1.59	2.4	2.56	3.88	3.9	2.82	3.09	0.74	5.16	6.66	2.44	1.86	5.32
Tm	0.13	0.24	0.34	0.39	0.65	0.63	0.44	0.45	0.13	0.76	1.01	0.41	0.34	0.80
Yb	0.78	1.4	2.31	2.59	4.18	4.07	2.58	2.9	0.9	4.99	6.65	3.16	2.96	5.20
Lu	0.1	0.17	0.37	0.39	0.54	0.53	0.32	0.41	0.12	0.75	0.98	0.58	0.61	0.78
ΣREE	253.73	227.94	358.36	135.52	145.37	195.00	310.94	107.12	164.34	173.36	372.26	611	427	278.44
LREE	243.81	212.05	338.62	119.20	119.91	168.89	287.93	88.96	156.97	144.89	333.31	585	407	247.89
HREE	9.92	15.89	19.74	16.32	25.46	26.11	23.01	17.75	7.37	28.47	38.95	26	19	30.55
LREE/HREE	24.58	13.34	17.15	7.30	4.71	6.47	12.51	5.01	21.30	5.09	8.56	22.5	21.16	8.15
Ce/Ce*	0.77	1.01	1.02	1.05	0.99	0.99	0.98	1.02	0.98	0.95	0.95	0.93	0.97	0.95
Eu/Eu*	0.77	0.69	0.47	0.79	0.61	0.64	0.96	0.76	0.85	0.56	0.51	0.95	0.81	0.55

 $Ce/Ce^{*} = (Ce_{sample}/Ce_{Chondrite})/(La_{sample}/La_{Chondrite})^{1/2}(Pr_{sample}/Pr_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})/(Sm_{sample}/Sm_{Chondrite})^{1/2}(Gd_{sample}/Gd_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})/(Sm_{sample}/Sm_{Chondrite})^{1/2}(Gd_{sample}/Gd_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})/(Sm_{sample}/Sm_{Chondrite})^{1/2}(Gd_{sample}/Gd_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})/(Sm_{sample}/Sm_{Chondrite})^{1/2}(Gd_{sample}/Gd_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})/(Sm_{sample}/Sm_{Chondrite})^{1/2}(Gd_{sample}/Sm_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})^{1/2}(Gd_{sample}/Sm_{Chondrite})^{1/2}. \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})^{1/2}(Gd_{sample}/Sm_{Chondrite})^{1/2}. \\ \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})^{1/2}(Gd_{sample}/Sm_{Chondrite})^{1/2}. \\ \\ Eu/Eu^{*} = (Eu_{sample}/Eu_{Chondrite})^{1/2}(Gd_{sample}/Sm_{Chondrite})^{1/2}. \\ \\ \\ Eu/Eu$

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ppm) (**Table 6**). The Post Archaean Australian Shales (PAAS) normalized REE patterns [15] reveal a negative Eu anomaly and no Ce anomaly in the global fraction (**Table 6**, **Figure 7**).

The concentrates showed enrichment in Sm compared to the global fraction with values ranging between 8.02 to 20.65 ppm. As for the global fraction, the total REE showed enrichment in LREE/HREE and negative anomalies for Eu and no anomaly in Ce.



Figure 6. Chondrite normalized REE distribution patterns from the study area [14].



Figure 7. Global fraction and rutile concentrate sediment AAS normalized REE distribution patterns [15].

4.4.4. Matrix of Correlation

Binary diagram of these elements with other existing elements in rocks showed a positive correlation of TiO_2 with SiO_2 , Fe_2O_3 , CaO, Nb, Ta and Cr in all the rock types, except with the micaschist sample (RM) from Otele (Figure 8).



Figure 8. Binary diagrams of: TiO_2 versus some selected major elements for the rocks (A) SiO_2 vs TiO_2 ; (B) Fe_2O_3 vs TiO_2 ; (C) CaO vs TiO_2 ; (D) Nb vs TiO_2 ; (E) Ta vs; TiO_2 ; (F) Cr vs TiO_2 ; (G) V vs TiO_2 ; (H) K_2O vs TiO_2 .

 TiO_2 also shows a positive correlation in both global fraction and concentrate with SiO_2 , Fe_2O_3 , CaO, Nb, Ta and Cr; except with the sediment concentrate sample (MTC) from Matomb (Figure 8).

5. Discussion

5.1. Polished Section Interpretation

Amphibolites were observed in the Otele area with the following mineral composition: (Amp + Bt + Pl + Kfs + Qz + Px + Grt + Op). Gneisses and micaschists encountered almost have the similar textural and mineral composition and exhibit the following mineral assemblages: gneisses (Fks + Bt + Qz + Ky + Pl + Msc + Grt + Op), and micaschists (Bt + Qz + Msc + Fks + Op + Ky + Grt). These mineral assemblages are similar to those observed in previous works at Matomb and Mandoga area as well as in the Yaoundé Group where they all belong [1] [4] [16] [17]. The difference could come from the temperature and pressure during metamorphism [9].

Regarding the mineral assemblage it is clear that, the primary source of kyanite is gneisses and micaschists. In the Yaoundé Group, mineralization has been tied to come from micaschists and gneisses in both host rock and quartz vein crosscutting the rock. Kyanite phenocrystals observed in micaschists attest this hypothesis [9]. Observed phenol-crystals of kyanite crosscutting micaschists confirm this assertion in quartz veins and in both rocks for the kyanite.

No rutile was observed in thin section. However, previous work attests the presence of rutile in amphibolites, gneisses and micaschists [4] [9] [16] [17]. This absence of rutile may be due to the fact that, the section chosen or the rock did not contain rutile.

5.2. Sedimentological Analyses and the Origin of the Mineralization

Angular shaped rutile and kyanite were observed in stream sediments. This presence of prismatic crystals of rutile and kyanite is indicative that these sediments come from surrounding rocks [18]. The angular shape of the majority of the grains of rutile, kyanite and quartz indicates immature sediment. These sediments are homometric well sorted and well classified.

Morphological statistics of sediments from the three locations (Otele, Matomb, Nguibassal) of the study area reveal a very low proportions of shiny blunt grains (8.15%); low sub-blunt grains (19.87%), and a clear dominance of unworn grains (64.62%). Unworn grains of rutile, kyanite and quartz observed in these locations are the most abundant (~65%) and are thought to result from short transport. It is known that, shiny dulls grains are characteristic of constant reworking or long transport in fluviatile environments, sub-rounded are characteristic of a relatively long hydromechanics transport, while the less abundant sub-blunt kernels have undergone slight shaping during transport by river waters [19] [20]. The polished appearance of the edges of these grains is caused by the phenomenon of collision between the grains during transport, stream bed attrition and abrasion. Moreover, unworn grains are the result of local sedimentation. Their abundance is linked to a short transportation and deposition [21]. This high percentage of unworn sediment therefore showed that the mineralization is found in location surrounding the area of deposition and therefore orientated primary search of kyanite and rutile toward rocks that are close to this area. Thus, the sediment morphological features are inherited from the sources rocks and marked a very low sedimentary process modification in a proximal source [22]. Therefore, on the basis of quartz, kyanite and rutile sediments morphology, it clearly appears that, the sediments exhibit two origins: 1) a local sedimentation with grains which retained their original shape; and 2) sediments deposited reworked by phenomenon of collision between the grains during transport, stream bed attrition and abrasion.

5.3. Geochemistry and Exploration

Provenance characteristics of clastic sediments can be deduced using various approaches based on the geochemical data. These are discussed below.

5.3.1. Major Elements

Major elements analysis showed that SiO_2 , Al_2O_3 , Fe_2O_3 are the main elements in both rocks and the sediments global fraction. The high content in SiO_2 associated to the low MgO may suggest a felsic protolith [18] [23].

 TiO_2 percentage in both rocks and the global fraction of sediments is similar and a drastic increase is observed in the sediment concentrate. This may suggest that the TiO_2 percentage encountered in minerals of the global fraction to come from the same minerals in the rock, and this percentage increases in the sediment concentrate due to panning of the fraction. It has been demonstrated that, high concentration in TiO_2 generally marks the presence of Ti rich mineral such as rutile and brookite [4]. Therefore, the high TiO_2 support the presence of these two minerals in these areas. Heavy mineral association in sediments highlights the presence of these two minerals. The presence of elevated TiO_2 in sediments is suggested to be related to the presence of rutile in the alluvium [9] [24] [25]. This therefore suggests the element to come from rutile or brookite in rocks. The less abundant brookite in sediments instead suggests the Ti percentage to mainly come from rutile.

Moreover, TiO_2 and SiO_2 positive correlation is indicative of the presence of rutile [4]. However, the high SiO_2 observed in the concentrate at Nguibassal is linked to the proportion of quartz. The positive correlation between TiO_2 and Fe_2O_3 , CaO, Nb, Ta and Cr reveal that these elements might be found in the same bearer-mineral in these rocks.

 Al_2O_3 and MgO permit to distinguished rutile from crustal and mantle source [26]. Mg and Al rich rutile are most likely derived from mantle rocks [27]. The absence of MgO and low Al_2O_3 in the rutile concentrate suggested rutile comes from a crustal source.

Na2O CaO and MgO are of low importance in gneisses and micaschists, and

are very low to absent in both global fraction and rutile concentrate. The progressive reduction of Na_2O and CaO in sediments is also due to the weathering of plagioclase [28]. The correlation matrix of CaO with TiO_2 is positive and suggests that the elements to be present in rutile in a very low amount as suggested by the chemistry of the global fraction and rutile concentrate of Matomb. In addition, the low concentration of MgO in sediments and high in all the rocks types (**Table 4**) suggests Mg to come from amphibolite or garnet in rocks as reported in previous works [29].

5.3.2. Trace Elements

Investigated rocks and sediments showed variability in the enrichment of trace elements. Barium, Ni, Sr, and Cu exhibit high concentrations in rocks and low concentrations in sediments as compared to Cr, Nb, V Zr, and Ta. Enrichment of these elements might suggest two different sources of rutile. Previous studies suggested sediment deriving from felsic rock weathering in the crust to be rich in Zr, La, Th, Rb and Sr, while those enriched in Cr, Co, Sc, Ni, and V derive from mafic rocks [30].

Alluvial rutile of the concentrate is characterized by high Nb contents (277 - 768.33 ppm) as compared to Cr (394 - 444.33 ppm), elements that are considered as major discriminant in the determination of sources rock [31]. It is suggested that, concentration of Cr is low as compared to that of Nb in felsic rocks (micaschists and gneisses) [32]. Field observations confirm the presence of these rocks. Moreover [33] diagram confirm the felsic sources of rutile concentrate (**Figure 9**). However, sample MBA showed enrichment in Cr as compared to Nb



Figure 9. Nb vs. Cr discrimination diagrams for rutile from different metamorphic lithologies according to Triebold *et al.* (2007). Positive log (Cr/Nb) values mostly indicate a metamafic source for rutile while negative values suggest derivation from metapelitic rocks.

suggesting another source for rutile. Rutile from mafic origin is rich in Cr and poor in Nb [32] [34]. This therefore suggested that rutile found come from the same area but with several source rocks and Cr to be present as trace impurities.

The high to moderate concentration in Cr, V, Mn, Fe, Mg, Ni, and Co are due to the presence of ferromagnesian minerals in metamorphic rocks such as amphibole, garnet, chlorite, as well as rutile and kyanite [29] [35]. High concentrations in Cr (>150 ppm) were observed in sediments and in one amphibolite sample. This could suggest an ultramafic source rock [36]. Thus, rutile may come from amphibolite. Moreover, a high concentration in Nb instead suggests a mafic felsic and therefore originated from micaschists.

Correlation matrix showed a positive correlation between TiO_2 and V, Nb, Ta and CaO. The good correlation between TiO_2 and these four elements confirms that, rutile contains a series of trace elements

The Zr percentage observed at Matomb concentrate 66.33 ppm is practically similar to values of alluvial zircon of the Yaoundé Group (91 ppm, [37]. Zr enrichment in the rutile lattice have been demonstrated by several authors [38] [39]. The high content of Zr at Nguibassal concentrate (>1000 ppm) remain questionable. Enrichment in Zr could be justified by the abundance of zirconium as observed in heavy mineral concentrate and thus part of the rutile lattice.

The high contents of Rb, Ba and Sr in rocks and sediments may be due to the presence of minerals such as muscovite and feldspars. It has been demonstrated that K-feldspars contains Rb, Ba while Sr is concentrated in plagioclase [40]. The reduction of Sr and Ba from rocks to global fraction and sediments concentrates is due to the weathering of plagioclase [29] [41] or to the recrystallisation of clay minerals [29].

5.3.3. Rare Earth Elements

The similarity of REE behavior in rocks and sediments explains the complexation of REE in solution during weathering [25]. Stream sediments geochemistry normalized with PAAS showed enrichment in LREE/HREE and a negative Eu anomaly. Previous works clearly showed that, REE normalization with negative Eu anomalies generally permits to understand the origin of terrigenous sediments [4] [42] [43]. These negative Eu anomalies in sediments derived from felsic rocks [44]. Elevated ratio of LREE/HREE coupled to the negative Eu anomalies in rocks and sediments is indicative of felsic source material that contained the mineralization [18] [23]. Again, it has been observed that, REE of Matomb, Mandoga and Yaoundé showed similar behavior with a negative Eu anomalies and enrichment in LREE [18] [45]. This suggests a unique source of sediments [18] [45]. However, recent data obtained in the Yaoundé Group suggested a pegmatitic source in the area [37].

6. Conclusions

They studied rocks that are characterized by a similar mineralogical pattern. Sedimentological analyses reveal the dominance of unworn grains of rutile quartz and kyanite. Silica is the most important major element. Sediment chemistry shows that silica and alumina are the notable elements with a high concentration of TiO_2 . The main conclusions are as follows:

1) Three rock types were encountered in the field: gneisses (Fks + Bt + Qz + Ky + Pl + Msc + Grt + Op), micaschists (Bt + Qz + Msc + Fks + Op + Ky + Grt) and amphibolites (Amp + Bt + Pl + Kfs + Qz + Px + Grt + Op).

2) Morphological shapes with the high percentage of unworn sediments from the three locations (Otele, Matomb, Nguibassal) showed that, they are inherited from the source rocks and marked a very low sedimentary process modification in a proximal source.

3) Sediments exhibit two origins: 1) a local sedimentation with grains which retained their original shape; and 2) sediments deposited reworked by phenomenon of collision between the grains during transport, stream bed attrition and abrasion.

4) TiO_2 percentage encountered in minerals of the global fraction and rutile concentrate come from the same minerals in the rock, and percentage increases associated to heavy minerals observation suggested the Ti percentage to mainly come from rutile.

5) Rutile was found to come from the same area originating from several source rocks.

Conflicts of Interest

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

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