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Tracing the Sources of Paleoproterozoic Metasediments in the Comoé Basin, Côte d'Ivoire, West Africa : Geochemistry Implication

Koffi Raoul Teha a*, Koffi Kossonou Jean-Marie Pria ^b , Augustin Yao koffi^a, Koffi Joseph Brou^a, **Brice Roland Kouassi ^c and Alain Nicaise Kouamelan ^a**

^a Université Félix Houphouët-Boigny Abidjan-Cocody, Laboratoire Ressources Minérale et Energétique (LGRME), UFR STRM, 22 BP 582 Abidjan 22, Côte d'Ivoire. ^b Département des Sciences de la Terre, Université Jean Lorougnon-GUEDE Daloa, Laboratoire Sciences et technologie de l'environnement, UFR Environnement, BP 150 Daloa, Côte d'Ivoire. ^c Département de Géosciences, Université Péléforo Gon Coulibaly Korhogo, UFR des Sciences Biologiques, BP 1328 Korhogo, Côte d'Ivoire.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Petrology and geochemistry have been used jointly to study the metasediments of the Comoé Basin. The main objective is to identify the sources of the metasediments. The entire Comoé metasedimentary basin is dominated by greywackes and shales. The mineralogy of the greywackes

**Corresponding author: E-mail: rkteha@hotmail.fr;*

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consists of biotite, plagioclase, quartz, muscovite, chlorite, ilmenite and other oxides. The shales contain andalusite, biotite, muscovite, quartz and chlorite. Overall, the geochemistry of the major elements shows an enrichment of Fe₂O₃, MgO, Al₂O₃, K₂O and TiO₂ in the metapelitic rocks. These oxides are controlled by the distribution of phyllosilicates. Observation of diagrams of rare earth elements has shown that the source of these elements in these metasediments for these elements is largely controlled by the TTG. On the other hand, a large quantity of felsic material, in particular felsic rocks, contributed to the composition of the sediments. Mafic rocks contributed to a lesser extent.

Keywords: Côte d'Ivoire; Comoé basin; metasediments; sources; TTG.

1. INTRODUCTION

The West African Craton (WAC) is formed by the Leo-Man shield and the Reguibat shield, separated by the Taoudeni Basin ([1-7], Fig. 1a). It underpins several countries including Côte d'Ivoire. The southern part of the West African Craton is represented by Côte d'Ivoire, which has two basins belonging to the paleoproterozoic domain: the Comoé basin and the Lobo basin ([1], Fig. 1b). The Comoé basin is located to the South-East of the Leo-Man shield. It extends from the south to the north of Côte d'Ivoire and is 17 km thick (Fig. 1b).

Several field and laboratory studies have been conducted [8-11]. These studies have provided insight into the tectonics, classification and origin of the metasediments. The Comoé metasedimentary basin is dominated by metapelites and metaarenites [12]. These rocks are intruded by a variety of granitoids [13- 15].

This paper will (i) compare the chemical compositions of the rocks to see if there is any variation in lithology and (ii) trace the sources of the Comoé basin sediments. Arenites and pelites are major groups of metasedimentary rocks. These rocks must be accurately identified by classification. Sampling was carried out on finegrained rocks. The collected rocks are rich in rare earths and record the intensity of weathering during transport and diagenesis processes. The petrology and chemical composition of major, minor and trace elements are analysed on these metasedimentary rocks in order to assess their chemical composition in space and time. The use of lithogeochemistry will allow us to establish correlations between macroscopically similar, metamorphosed and deformed sedimentary units [16,17]. Mechanically and chemically stable minerals from a source are of great use for this study [18].

Fig. 1. Regional geologycal maps

a) Geological sketch map of the West African Craton (WAC) (modified after [19, 20]). The map shows the capitals of the countries. b) Simplified geological map of Leo-Man shield (modified after [21, 22]), location of Comoé basin in the South-East part of Leo-Man shield

1.1 Geological Setting

The Leo-Man ridge consists of the Kenema-Man domain and the Baoulé-Mossi domain [23-25]. The two domains are separated by the Sassandra shear zone [26]. The Kenema-Man domain is located west of the Sassandra shear zone. It composed of tonalite-trondhjemitegranodiorite (TTG) plutons, extensive gneissic domains and volcano-sedimentary meta belts [27,4,28,29]. The metavolcanic-sedimentary belts are delimited by shear zones and alternate with TTG granitoids and gneissic domains.

The Baoulé-Mossi domain is also called the Paleoproterozoic domain. It is located to the east of the Sassandra shear zone and covers a large part of the Leo-Man shield. This vast domain is made up of deformed and metamorphosed volcanic, volcano-sedimentary and metasedimentary rocks. These rocks are intruded by several generations of granitoids with alkaline, calc-alkaline geochemical signatures and peraliminous [30-33,13].

1.2 Geology of Comoe Basin

The study area consists of volcano-sedimentary, meta-sedimentary and granitoids intrusions (Fig. 2). The Comoé domain is located to the South-East of the Palaeoproterozoic domain. The lithostratigraphy of the Comoé unit is essentially composed of quartzites, basic to acid vulcanites [34], shales and sandstones [35,36] resting unconformably on an antebirimian granitomigmatitic basement. Volcanic formations are very little represented and essentially on the periphery.

The metasediments are composed of sericitoschistes, chloritoschistes and poundingues, with compositions of quartz arenite, litharenites and sandstone (arkose and ferruginous sandstone) [10]. The petrographic and structural study permits to characterize, in part, thirteen different facies of granitoids in the Tiassalé region (southern Côte d'Ivoire) [14]. The absence in the region of gneiss and migmatites, the presence of enclaves of varied petrographic type in the studied different facies, in favor of the hypothesis of a mantle or mixed origin of the the magmas for these granitoid facies [14]. For [13], the absence of contact metamorphism indicates that the sedimentary series must be deposited on these granites. These massifs may correspond to the complex TTG units of the Nassian domain that were emplaced very early during eburnean history. The protoliths of metasediment are ranging from gabbro to granodiorite, all have been affected by strong to moderate alteration (62 $<$ CIA $<$ 97) [9,10].

2. ANALYTICAL METHODS

Petrography and geochemical analysis are the main methods used to achieve these objectives.

2.1 Petrography

The petrographic study of the rocks was carried out by traversing the region from north to south. Petrography consisted in describing the lithological units observed in the various outcrops encountered. Eight thin sections were prepared at the Laboratoire des Sciences de la Terre et des Ressources Minières (UFR-STRM) of the Université Félix Houphouët Boigny d'Abidjan - Cocody. The samples are located on the litho-structural map. They are numbered MS01 to MS08 (Fig. 2).

metasedimentary rocks from the Comoé basin were analysed (Table 1). ICP-AES and ICP-MS methods were used to determine major and trace elements respectively. Sample preparation consists of grinding some of the fresh rock into powder. To do this, the samples are sawn, washed several times to remove the dust and dried in an oven. The loss on ignition is measured. It allows the degree of weathering, water and carbonate content to be quantified. The loss on ignition is determined according to the formula :

Loss on ignition $=$

$$
\frac{\text{Sample weight} - \text{Calcined sample weight}}{\text{Sample weight}} \times 100
$$

The geochemical data was used to draw up diagrams that provide information on the geochemical characteristics and geotectonic environments of the petrographic facies.

Fig. 2. Litho-structural map of the Comoé basin [12], modified *Black squares show the location of the studied rocks of the Comoé basin*

2.2 Geochemistry

The chemical composition was determined in the BUREAU VERITAS laboratory. Eight

Table 1. Whole rock major and trace element composition

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a : Detection Limit

b : Chemical Index of Alteration

3. RESULTS AND DISCUSSION

3.1 Results

The main results of the petrographic and geochemical data are highlighted in this section.

3.1.1 Petrography characteristic

Metasedimentary rocks are observed in the Bandama (Fig. 3a) and N'Zi (Fig. 3b) rivers. These are rocks that form alignments of sometimes thin bands. The outcrops have a foliated appearance, generally derived from arenites with relatively abundant cement (20%). The main foliation S1 is N-S to NNE-SSW trending with subvertical dips (Fig. 3). In this section, we have distinguished between the metasediments of the Tiassalé group and those of the Toumodi group.

3.1.1.1 Metasediments of the Tiassalé group

The Tiassalé sector includes the localities of Tiassalé, M'Brimbo and N'Zianoua. We collected five metasedimentary rocks in this area (MS02, MS03, MS04, MS05 and MS06). Macroscopically, these samples are dark-green, fine-grained and foliated. They are composed of greywacke (MS02 and MS03) and orthoschist (MS04, MS05 and MS06). The greywacke consists of 40% quartz, 35% plagioclase and 20% biotite. Quartz and plagioclase crystals are subrounded. Accessory minerals are mainly represented by oxides (Fig. 4a). The shales show a variety of compositions (Fig. 4b and c). Sample MS04 is an andalusite micaschist. It consists of small micas crystals (biotite and muscovite) reaching 50% and quartz (40%). The coarse grains are andalusite (5%). Micas form the main minerals of the S1 main foliation (Fig. 4b). The foliation in the orthoschist is materialised by brown biotite and muscovite, which represent 60% of the minerals in the rock. The mica beds alternate with quartz (35%) (Fig. 4c).

3.1.1.2 Metasediments of the Toumodi group

This group includes the localities of Kalégoua, Laourébo and Kouadiotèkro. We collected three samples in the Toumodi area (MS01, MS07 and MS08). The metasediments are dense, very coherent, with a fine texture (Fig. 4d, e and f). Samples MS01 and MS07 are greywackes with

contrasting mineralogical compositions (Fig. 4d and e). Chlorite and muscovite represent 70% of the minerals in sample MS01 (Fig. 4d). Together with the quartz (25%) beds they form the foliation in the rock (Fig. 4d). Accessory minerals are ilmenite (5%) (Fig. 4d). However MS07 is very abundant in quartz of various sizes (60%) (Fig. 4e). The quartz crystals are surrounded by fine beds of brown biotite (30%) (Fig. 4e). Accessory minerals are oxyde (3%) (Fig. 4e). Sample MS08 is composed of chlorite (35%), quartz (30%), muscovite (20%) and biotite (15%). These minerals are the main foliation of the rock (Fig. 4f). The coarse grains are staurotite, moulded by the S1 foliation (Fig. 4f).

3.1.2 Geochimical characteristic

3.1.2.1 Classification of Comoé metasediments

In this section, we used several diagrams to discriminate the metasedimentary rocks of the Comoé. According to the classification diagram $Log(Fe₂O₃/K₂O)$ versus $Log(SiO₂/Al₂O₃)$, proposed by [37], the samples of the Tiassalé and Toumodi groups are related to greywackes and shales (Fig. 5a).

In Fig. 5b, these metasedimentary rocks show mostly alkaline affinities in the $(Na₂O+CaO)/K₂O$ versus SiO² diagram [38]. However, some samples (shale) from the Tiassalé group show potassic characteristics (Fig. 5b). The variation of K_2O/Na_2O versus SiO_2 ratios (Fig. 5c), in the discrimination diagram of [16], places the samples of the Toumodi group and some of the Tiassalé samples in the active continental margin field. Some samples (shales), mainly those from Tiassalé, are in the island arc field.

3.1.2.2 Major oxides

The degree of alteration of the metasediments during chemical weathering is determined from the Chemical Index of Alteration (CIA) diagram [39]. CIA is calculated from the molecular proportions:

$$
CIA = [Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)]
$$

x100.

CaO* is the concentration of CaO incorporated in the silicate fraction of the rock. The diagram in Fig. 6a shows the results of the calculation of the Chemical Index of Alteration.

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Fig. 3. Foliated metasedimentary rocks in the Bandama and N'Zi river beds *a) NNE-SSW oriented millimetre thin bands make up the Bandama metasediments. b) NNE-SSW foliation observed in the decimetric beds of the N'Zi River*

Fig. 4. Photographs and microphotographs of studied metasedimentary rocks of Comoé basin. *Abbreviations : MS01 = Sample identification ; q = quartz ; pl = plagioclase ; bi = biotite ; and = andalusite ; mu = muscovite ; ox = oxide ; ilm = ilmenite ; chl = chlorite ; st = staurolite*

Fig. 5. Discrimination diagrams of the metasedimentary rocks of the Comoé basin.

a) Log(Fe2O3/K2O) versus Log(SiO2/Al2O3) diagram according to [37]. The metasediments are composed of greywackes and shales; b) Diagram (Na2O+CaO)/K2O versus SiO² showing the alkaline and potassic characters of the metasediments, after [38] ; c) Discrimination diagram of K2O/Na2O versus SiO² of the geotectonic context of the metasediments, after [16]

The general trend indicates an increase in the chemical index of alteration in the Comoé metasediments. This index is above 78. For metasediments with SiO₂ contents between 65-75%, the chemical index of alteration varies from 60 to 70. $SiO₂$ contents of 53-63% show chemical index of alteration of 70-80. The chemical index of alteration between 60-80 reflects low to moderate alteration of the source rock [40,41]. In addition, the compositional poles of the source rocks (TTG and mafic rocks) have lower index than the metasediments. However there is a negative correlation between the chemical index of alteration of metasediments, felsic rocks and SiO2. The approximately linear distribution indicates the intervention of a felsic source. The shales of the Tiassalé Group have the highest indexes. The material of these rocks is more altered than the other rocks of the basin.

In detail, the samples vary inversely with silica content (Fig. 6b, c). There is an increase in Fe

and Mg in the metasediments. Some samples of Tiassalé shale are rich in Fe (about 10%, for a SiO² content of 53.82%). They are similar to mafic rocks. The SiO₂ vs MgO diagram indicates that the Fe-rich samples are also enriched in Mg. In both diagrams, there is an excellent correlation between the metasediments and the TTG. However, in the SiO₂ vs. Fe₂O₃ diagram, this negative correlation is also associated with mafic and felsic rocks. The linear trend of the rocks would indicate that the metasediments come from the same source.

In the diagram in Fig. 6d, the correlation is negative between metasediments, TTG and felsic rocks. Al₂O₃ content varies inversely with silica. There is a high proportion of aluminiumrich minerals. Aluminium content varies between 10% and 25%. Samples rich in Al_2O_3 are the poorest in SiO2. These aluminium-enriched samples suggest the presence of aluminous minerals such as kaolinite in the initial sediments [42,43].

Fig. 6. Distribution of metasediments in SiO² vs oxide diagrams of Harker

The black arrow indicates the enrichment or depletion of oxides relative to silica. The stars represent the location of mafic, felsic and TTG rocks. The dotted vertical line corresponds to the boundary between shales and greywackes

The $SiO₂$ vs $K₂O$ diagram also shows a negative correlation (Fig. 6e). $K₂O$ is a component of white micas and alkali feldspars. The slope indicates a gain in potassium in the residual alteration minerals $[42]$. Similarly, $SiO₂$ vs TiO₂ and SiO₂ vs P₂O₅ show negative slopes. However, a slight dispersion can be seen in the diagram in Fig. 6h. $TiO₂$ and $P₂O₅$ are considered to be immobile elements during weathering. TiO₂ would be contained in the ilmenite described in the petrography. The slight enrichment in P₂O₅ suggests that apatite and monazite are present in greater quantities. Both diagrams show a relationship between metasediments and TTG. There is also a good correlation between metasediments, mafic rocks (Fig. 6g) and felsic rocks (Fig. 6h). The TTG could be the source of the metasediments, with mafic and felsic material

participating. This observation will be verified with the following diagram.

The diagram in Fig. 6f shows a positive $correlation$ between $SiO₂$ and CaO. However, there is no correlation between the metasediments and the felsic, mafic and TTG rocks. In this diagram, the positive slope indicates a loss of CaO in the alteration solution.

3.1.2.3 Rare earth elements

The chemistry of the metasediments shows La contents ranging from 18.2 to 43.4 ppm, Ce from 37.1 to 81.2 ppm, Pr from 4.45 to 9.83 ppm and Nd from 17.4 to 35.2 ppm (Tab. 1). The HREE show lower values than the LREE. The rareearth spectra of metasediments normalized to the chondrites of [44], indicate a moderate fractionation in LREE, reflected by their ratio (La/Sm)n between 3.15 and 4.36. The (Gd/Yb)n ratio is in the range 1.53-1.97, suggesting subflat HREE spectra. The metasediments show enrichments in light rare earths relative to the chondrite of the order of more than 55 to more than 100 times for La, 45 to 100 times for Ce, 35 to 90 times for Pr and 30 to 65 times for Nd. The contents of heavy rare earths (Er, Tm, Yb) are grouped together and do not exceed 15 times the in the chondrite. There is also a small negative anomaly in Eu (Eu/Eu^{*} = 0.83-0.95) (Fig. 7). The almost identical spectra suggest that the metasediments may have the same sources, with slight variations.

3.1.2.4 Characterisation of the source of metasediment

Some rare earth elements and other elements with a high ionic potential are characterised by their low mobility, small size and high electronic charge. Zircon contains a portion of these elements transported in sedimentary rocks during alteration and transport. They reflect the signature of the parent material [45,42]. These elements will be used to determine the source of the metasediments and the provenance of the clastic sediments.

The diagrams in Fig. 8 use constituents from mafic rocks (TiO₂, Y) and felsic rocks (Zr). In Fig. 8a (Zr vs. TiO₂), the metasediment samples are outside the field defined by the TTGs, mafic and felsic rocks. They cluster around the TTG. A wide dispersion is observed in the Y vs. $TiO₂$ diagram (Fig. 8b). The samples are closer to the poles of the TTG and mafic rocks. In both diagrams, zirconium (Zr) , yttrium (Y) and titanium (Ti) are elements controlled by sources close to the TTG that have been diluted by a mafic source.

Trace elements are also influenced by their source, erosion and diagenesis [38]. Like Zr, Hf is an immobile element that is distributed mechanically. Their concentration depends on the heavy minerals. Th is transported in clasts and reflects the geochemistry of the source [38]. The Th vs U binary digram shows a good distribution and correlation (Fig. 9a). U/Th ratios range from 0.18 to 0.36. The chondritic ratio is around 0.28.

The Hf vs Zr diagram in Fig. 9b also shows a good distribution and a positive correlation. Zr/Hf ratios are generally greater than 36 (chondritic ratio). The trace elements used in these two diagrams reflect signatures characteristic of a felsic source (TTG).

There are two trends in the La vs Th diagram (Fig. 9c). The first trend shows a high La/Th ratio of 10.09. This ratio reflects Th depletion in some metasediments. The second trend shows a slight enrichment in Th. The La/Th ratio is 6.53. This diagram shows that a large quantity of felsic material contributed to the formation of the sediments in the Comoé basin. Both trends would explain the distinct tectonic environments [46].

Fig. 7. Rare earth spectra

a) Rare earth spectra of metasediments normalized to chondrites, [44]. b) General trend in metasediment spectra

Fig. 8. Source identification diagrams, after [38], modified

a) Zr vs TiO² ; b) Y vs TiO2. The stars represent the location of possible sources

Fig. 9. Trace element variation diagrams for metasedimentary rocks

a) Th vs U ; b) Hf vs Zr ; c) La vs Th to determine the source of the initial sediments, the black arrows represent the increase in La and the increase in Th

3.2 Discussion

Petrographic studies of metasediments have revealed greywack, shale and micaschist in the Comoé Basin. These metasedimentary rocks are also highlighted by [9], in the SASCA transition zone by [47], and in southern Ghana by [48].

The geochemical aspect indicates low to moderate CIA, similar to the metasediments described in north-eastern Canada [49]. The enrichment of $Fe₂O₃$, MgO, Al₂O₃, K₂O and TiO₂ indicates that the Comoé basin has a mafic component in its composition and a volume of clay minerals. The P_2O_5 enrichment suggests a large quantity of minerals resistant to alteration, such as apatite and monazite [42] This volume of minerals can be explained by a proximal source or a source rich in P_2O_5 . CaO depletion reflects a small proportion of calcium plagioclase. However, there is an increase in NaO₂. This enrichment reflects a greater input of felsic material or a proximal source.

Diagrams using rare earths and trace elements are the most discriminating. Slight variations can be observed in the rare earth profiles. The factor that justifies these variations in rare earth profiles in metasedimentary rocks is their origin [50,51]. Rare earth profiles revealed slight negative anomalies in Eu, like the metasediments described by [42,38]. This trend towards negative Eu anomalies in metasediments suggests that the source was derived from a fractionated magma [52]. The weak Eu anomaly also reflects the erosion of a high relief followed by a relatively short transport [38]. Plagioclase minerals are therefore preserved in certain metasediments. Interpretation of the diagrams suggests that the composition of the metasediments in the Comoé basin is mainly controlled by the TTG at source. However, a non-negligible quantity of mafic and felsic material have contributed to the composition of the metasediments. These observations were made in the Kumasi basin by [48, 53]. Indeed, after modelling the source of the Kumasi Basin shales, [53] showed that it is composed of 62% TTG, 22% basalt and a minority of granite. Conversely, [9] and [10] have respectively shown that the protoliths of metasediments are closer to gabbros and evolve towards granites and granodiorites. Based on the work of [54], a fractionated LREE model with an almost flat HREE trend and low to moderate Eu anomalies $(Eu/Eu^* = 0.83$ to 0.95) could indicate that feldspar granite-granodiorite is a likely composition in the provenance.

Finally, the geochemical data show that the majority of the metasediments were formed on active continental margins and a minority on the margins of oceanic island arcs. This dual tectonic environment has contributed to the formation of metasediments in Côte d'Ivoire [55-57,9,47,10], in India [58] and Canada [42]. These tectonic environments could suggest that the sediments accumulated at different times. This observation needs to be corroborated by U-TH-PB isotopic studies [59]. The aim of this work is to model the source of the Comoé metasediments more accurately.

4. CONCLUSION

A petrographic and geochemical study of the Comoé basin was carried out to determine the composition and origin of the sediments. This study provided evidence of the existence of varied lithologies within the same basin. Petrography revealed shales and greywackes with varied mineralogical compositions. The metasediments have alkaline and potassic affinities. A chemical alteration index of between 60 and 80 indicates atmospheric alteration of the source rocks. The composition of metasediments in the Comoé basin is controlled mainly by the presence of TTG at source. A rich quantity of mafic and felsic material also contributed to the formation of the metasediments. The Comoé metasediments were emplaced in the context of an active continental margin and an oceanic island arc margin.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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