

CONTRIBUTION OF MAJOR, TRACE AND RARE EARTH ELEMENTS IN THE DETERMINATION OF SANDSTONE AND PELITE SOURCE ROCKS IN BANGUE (CAMEROON).

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ABSTRACT

The Ngola series (upper part of the Low Dja Series) is mainly composed of fine grained rocks commonly called pelites, associated with sandstones. The qualitative and semi-quantitative measurements of clay abundance with Macdif software were carried out by Bruker X-ray diffractometer. These measurements were done on normal sample, heated sample, and sample with glycerol. The major element geochemical analysis was performed by X-ray fluorescence spectrometry; whereas trace and rare earth elements abundance were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The mineralogical suites in Bangué sandstones and pelites include: argillaceous minerals (Illite and Kaolinite) and non argillaceous minerals (goethite, gibbsite...). Elementary grouping based on their correlation suggests a slightly dominance of mafic minerals (biotite, amphibole and a titanium mineral), apatite, and Ce enriched mineral (zircon).

Chemical results indicate that Bangué sandstones and pelites were deposited and lithified in a marine environment. Various elementary ratios and the high value of the chemical weathering index ($CWI \geq 90\%$) is typical of harsh weathering activities within the lithified sediments source area. The use of La-Th-Sc ternary diagram, and samples distribution pattern in Co/Th versus La/Sc and K_2O , show that the distributed elements found in the lithified clasts were sorted from mafic to intermediate source rocks.

Key words: Chemical composition, source rock, pelites, sandstones, SE Cameroon

RÉSUMÉ

La série de Ngola est principalement constituée de roches à grain fin, communément appelées pélites, auxquelles sont associées les grès. Ces formations constituent la partie sommitale de la série du Dja inférieur. Les mesures qualitatives et semi-quantitatives d'argiles avec le logiciel Macdiff, sont réalisées grâce à un diffractomètre DRX Bruker, D4 Endeavor à anticathode de cuivre. Ces mesures sont effectuées sur un échantillon normal, un échantillon chauffé et un échantillon glycolé. L'analyse géochimique des éléments majeurs a été réalisée par fluorescence X. Tandis que les analyses géochimiques des éléments traces et Terres Rares ont été effectuées par Plasma Inductif Couplé à un Spectromètre de Masse (ICP-MS).

L'assemblage minéralogique global, tel que déduit des deux méthodes minéralogique et chimique est formé de minéraux argileux, tels que l'illite, la kaolinite et les minéraux non argileux tels que la gibbsite, la goéthite. Le regroupement d'éléments selon la base de leur corrélation suggère une faible dominance des minéraux mafiques (biotite, amphiboles, et un minéral titanifère), l'apatite et un minéral enrichi en Ce comme le zircon.

Les résultats des analyses géochimiques indiquent que les grès et pélites de Bangué se seraient déposés et consolidés dans un environnement marin. Divers rapports d'éléments et les valeurs élevées du CIA ($\geq 90\%$) reflètent une météorisation rigoureuse. L'emploi du diagramme ternaire La-Th-Sc, la distribution des échantillons dans les diagrammes, de Co/Th versus La/Sc montre une distribution caractéristique d'une contribution de sources mafiques à intermédiaires (60-50%).

Mots clés : Composition chimique, roche source, pélites, grès, SE-Cameroun.

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INTRODUCTION

The composition of a detrital sediment is a cumulative result of four main factors: (1) the composition of the source rock, (2) the intensity of chemical weathering in the source area, (3) the prevailing processes during sediments transportation and accumulation (sorting and maturity), and (4) element mobility during weathering (Nesbitt et al., 1980; McLennan et al., 1983a; Cullers, 1995). Detailed studies on palaeoenvironmental

reconstitution (Bolhar et al., 2007; Nedelec et al., 2007; Caron et al., 2010), and influence of the nature of the source rocks (Sawyer, 1986; Moisan, 1992; Abderrahim, 1996) have been carried on sedimentary rocks. There are two ways (mineralogy and geochemistry) to evaluate the compositional changes due to cumulative results of the above mentioned factors. Mineralogically, many studies (Underwood et al., 1993) have proven the reliability of information on weathering processes that took place in sediment source area, and their various sources obtained

from analysis of clay minerals. Although, the mineralogy of clays seems to be a good tool for the interpretation of certain factors (the climatic condition in the source area, weathering, and diagenesis) which can influence the genetic history of sedimentary rocks, it is some time very difficult to be settled on other factors like provenance and the tectonic environment.

The geochemistry of sedimentary rocks mainly reflects the nature and proportion of their detrital components, and consequently their provenance (Taylor and McLennan, 1985; Gibbs et al., 1986). Although, it is possible that diagenesis can modify the original chemical composition of detritus, changes can also be related to the tectonic setting (Bhatia, 1983), and in this manner, help to develop source discrimination properties based on chemistry and petrography.

Bangué sandstones and pelites have two main problems that need to be resolved: (1) The nature of the source rocks is still to be determined, and the relationship between the underlying igneous basements (granodiorite: 2.66 Ga, and dolerites: 2.1 Ga), and those lithified sediments are still to be established; and (2) the distinction between those rocks, and that of their bed rocks of the lower Dja, and Lobéké series. The mineralogical and geochemical studies of the Bangué sandstones and pelites will help to determine the source of the lithified sediments, the nature of their depositional environment, and the existing relation between the mineralogical and chemical components of the sediments.

Geological Settings

The studied sedimentary formations are found in the southeastern part of the East Region of Cameroon (Fig. 1), at about 70 km to Yokadouma. The south east of Cameroon is made up of two main lithostratigraphic units (Vicat et al, 1998; Moloto, 2002) : (1) the folded unit (autochthonous) including the Lower Dja Series of Lobéké and Ngola, is superposed on the Congo craton. The lithologic series of this unit are cross-cut by post-metamorphic and post-deformation intrusions; both covered by discordant glacial deposits overlain by carbonate formations of the upper Dja series called Mintom Formation (Caron et al., 2010); and (2) the overthrusting unit (allochthonous) including the Yokadouma series overlapping the folded unit.

The Lower Dja series is the extension in Cameroon of the pelitic sandstone series of Sembé (Alvarez, 1995; Moloto, 2002). This series is made up of lower sequence of coarse grained to arkose sandstones, and conglomeratic sandstones. This lower sequence is overlain by an argillaceous formation, sometimes ampelitic, alternating with sandstones and cross-stratified quartzitic layers, with rare dolomitic and jaspe occurrences. Interbedded metabasites in quartzitic sandstones and metapelitic layers are found in Lokomo close to Cameroon- Centrafrican Republic border. The type of folding which affected this area is similar to that of Sembé (Alvarez, 1995; Vicat, et al., 1997; Moloto, 2002).

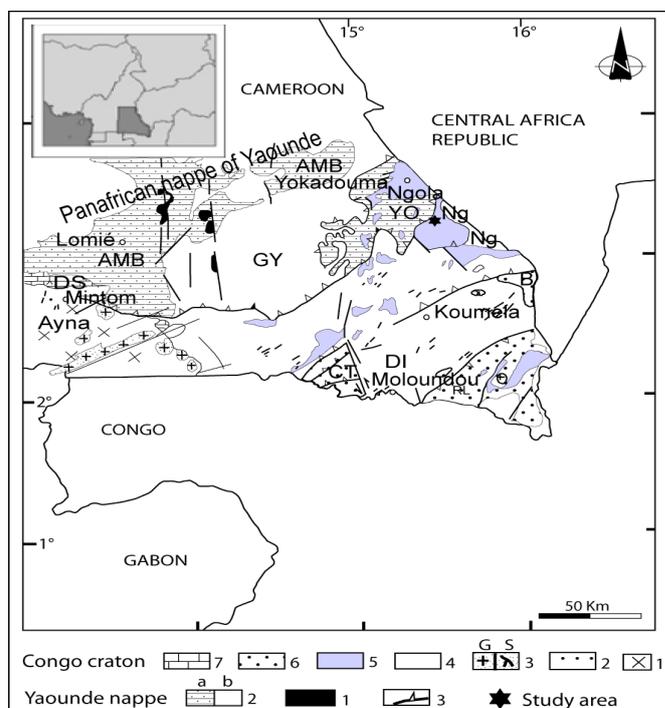


Fig 1: simplified geological map and location of the study zone (Vicat et al., 1998), modified. Congo craton: 1: Ntem archean group. 2: sericitoschists and micaschist of the basal formation of the palaeoproterozoic cover of the craton; RL Lobéké ridge. 3: eburnean intrusion (about 2Ga); G = granodiorite, S = syenite. 4: quartzite, sandstone and pelite of the upper formation of the palaeoproterozoic cover of the craton; DI: Lower Dja; Ng : Ngola series; YO: Yokadouma series. 5: doleritic complex of Palaeoproterozoic to Neoproterozoic age. 6: cryogenian tillite. 7: schisto-limestone supergroup; Ds Upper Dja series renamed the Mintom formation. Panafrican chain: 1 ultrabasic rocks. 2: neoproterozoic metasediments; 2a = epimetamorphic formation of the Ayo-Mbalmayo-Bengbis (AMB); 2b = micaschists, migmatitic gneisses of the Yaoundé group (GY). 3: principal panafrican overlappings.

The Lobéké Series is the extension in south east Cameroon of the schisto-quartzitic series of Ouessou (Alvarez, 1995; Vicat et al., 1997; Moloto, 2002). The lithostratigraphy of this series is characterized by an alternation of quartzites, quartz-rich phyllites, sericite schists, clays and jaspes. Within the quartzitic levels found in Koka, interbedded metabasites were located near the river Mokopaka (Moloto, 2002). Quartzitic sandstones were found in its southern part during the 1987 south east Cameroon mining project. Those rocks are probable the extension in Cameroon of the Koka sandstones (Moloto, 2002). The rocks found in the Lobéké Formations are folded with their fold axis parallel to N20°E and N40°E direction. They are cross-cut by a multitude of doleritic dykes.

The studied formation is part of the Ngola series characterized by basic volcanic activities with interbedded lava flows occurring within metasediments. The nature of these metasediments is closed to that of the Nola and Bolé-north series (Vicat et al., 1997; Moloto, 2002). The Ngola series is slightly folded with an upper epizonal

metamorphism (Vicat et al., 1997; Moloto, 2002), and forms the upper part of the Lower Dja series (Vicat et al., 1997, 2001; Moloto, 2002) The age of the Bangué sandstones and pelites is unknown. Vicat et al. (2001) suggested a Paleoproterozoic age for those covered rocks overlying the Congo Craton.

Formations of the pan-African sheet form the Yokadouma series (Vicat et al., 1997, 2001; Moloto, 2002), and are made up of garnet orthogneiss, augen gneiss, mylonitic gneiss, mylonitic quartzites and basic gneiss. Rocks of this series overlap the northern part of the Congo craton cover in Cameroon (The lower Dja and Ngola series). The contact zone between the Yokadouma series and that of Ngola is not well-defined. It could be found in Badékok, where samples from the overlapping rocks were collected, or in Bangué where rock formations are metapelitic (Moloto, 2002).

Sampling and analytical methods

The Bangué sandstones and pelites are located at latitude N03°00'00" to N03°21'36", and longitude E15°16'12" to E15°45'36", and at about 70 km to Yokadouma town in the south east of Cameroon. They underlie thick soil profiles in a tropical humid forest. They crop out near river Lokomo, and can be access and visible mainly during the dry season (January-February). These rocks are fairly weathered. Six samples were collected from four different facies, from bottom to the top (Fig 2): coarse-grained sandstone (BS01), medium-grained sandstone (BS02), silty fine-grained sandstone (BS03), and pelites (BS05-1 and BS05-2). Sample BS04 was collected at the contact zone between pelite and silty fine-grained sandstone. The contact between the basement formation and the coarse grained sandstones was not found on the outcrop.

Part of the collected samples was sent to the University Lille 1 for clay analysis, and another part was sent to the Geosciences laboratory in Canada for XRD mineralogical analysis, and also for major, trace and rare earth element geochemical analyses.

Qualitative and semi-quantitative measurement of clays in collected samples was carried out by a Bruker X-ray diffractometer, D4 Endeavor with copper anticathode. The goniometers were controlled by a micro-computer with the use of the PC-APD and DIFFRAC softwares, used to determine the optimized 2θ angles ranging from 2 to 32° and in which all clays are mainly diffracted. The obtained data are later treated on MacDiff 4.2.5. When the incident X ray beams arrive the network of a crystalline surface, they are then diffracted following Bragg law: $\lambda = 2d \sin\theta$ with: λ : the wavelength; d : the distance of crystalline network plan; and θ : the incident angle of X ray beams on the crystalline surface. By rotation of θ of each sample around an axis perpendicular to an incident beam, it is possible to determine all the distances d ; characteristics of the minerals found (Holtzapffel, 1985). The quantification is carried out on a fresh sample, heated sample, and sample treated with glycerin. The examination of the three X-ray diffraction diagrams by Macdiff software, leads to

the qualitative and semi-quantitative studies of the clay minerals found in each thin section. The error of this method is estimated at 5% of the percentage of clay in study sample.

The geochemical analysis of the major element was carried out by X-ray fluorescence spectrometer at the Geosciences Laboratory in Canada. Six samples were alkaline melted in lithium metaborate, and the remaining material was treated with hydrochloric acid. At about 5 ml of filtered solutions were later diluted with 35 ml with nitric acid and their quantity was doubled or tripled.

The geochemical analysis of trace and rare earth elements was carried out by ICP-MS (Inductively Coupled Plasma Mass Spectrometry). Before any ICP-MS analysis of collected sample, it was first mineralized in microwave oven. This was aimed to dissolve all elements found in each sample matrix. 250± 2.5 mg of each sample are mixed to 10 ml of nitric acid at 65% in closed bomb, later heated at a defined temperature in micro wave oven (Ethos plus, Milestone). The obtained mineralized product is later filtered, and poured in a 100 ml polypropylene bottle. ICP and spectrometric treatment of the filtered product lead to the quantification of those elements.

RESULTS

Outcrop Description and Petrography

In general, sandstones within the Ngola series are gray, graded bedded, and exhibit yellow and oxidized patinas from local weathering. These sandstones outcrop along river Lokomo, forming a slab on which this river flows. At latitude N03°14'27.8" and longitude E15°27'25.6" along the bank of the Lokomo River, sandstones and pelites crop out in form of scarp of about 4 m high (Fig. 2). Quartz-rich and variable meters (1- 3 mm to 2.5- 3 cm of thickness) coarse-grained sandstones occur at the bottom of the series. These sandstones are mainly composed of variable shape quartz grains with few quartzite fragments interlinked by friable yellow clay. Medium-grained sandstones overlying the above described rocks are made up of quartz with clast sizes ranging from 1 mm to 1 cm in diameter (being coarser at the bottom and medium at the top). Those quartz grains are linked by a yellow argillaceous material. The height of the medium-grained sandstones is up to 2 m.

The medium-grained sandstones are overlain by fine-grained silty sandstones, whose height is about 1.5 m. Yellow pelitic laminae locally occur in the silty sandstones. The thickness of laminae increases when moving close to the yellow pelitic overlying layer (height: up to 1 m). Microscopically, the quartz grains mostly form single crystals in fine-grained silty sandstones (BS03) and pelitic sandstones (BS04). They are sub-angular to sub-round with wavy extinction. Few polycrystals are visible. Those polycrystals were recrystallized and show a well-developed polygonal texture. Some quartz grains show a melting texture. The quartz grains in fine grained silty sandstones are granular whereas; those in pelitic sandstones are microgranular. Quartz grains in those two textural (granular and microgranular) features are scattered

within an argillaceous matrix.

Non argillaceous and argillaceous mineralogy

The main identified very fine-grained non argillaceous (grain size < 1/256) minerals in Bangué sandstones and pelites are quartz, hematite, goethite and gibbsite (Fig. 3A). Quartz is δ -quartz type which is the most common silicate mineral in sedimentary rocks. This type of quartz was easily identified by its two reflection characteristics at 4.26 and 3.34 Å. Gibbsite and goethite are respectively aluminum and iron oxide. They are easily identified at the respective peaks 2.69, 4.85, and 4.14 Å.

Clay minerals were identified by oriented specimens of X-ray diffraction (Fig. 3B). The obtained results show that the main clay peaks are at 10, 5 and 7.15 Å. The most common clay minerals in sedimentary rocks with the above reflections are illite and kaolinite.

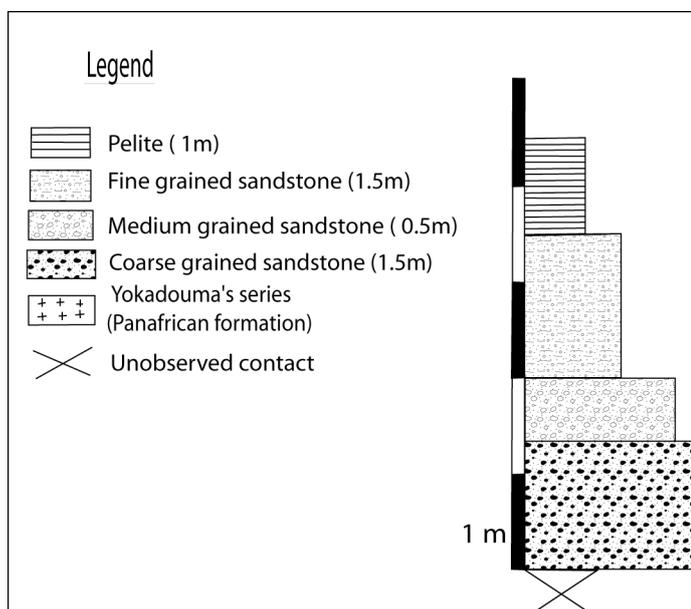


Fig. 2: Lithostratigraphy of Bangué's sandstone and pelite. The different formation thickness are given into brackets.

Geochemistry

Elements chemical distribution and source mineral

From the geochemical results (Table 1), a correlative matrix was constructed (Fig. 4) with the aim to identify a possible link between elements; from correlative eventualities. From these identified links, we propose mineralogic phases controlling the distribution of chemical elements. The study of the correlative matrix helps to group elements and their specific minerals; (1) oxides: in sample, the medium rare earth elements (MREE: Eu and Sm), and light rare earth elements are correlated amongst them, and also correlated with P_2O_5 and TiO_2 . The distribution of MREE and LREE seems to be highly influenced by the heavy minerals. Those minerals may be apatite, and titanium oxide like titanite. Zircon may be the Ce bearer. Therefore, the positive correlations between Zr and Ce, Hf, Nb, Ba, Bi, Cd, Cr, Cu, Ga, In, Th, W, and Mo can be due their presence in zircon; (2) clays and accessory

minerals: the highly and significant correlations between heavy rare earth elements (HREE) and K_2O , Al_2O_3 , Na_2O and Fe_2O_3 is due to the presence K_2O rich clay such as illite; and accessory minerals such as gibbsite and goethite. The positive correlation between K_2O - Co, K_2O - Cs, K_2O - Li, K_2O - Rd, K_2O - W, K_2O - U, and K_2O - Zn suggests that, those elements are found in illite which is the main potassium bearer.

From the correlative diagrams (Fig. 4), it is also possible to share out the identified chemical elements into two main systems; the felsic and mafic system (Moisan, 1992; Abderrahim, 1996). These elements were divided into three main groups: the felsic group enclosing elements which are normally associated to felsic minerals; the mafic with elements associated to mafic minerals, and REE group which comprises elements associated to heavy minerals. The REE are treated as a separated group, but often behave like elements in mafic and felsic group (Sawyer et al.; 1989; Moisan, 1992; Abderrahim, 1996).

Table 1

Elements	L.D	BS01	BS02	BS03	BS04	BS05-1	BS05-2
SiO2 (%)	0.04	16,88	4,49	58,45	25,91	4,97	4,44
Al2O3	0.02	13,49	5,79	1,66	9,05	5,93	5,82
Fe2O3	0.01	53,90	74,86	33,27	49,71	74,67	75,19
MnO	0.01	0,09	0,01	0,01	0,02	0,02	0,02
MgO	0.01	0,11	0,12	0,01	0,01	0,11	0,12
CaO	0.01	0,01	0,01	0,02	0,02	0,01	0,01
Na2O	0.02	0,10	0,11	0,09	0,09	0,12	0,11
K2O	0.01	0,41	0,56	0,04	0,02	0,54	0,56
TiO2	0.01	0,80	0,24	0,12	0,72	0,28	0,24
P2O5	0.01	0,82	0,88	0,08	1,93	0,75	0,89
LOI	0.05	13,64	13,26	5,94	11,56	13,00	12,82
Total	/	100,33	99,68	99,04	100,40	100,22	100,22
CIA	/	96,36	89,63	92,74	98,80	89,98	89,68
Ba (ppm)	0,80	130,00	643,00	4,30	78,10	99,00	107,80
Be	0,04	3,08	1,09	1,15	3,55	4,24	4,47
Co	0,13	19,96	35,62	9,39	14,92	29,04	27,26
Cr	3,00	747,00	2347,00	39,00	1323,00	89,00	62,00
Cs	0,01	1,11	0,24	0,05	0,16	1,13	1,19
Ga	0,04	16,83	32,87	2,21	17,86	7,60	6,97
Hf	0,14	3,30	6,90	0,50	2,46	1,31	1,18
In	0,01	0,10	0,22	0,01	0,13	0,031	0,03
Ni	1,60	179,00	142,60	83,30	271,60	594,70	603,50
Pb	0,60	44,10	105,30	8,70	44,00	15,20	16,10
Sc	1,10	54,0	>63	9,60	43,70	29,80	26,00
Sr	0,60	4,80	11,40	1,30	36,40	3,30	2,40
Th	0,02	7,33	13,62	0,78	6,02	3,69	3,29
U	0,01	5,74	4,16	1,49	2,36	3,61	3,07
V	0,80	349,50	>370	39,50	>370	76,80	57,80
W	0,05	0,68	1,18	0,17	0,44	0,52	0,48
Y	0,05	24,14	17,60	13,37	39,18	47,65	92,04
Zn	7,00	187,00	144,00	460,00	378,00	674,00	663,00
Zr	6,00	125,00	277,00	21,00	99,00	50,00	44,00
La	0,04	16,69	26,36	2,89	133,67	11,21	11,13

Ce	0,12	51,10	234,15	6,12	104,64	17,46	15,55
Pr	0,01	4,55	5,389	1,33	25,26	3,88	4,40
Nd	0,06	18,35	19,45	6,38	81,03	18,07	21,00
Sm	0,01	5,54	4,87	2,19	12,87	6,10	7,14
Eu	0,01	1,46	1,22	0,70	3,02	1,85	2,32
Gd	0,01	5,02	4,03	2,78	9,32	7,94	10,78
Tb	0,01	1,01	0,79	0,57	1,57	1,57	2,11
Dy	0,01	6,91	5,20	3,92	9,65	10,61	14,97
Ho	0,01	1,39	1,02	0,78	1,84	2,20	3,33
Er	0,01	4,28	3,09	2,25	5,27	6,61	9,90
Tm	0,01	0,70	0,51	0,33	0,81	0,96	1,42
Yb	0,01	5,080	3,567	2,130	5,531	6,273	8,757
Lu	0,01	0,70	0,51	0,29	0,763	0,89	1,30
ΣREE	/	16,41	15,61	7,51	30,694	21,493	29,72
ΣLREE	/	2,14	4,82	0,49	10,07	1,49	1,61
ΣMREE	/	3,42	2,87	1,63	7,11	4,52	5,75
ΣHREE	/	10,85	7,93	5,38	13,52	15,49	22,37
ΣLREE/ΣHREE	/	0,20	0,61	0,09	0,75	0,10	0,07
ΣLREE/ΣMREE	/	0,62	1,68	0,30	1,42	0,33	0,28
Ce/Ce*	/	1,35	4,53	0,72	0,42	0,61	0,51
Eu/Eu*	/	1,30	1,30	1,34	1,30	1,25	1,25
(La/Yb)N	/	0,24	0,55	0,10	1,78	0,13	0,09
Y/Ho	/	17,32	17,26	17,14	21,29	21,68	27,68
La/La*	/	0,94	1,01	1,00	0,92	1,16	1,14
Gd/Gd*	/	0,95	0,92	0,94	1,01	0,95	1,03

The felsic group of elements includes: K₂O, Al₂O₃, Ba, Rb, Th, U, Zr and Y (Moisan, 1992; Abderrahim, 1996). These elements generally show positive correlation amongst them. Ba, Th and Zr often have affinity amongst them. This is the same for Rb, Cs, and Y. Yttrium is found in three different groups (felsic, mafic and REE); The reason of this presence within felsic group is due to its good correlation with Rb and Cs at 0.70 and 0.63 respectively, and also with Al₂O₃ (0.55), and because it was not correlated with any other element of this group (Ba, Th, Zr and U). In order to explain the influence of certain minerals on felsic elements group, correlation eventualities between K₂O- Al₂O₃ and K₂O- Rb were analyzed. This same study was carried out in other sedimentary rocks by Sawyer et al.; (1989). Rubidium and Cs can replace K in illite structure (Deer et al., 1992), which therefore shows a good correlation with K₂O. They are correlated with Al₂O₃, Na₂O and other mineralogical components not showing any influence on their distribution (MgO and Fe₂O₃) and consequently support the fact that those elements are controlled by potassic micas and other minerals such as biotite, amphibole and goethite which are not felsic minerals. Their influences on felsic group are due to the fact that Al₂O₃ belongs to both the felsic and mafic group of elements. The correlative diagrams show that K₂O has affinity with Th, Ba, and U. These trace elements are mainly found in zircon, sphene, and apatite which can contain a very low proportion of Al₂O₃ and K₂O (Deer et al., 1992). This is why the correlation values between these trace elements and felsic group major oxides are not very

Felsic group

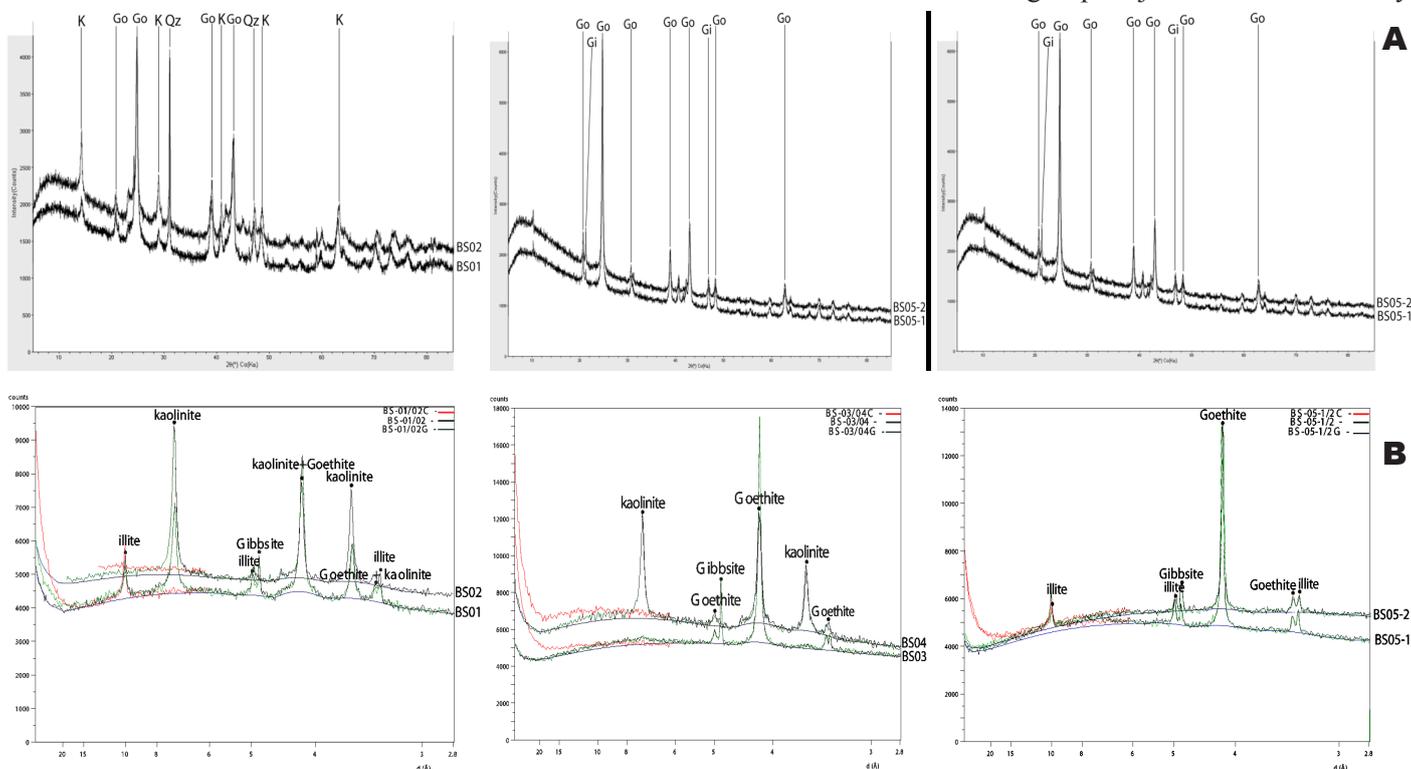


Fig. 3: X-rays diffractograms (open air) showing all the non-clay mineralogical phases (A). X-rays diffractograms (open air; ethylene, glycol and heating) showing all the clay mineralogical phases and some accessory minerals (B)

high (not above 0.63). But, based on correlative matrix, it is possible to determine trace elements that are found in zircon. This is because, they have a good factor of

	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu	Ga	Hf	In	Li	Mo	Nb	Ni	Pb	Rb	Sb	Sc	Sn	Sr	Ta	Th	Ti	Tl	U	V	W	Zn	Zr	Al2O3	CaO			
Ba	1,00																																		
Be	-0,48	1,00																																	
Bi	0,96	-0,60	1,00																																
Cd	0,91	-0,17	0,82	1,00																															
Co	0,74	0,14	0,61	0,77	1,00																														
Cr	0,85	-0,47	0,84	0,87	0,41	1,00																													
Cs	-0,21	0,75	-0,23	-0,11	0,40	-0,47	1,00																												
Cu	0,79	-0,27	0,88	0,74	0,61	0,74	0,12	1,00																											
Ga	0,88	-0,37	0,89	0,91	0,54	0,97	-0,27	0,86	1,00																										
Hf	0,94	-0,46	0,96	0,89	0,60	0,94	-0,23	0,90	0,98	1,00																									
In	0,83	-0,40	0,84	0,87	0,43	0,99	-0,38	0,80	0,99	0,95	1,00																								
Li	-0,22	0,78	-0,26	-0,11	0,43	-0,49	0,99	0,06	-0,30	-0,27	-0,40	1,00																							
Mo	0,89	-0,63	0,96	0,80	0,42	0,93	-0,39	0,86	0,94	0,97	0,93	-0,43	1,00																						
Nb	0,94	-0,45	0,96	0,90	0,62	0,93	-0,21	0,91	0,98	1,00	0,94	-0,24	0,97	1,00																					
Ni	-0,27	0,87	-0,46	-0,05	0,42	-0,49	0,73	-0,31	-0,39	-0,42	-0,45	0,79	-0,61	-0,40	1,00																				
Pb	0,93	-0,49	0,94	0,90	0,54	0,97	-0,33	0,85	0,99	0,99	0,97	-0,36	0,98	0,99	-0,45	1,00																			
Rb	-0,26	0,77	-0,30	-0,16	0,39	-0,55	0,99	0,01	-0,36	-0,32	-0,47	1,00	-0,48	-0,29	0,80	-0,41	1,00																		
Sb	-0,05	-0,79	0,06	-0,40	-0,45	-0,16	-0,55	-0,27	-0,28	-0,15	-0,24	-0,57	0,04	-0,17	-0,62	-0,14	-0,52	1,00																	
Sc	0,73	-0,13	0,78	0,80	0,53	0,85	0,02	0,93	0,93	0,90	0,91	-0,03	0,83	0,90	-0,26	0,88	-0,10	-0,48	1,00																
Sn	0,94	-0,35	0,94	0,94	0,68	0,93	-0,16	0,90	0,98	0,99	0,95	-0,18	0,94	0,99	-0,30	0,98	-0,24	-0,26	0,91	1,00															
Sr	0,05	0,08	-0,01	0,33	-0,21	0,53	-0,49	0,02	0,42	0,23	0,52	-0,48	0,24	0,22	-0,18	0,33	-0,52	-0,42	0,37	0,26	1,00														
Ta	0,95	-0,44	0,97	0,90	0,64	0,92	-0,19	0,92	0,97	1,00	0,93	-0,22	0,96	1,00	-0,38	0,98	-0,27	-0,17	0,90	0,99	0,19	1,00													
Th	0,92	-0,35	0,93	0,91	0,63	0,93	-0,16	0,92	0,99	0,99	0,96	-0,19	0,94	0,99	-0,33	0,98	-0,25	-0,27	0,94	1,00	0,29	0,99	1,00												
Ti	0,92	-0,46	0,93	0,89	0,54	0,97	-0,30	0,87	0,99	0,99	0,98	-0,33	0,97	0,99	-0,44	1,00	-0,39	-0,17	0,90	0,98	0,34	0,99	0,99	1,00											
Tl	0,99	-0,47	0,97	0,87	0,77	0,78	-0,11	0,83	0,84	0,93	0,78	-0,12	0,87	0,93	-0,25	0,90	-0,17	-0,03	0,72	0,92	-0,08	0,94	0,90	0,88	1,00										
U	0,40	0,13	0,51	0,38	0,51	0,30	0,58	0,84	0,50	0,54	0,41	0,51	0,45	0,56	0,00	0,44	0,46	-0,44	0,74	0,55	-0,21	0,57	0,58	0,48	1,00										
V	0,53	-0,22	0,61	0,63	0,14	0,85	-0,27	0,74	0,86	0,77	0,89	-0,33	0,78	0,77	-0,49	0,79	-0,39	-0,37	0,90	0,76	0,64	0,75	0,81	0,82	0,48	0,51	1,00								
W	0,95	-0,27	0,93	0,91	0,80	0,82	0,04	0,92	0,91	0,95	0,84	0,01	0,87	0,96	-0,16	0,92	-0,04	-0,29	0,88	0,97	0,06	0,97	0,96	0,92	0,95	0,65	0,64	1,00							
Zn	-0,60	0,64	-0,77	-0,49	-0,04	-0,79	0,41	-0,78	-0,79	-0,80	-0,81	0,49	-0,89	-0,79	0,82	-0,80	0,53	-0,13	-0,76	-0,72	-0,27	-0,77	-0,77	-0,81	-0,59	-0,49	-0,85	-0,62	1,00						
Zr	0,95	-0,48	0,96	0,90	0,59	0,94	-0,26	0,89	0,98	1,00	0,95	-0,29	0,97	1,00	-0,42	0,99	-0,35	-0,13	0,89	0,99	0,24	1,00	0,99	0,99	0,93	0,51	0,77	0,95	-0,79	1,00					
Al2O3	0,53	0,43	0,35	0,64	0,95	0,21	0,57	0,42	0,35	0,38	0,24	0,62	0,17	0,40	0,67	0,32	0,58	-0,62	0,39	0,48	-0,17	0,42	0,44	0,32	0,55	0,44	0,01	0,62	0,21	0,37	1,00				
CaO	-0,29	-0,22	-0,31	-0,20	-0,66	0,16	-0,78	-0,45	-0,05	-0,18	0,09	-0,76	-0,07	-0,20	-0,39	-0,07	-0,76	0,17	-0,19	-0,21	0,75	-0,23	-0,19	-0,07	-0,41	-0,67	0,20	-0,42	-0,07	-0,16	-0,66	1,00			
Fe2O3	0,53	0,43	0,35	0,64	0,95	0,21	0,57	0,42	0,35	0,38	0,24	0,62	0,17	0,40	0,67	0,32	0,58	-0,62	0,39	0,48	-0,17	0,42	0,44	0,32	0,55	0,44	0,01	0,62	0,21	0,37	1,00				
K2O	0,51	0,28	0,43	0,49	0,91	0,08	0,70	0,53	0,27	0,37	0,13	0,71	0,19	0,39	0,52	0,27	0,69	-0,40	0,36	0,43	-0,51	0,42	0,40	0,28	0,59	0,63	-0,07	0,63	0,10	0,35	0,91	-0,90			
MgO	0,49	0,28	0,46	0,48	0,86	0,10	0,74	0,61	0,30	0,40	0,17	0,73	0,24	0,42	0,45	0,30	0,70	-0,42	0,44	0,46	-0,51	0,45	0,44	0,31	0,58	0,74	0,02	0,65	-0,01	0,38	0,85	-0,93			
MnO	-0,08	0,17	0,13	-0,07	-0,05	0,03	0,48	0,54	0,18	0,18	0,14	0,39	0,18	0,19	-0,18	0,10	0,36	-0,30	0,48	0,16	-0,10	0,19	0,22	0,15	0,00	0,83	0,46	0,20	-0,47	0,15	-0,07	-0,37			
Na2O	0,36	0,39	0,23	0,36	0,87	-0,06	0,66	0,29	0,10	0,18	-0,02	0,70	-0,02	0,20	0,69	0,10	0,68	-0,42	0,17	0,26	-0,46	0,23	0,22	0,10	0,42	0,42	-0,25	0,46	0,35	0,17	0,91	-0,73			
P2O5	0,06	0,43	-0,03	0,43	0,06	0,45	-0,07	0,14	0,43	0,24	0,48	-0,06	0,15	0,23	0,17	0,30	-0,11	-0,77	0,49	0,31	0,90	0,21	0,33	0,32	-0,04	0,06	0,62	0,18	-0,14	0,24	0,18	0,42			
SiO2	-0,49	-0,51	-0,36	-0,67	-0,89	-0,29	-0,63	-0,55	-0,45	-0,44	-0,35	-0,66	-0,23	-0,47	-0,61	-0,39	-0,61	0,78	-0,57	-0,55	0,02	-0,48	-0,52	-0,40	-0,51	-0,62	-0,23	-0,67	-0,05	-0,43	-0,95	0,63			
TiO2	-0,17	0,31	-0,05	0,04	-0,25	0,24	0,15	0,34	0,29	0,16	0,33	0,08	0,16	0,16	-0,17	0,16	0,04	-0,55	0,54	0,17	0,55	0,14	0,23	0,21	-0,19	0,50	0,71	0,08	-0,44	0,14	-0,19	0,20			
La	-0,07	0,17	-0,13	0,23	-0,27	0,43	-0,43	0,07	0,32	0,12	0,42	-0,42	0,12	0,11	0,21	-0,45	-0,45	0,30	0,15	0,99	0,08	0,18	0,23	-0,20	-0,24	0,58	-0,05	-0,19	0,13	-0,20	0,76				
Ce	0,91	-0,50	0,88	0,91	0,51	0,99	-0,45	0,73	0,96	0,95	0,97	-0,46	0,93	0,94	-0,42	0,98	-0,52	-0,12	0,80	0,94	0,44	0,94	0,94	0,97	0,85	0,27	0,75	0,86	-0,72	0,96	0,30	0,08			
Pr	-0,10	0,24	-0,17	0,21	-0,26	0,38	-0,37	-0,09	0,28	0,08	0,38	-0,36	0,07	0,07	-0,05	0,18	-0,39	-0,50	0,28	0,12	0,98	0,04	0,15	0,19	-0,23	-0,23	0,55	-0,07	-0,14	0,09	-0,17	0,73			
Nd	-0,12	0,31	-0,20	0,21	-0,23	0,35	-0,31	-0,10	0,26	0,06	0,36	-0,29	0,03	0,05	0,02	0,15	-0,32	-0,55	0,27	0,10	0,97	0,02	0,13	0,16	-0,24	-0,21	0,53	-0,07	-0,09	0,06	-0,12	0,69			
Sm	-0,15	0,56	-0,26	0,24	-0,06	0,24	-0,02	-0,08	0,20	0,00	0,27	0,01	-0,08	0,00	0,29	0,07	-0,03	-0,76	0,28	0,08	0,86	-0,02	0,10	0,09	-0,25	-0,08	0,44	-0,04	0,07	0,00	0,11	0,47			
Eu	-0,23	0,75	-0,38	0,18	0,03	0,04	0,20	-0,18	0,04	-0,14	0,08	0,23	-0,26	-0,14	0,54	-0,09	0,21	-0,82	0,14	-0,04	0,69	-0,15	-0,04	-0,08	-0,32	-0,09	0,23	-0,11	0,30	-0,15	0,26	0,29			
Gd	-0,31	0,90	-0,49	0,07	0,18	-0,24	0,48	-0,30	-0,20	-0,33	-0,21	0,54	-0,49	-0,32	0,82	-0,31	0,53	-0,78	-0,0																

U is controlled by zircon.

Mafic Group

The mafic group includes: Al_2O_3 , CaO, Fe_2O_3 , MgO, MnO and TiO_2 , and trace elements such as Ni, Sc, Sr and Y (Moisan, 1992; Abderrahim, 1996). The correlative diagrams show that Al_2O_3 , Fe_2O_3 , and MgO have good correlation within them. Those three oxides also show good correlation with K_2O . Their distribution may be controlled by illite, and minerals such as biotite, amphiboles, gibbsite and goethite. MnO and TiO_2 show a good correlation ($R = 0.76$). TiO_2 show a good correlation with P_2O_5 . Their distribution may be controlled by apatite. The correlative diagrams show that Al_2O_3 and Fe_2O_3 although present in felsic group of elements, have affinities with Ni and Y. These two trace elements are correlated, and may be found in goethite and gibbsite. Scandium is well correlated with Zr and Ti. These two elements are respectively found in zircon and a titanium mineral. Strontium shows a positive correlation with P_2O_5 and CaO. These two oxides are found in apatite. The distribution of Sr is surely controlled by apatite.

The main minerals which have controlled the distribution of mafic group elements are apatite and titanium mineral. Accessory minerals like zircon, goethite, gibbsite, amphibole, and biotite also control the distribution of these elements.

REE Group

The rare earth element group is divided into three parts including the light rare earth elements (LREE: La, Ce, Pr, and Nd), the medium rare earth elements (MREE: Sm, Eu, and Gd) and the heavy rare earth elements (HREE: Tb, Dy, Ho, Er, Tm, Yb, and Lu). The rare earth elements shows a good correlation with Al_2O_3 , CaO, P_2O_5 , Fe_2O_3 , MgO, MnO, TiO_2 , Th, U, Zr, Y, Sc and Sr. All of these elements are compounds in amphiboles, zircon, and apatite (Deer et al., 1992). As most of these oxides and elements have already been studied in mafic or felsic group, only correlations between HREE- Al_2O_3 , LREE- CaO, HREE- Fe_2O_3 , LREE- P_2O_5 , LREE- TiO_2 , Ce-Zr, HREE-Cs, HREE-Rb, and HREE-Ni will be used to explain the rare earth elements distribution control by minerals. HREE show positive correlation with Al_2O_3 , Fe_2O_3 , Cs, Ni and Rd. These oxides and trace elements are found in gibbsite, goethite, illite, biotite and amphibole. Most LREE and MREE show a good positive correlation with P_2O_5 , and Sr; with the exception of Ce that shows a positive correlation with Zr and Ti. P_2O_5 and Sr are mutually correlated. Most LREE and MREE are found in apatite, whereas Ce is associated to zircon and a titanium mineral.

The distribution of HREE is probably controlled by illite, gibbsite, goethite, and biotite and amphibole. The distribution of LREE and MREE is controlled by apatite,

except Ce whose distribution is controlled by zircon and titanium mineral.

Source of sediments

The most important elements used for provenance study of a sedimentary material are REE, Th, Sc (Moisan, 1992; Abderrahim, 1996; Singh, 2009). These elements have a very low concentration in rivers and sea water. They can not persist for a very long time in ocean. Their proportion is not affected by diagenesis and metamorphism. These elements are exclusively transported as detrital fraction of sediment, and consequently reflect the chemistry of their source area (McLennan et al., 1983a; Taylor and McLennan, 1985). The plotted data for Bangué sandstones and pelites in La-Th-Sc sources discrimination ternary diagram (Fig. 5A) places these rocks within the mafic field with very high Sc content, average Th/Sc ratio (1.5), and La/Sc ratio (0.89). The presence of the relatively less mobile elements may reflect a local provenance of the studied samples. The Th/Sc ratio is probably more sensitive to the source average concentration than the REE. This is because the REE variation may typify different characteristics of their provenance (McLennan et al., 1990) or due to the effect of some REE bearer minerals (Cullers et al., 1987; Cathélineau, 1988). The REE mobility during diagenesis has been mentioned by Milodowski and Zalasiewicz (1991). The sample distribution in Co/Th versus La/Sc plot diagram shows a contribution from a more mafic to intermediate sources (60 to 50%), when compare to McLennan et al. (1983a) same diagram; but, with high Co and Sc content, and low Th and La contents (Fig. 5B).

Depositional environment

The palaeoenvironmental reconstitution of Bangué sandstones and pelites was difficult because of the presence of very thick soil profile, the scarcity of outcrops, the discontinuity of outcrops, and a very high chemical weathering index ($CWI \geq 90\%$). However, the up to 4m scarp shaped outcrop found at the bank of river Lokomo, shows a decrease in quantity and grain size of quartz and quartzite from bottom to the top (normal grading). The disposition and succession of graded bedding sediments suggest that, sedimentation took place in lower energy environment. This low dynamic environment of sedimentation can be marine or continental (Lacustrine or fresh water). Due to those difficulties many authors (Bolhar and Kranendok, 2007; Frimmel, 2009; Caron et al., 2010) have used the nature and abundance of rare earth element and Y, to characterize sediments depositional environment. Those elements are characteristics of every depositional environment: marine, lacustrine, and fresh water, only if detrital contaminations,

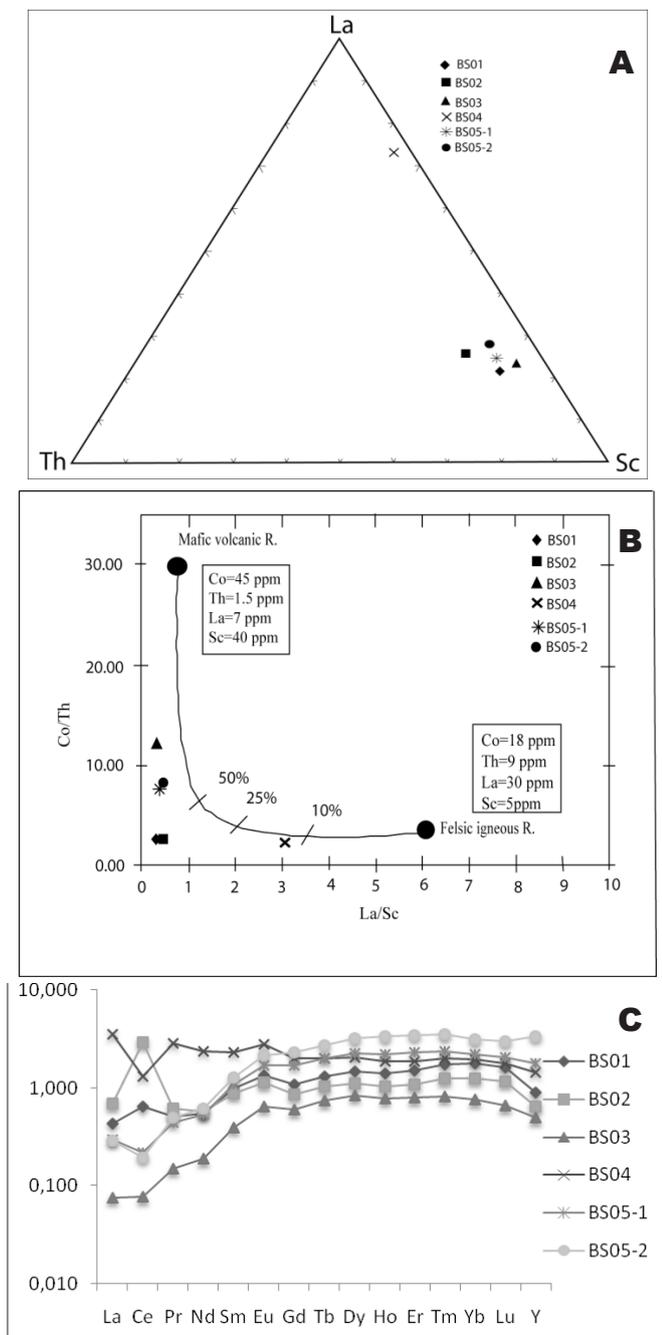


Fig. 5: Sample plot of sandstones and pelite from Bangué in the La-Th- Sc ternary diagram (A). Co/Th versus La/Sc diagram of the sandstones and pelite from Bangué. The ligne represents the average of the mafic volcanic and felsic igneous rocks (after McLennan et al., 1983). The average concentrations for the extreme composition of the line are from Jahn et al.1983) and Glikson and Hickman (1981) except the concentrations of Sc, the average archean from values McLennan (1981). Percentage values indicate the percentage of the contribution of mafic volcanic. R. volcanic = volcanic rocks (B). REE+Y spider diagram of the sandstones and pelites from Bangué normalized to PAAS (C).

diagenetic and metamorphic changes have not rubbed out the primary elementary signatures. A marine depositional environment is characterized by: a negative Ce (Ce/Ce^*) anomaly, HREE enrichment, and a positive Eu (Eu/Eu^*), Gd (Gd/Gd^*) and La (La/La^*) anomalies (Bolhar and Van Kranendonk, 2007; Caron et al., 2010). The normalized

rare earth element data for Bangué sandstones and pelites show flat spectrums for HREE (Fig. 5C). Those spectrums display a positive Ce (Ce/Ce^*) anomaly for two samples (BS01 and BS02) from quartzitic sandstones found at the bottom of scarp shape outcrop, and a negative anomaly of this same element for other samples. In addition, all samples from Bangué sandstones and pelites are HREE enriched, and have a positive Eu (Eu/Eu^*) anomaly. They also present positive and negative anomalies for Gd (Gd/Gd^*) and La (La/La^*). The Y/Ho ratios are less than 40.

DISCUSSIONS

Sandstones and pelites are sensitive to weathering, diagenesis, and particularly to mineralogic and chemical variations (Moisan, 1992; Abderrahim, 1996). Bangué sandstones and pelites are made up of goethite, gibbsite, kaolinite, and illite. These minerals are often products of weathering processes, but can also be inherited (Potter et al., 1980; Reynolds and Moore, 1989). The presence of kaolinite, goethite and gibbsite which are mainly found ferrallitic soils suggests that the paleoclimate was equatorial (Cailler et al., 1989; Comment G, 2006). The chemical weathering index (CWI) for rocks in Bangué are greater than 90%. CWI values ranging from 75 to 86 suggest that the source rocks of Bangué sandstones and pelites were subject of intensive weathering activities (McLennan et al., 1983a). This suggestion is supported by the good correlation between Ni and Al_2O_3 (0.67), based on studies by Feng and Kerrich (1990). Consequently, some soluble and mobile elements (CaO , Fe_2O_3 , Na_2O , MgO , MnO and K_2O) found in these rocks will be treated with precaution. They are less sensitive when used to identify specific bearer minerals, when applied in provenance study, and to determine the nature of sediment depositional environment (McLennan et al., 1990). Elements such as Cr, Ni, Co, and Ba are weakly or strongly affected by weathering, dissolution, transportation, depositions, and diagenesis (McLennan et al., 1990). For Taylor and McLennan (1985) and Bhatia and Crook (1986), Zr, Sc, Nb, Hf, Y and Th are generally resistant to changes during weathering. In addition, Zr and Hf can be mechanically distributed. This distribution is controlled by the nature and grain size of heavy minerals. Those felsic source elements can be found in zircon, which can also play an important role on the rare earth elements budget in sediment (Cullers et al., 1987; Cathélineau, 1988). The Bangué sandstones and pelites have a high Zr content (BS01, BS02 and BS04). The Ce (Ce/Ce^*) anomalies can be due to the high Zr abundance. In many igneous processes, V is often related to Cr and Ni (Feng and Kerrich, 1990). The separation of V from Cr and Ni are in some case due to weathering. The negative correlation between V and Ni (-0.49), and very high positive correlation between V and Cr (0.85) suggest that these elements were separated by weathering, or were

not related in their source rock (fairly ultramafic and mafic source). The high Cr (39.0-2347.0 ppm) and Ni (83.3-603.5 ppm) contents and the positive correlation between MgO and Cr, Ni, and Co may suggest an ophiolitic source (ultramafic) if based on Hiscott, (1984) and Abderrahim, (1996) studies.

The observed REE spectrums (Fig. 5C) for the Bangué sandstones and pelites are flat for HREE, truncated for LREE, and do not show any intense marine water signature. For Frimmel (2008) and Caron et al. (2010) contamination from continental source can modify the chemical properties of sea water, and greatly impact the REE spectrums of this water. These spectrums are generally flattened. The geochemical anomalies are also modified, and the Y/Ho ratio is closed to that of PAAS (27.3). The Y/Ho ratios for Bangué sandstones and pelites range from 17.2 to 27.6. Zirconium, Thorium and aluminum abundances are often used as tracers for contamination from schistose rocks, because they are found in argillaceous and other detrital materials. Moreover, correlations between Zr-Y/Ho; Zr- Σ REE, and Al-Th can typify contamination from schistose rocks (Bolhar and Van Kranendonk, 2007; Caron et al., 2010). The Bangué sandstones and pelites are characterized by high Zr content, ranging from 44 to 277 ppm. This element has an average correlating coefficient with Al ($R_{Zr-Al_2O_3} = 0.47$), and a low negative correlating coefficients with the Σ REE ($R_{Zr-\Sigma REE} = -0.12$), and Y/Ho ($R_{Zr-Y/Ho} = -0.44$).

CONCLUSION

The Bangué sandstones and pelites belong to the Ngola series, which is the upper part of lower Dja series. The X-ray diffraction mineralogical analysis of these sandstones and pelites identified non argillaceous and argillaceous minerals. The major and trace element geochemical analyses helped to identify elements bearer minerals phases, and also to determine the tectonic settings and depositional environment of these lithified sediments.

The mineralogical budget obtained by x-ray mineralogy and geochemistry includes: argillaceous minerals (illite and kaolinite), and non argillaceous (quartz, goethite, gibbsite, zircon, apatite, biotite, amphibole, and a titanium mineral).

The geochemical method supports the idea of a distribution of mainly one elementary population during the depositional phase of the lithified sediments. This population is dominated by mafic elements (45%) with limited contribution from felsic source. They were probably sorted from mafic to intermediate source rocks.

The high and low positive correlations between MgO and Co, Ni, and Cr show that the lithified materials forming the Bangué sandstones and pelites were probably sorted from ophiolitic rock. The flat HREE spectrums

and positive correlation between HREE and CaO, Fe₂O₃, Na₂O, Al₂O₃, and K₂O, characterize contaminated patterns by elements from clay, gibbsite and goethite. The analyzed samples mostly show negative Ce (Ce/Ce*) anomaly, except in BS01 and BS02 which are Zr-enriched. Zirconium has largely influenced the rare earth elements patterns, particularly the Ce behavior. The Bangué sandstones and pelites were deposited and lithified in a marine environment characterized by HREE enrichment, and positive and negative Gd (Gd/Gd*) and La (La/La*) anomalies, due to contaminations from detrital sources.

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