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Petrography and Geochemistry of Upper Paleozoic Sandstone around Kuch Area, Blue Nile Basin, Central Ethiopia: The implication for Provenance, Paleoclimate and Tectonic

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Petrography and Geochemistry of Upper Paleozoic Sandstone
around Kuch Area, Blue Nile Basin, Central Ethiopia:
The implication for Provenance, Paleoclimate and Tectonic
Setting

By
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A Thesis Submitted to the School of Earth Sciences, Bahir Dar University in
partial fulfillment of the Degree of Master of Sciences in Petrology

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Approval of the thesis for defense

I hereby confirm that I have supervised, read, and evaluated this thesis/dissertation titled "Petrography and Geochemistry of Upper Paleozoic Sandstone around Kuch Area, Blue Nile Basin, Central Ethiopia: the implication for Provenance, Paleoclimate and Tectonic Setting" by Tigist Birhanu prepared under my guidance. I recommend the thesis/dissertation be submitted for oral defense (mock viva and viva voce).

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Declaration

I hereby certify that the entire work to this thesis entitled "Petrography and Geochemistry of upper Paleozoic Sandstone around Kuch Area, Blue Nile Basin, Central Ethiopia: the implication for Provenance, Paleoclimate and Tectonic Setting" was done by me, Tigist Birhanu, for partial fulfillment of the requirements for the award of the Degree of Master of Science in petrology to the School of Earth Sciences, Bahir Dar University (BDU) under the supervision of Minyahl Teferi (PhD.) and Dawit Libene (P.D.).

I announce that the entire material my original work and only with the use of the referenced literature and the described methods. The results embodied in this thesis have not been submitted in part or whole to any other university or institute for assessment or award of another degree.

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ABSTRACT

Paleozoic sedimentary rocks in the Blue Nile of central Ethiopia are related to two major Gondwana glaciations: namely, the Late Ordovician-Silurian and the Carboniferous-Permian glaciation. The present study investigates sandstone sections cropping out in the Bokotabo Sentom and Daguja town, both which are found around the Kuch area, in the western parts of Blue Nile basin, central Ethiopia. The upper Paleozoic sandstones are composed of mudstones, siltstones and sandstones in the Bokotabo Sentom area and deposited as sandstone and tillite in the Daguja area. The present study is aimed at investigating the petrography and geochemistry of these sandstones to evaluate the provenance, the tectonic setting, and the paleoclimate conditions under which the upper Paleozoic sandstones were deposited. The study was conducted using a transmitted microscope, inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Based on major, trace and rare earth element analysis and petrography, the upper Paleozoic sandstones are dominated by Quartz (on average of 64.5% in Bokotabo Sentom area and 58.4% in Daguja area) and followed by feldspars (on average of 31.0% in Bokotabo Sentom area and 36.6% in Daguja area) and rock fragment (on average of 3.2% in Bokotabo Sentom area and 4.9% in Daguja area). The sandstone is medium to coarse grained, texturally immature to sub mature, and poorly to moderately sorted. The sandstone was derived from transitional continental and basement uplift rocks. The sandstone could be classified as arkosid lithic arenite. The chemical index of alteration, plagioclase index of alteration, and chemical index of weathering values identify the upper Paleozoic sandstone has moderate to high weathering history in the Bokotabo Sentom area and low to moderate in the Daguja area. Based on trace and rare earth element concentrations, its sources possibly are juvenile material, the basement nearby.

Keywords: upper Paleozoic, Sandstone, Blue Nile basin, Petrography, Geochemistry, Provenance

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ACRONYMS

ACM ,, active continental margin	REE ,, rare earth element (HREE heavy REE; LREE,, light REE)
Afsp ,, alkali feldspar	PI- Paleozoic
ALS ,, Australia laboratory service	SIT ,, siltstone
ANS ,, Arabian-Nubian Shield	SRF,, Sedimentary rock fragment
CIA ,, chemical index of alteration	SST,, sandstone
CIW ,, Chemical Index of Weathering	TIL,, tillites
DF ,, discriminant function	TTE ,, transition trace elements
Gr ,, granitoid	UCC,, Upper Continental Crust
HFSE,, high field strength elements	
ICP-AES ,, inductively coupled plasma atomic emission spectroscopy	
ICP-MS ,, inductively coupled plasma mass spectrometry	
IRF ,, Igneous rock fragment	
LILE ,, large-ion lithophile elements	
LOI ,, Loss on ignition	
MRF ,, Metamorphic rock fragment	
Mc ,, microcline	
Md ,, mudstone (for thin section)	
MST- mudstone (for thin section)	
PAAS ,, PostArchean Australian Shale	
PIA ,, plagioclase index of alteration	
Plg,, plagioclase	
PM ,, passive margin	
QFL- Quartz Feldspar Lithics	
Qm- monocrystalline quartz	
QmFLt ,, monocrystalline quartz-feldspar lithic fragment	
Qp- polycrystalline quartz	

1. INTRODUCTION

1.1. BACKGROUND OF THE STUDY

In the Paleozoic, two main glaciation events have been reported from various locations within the Gondwana continent. However, the period and the areal coverage of the glaciated areas are not completely understood (Lewin et al., 2018; Elhebery et al., 2019). The lower Paleozoic (upper Ordovician to Silurian) glaciation was depicted, relatively, as a limited, momentary (~10 Ma) Hirnantian event and the upper Paleozoic (Carboniferous to Permian event) lasted for tens of millions of years (>70 Ma) (Isbell et al., 2012). During the Ordovician glaciation, a wide range of glacial deposits such as glacial landforms including tunnel valleys, megalake glacial lineation, and paleo-ice streams have been formed, particularly in northern Gondwana (Armstrong et al., 2005). During the upper Paleozoic (Permian to Carboniferous) glaciation, the southwestward migration of the glaciogenic deposits was in response to movement of the southern pole across Gondwana from NW Africa to central Antarctica (Scottese and Barrett, 1990; Torsvik and Cocks, 2013). Both Paleozoic glaciations are identified in northern Central Africa (Niger and Chad), Horn of Africa (Eritrea and Ethiopia) and southern Saudi Arabia, while Carboniferous to Permian glaciogenic deposits have been well documented from southern Arabia (i.e. Yemen and Oman) (Elhebery et al., 2019). The upper Paleozoic glacio-lacustrine and glacio-lacustrine deposits occur in East Africa (Wopfner and Kreuser, 1985). The upper Paleozoic siliciclastic sedimentary rocks are recognized from the south of the Equator, starting from Ethiopia in the north up to South Africa in the south (Elhebery et al., 2019).

In Ethiopia, there are two types of Paleozoic sedimentary rocks which are related to the two major Gondwana glaciations: Enticho sandstone (Late Ordovician to early Silurian) which is exposed in the Mekelle basin and the upper Paleozoic sandstone (the Carboniferous to Permian) which are exposed in Mekelle basin (Edaga arbi glacials) and Blue Nile basin (Bussert, 2010; Lewin et al., 2018). They are underlain by Neoproterozoic basement rocks and covered by Mesozoic clastic and carbonate sediments (Erturk, 2010; Lewin et al., 2018).

The study area, Kuch area, is located in the Blue Nile Basin, central Ethiopia. The geological units that cover the Kuch area belong to the following three major categories: (i) the Precambrian

basement, ii) the Paleozoic/Mesozoic sediments, and iii) the Cenozoic Volcanic rocks (Tsegaye, 2008; Gani et al., 2009). The Paleozoic sedimentary rocks occur in the south and southeastern part of the study area, in the western part of the Blue Nile basin (Dawit, 2014; Lewin et al., 2018). They are exposed in narrow zones and discontinuous bodies that have a generally north-south trend. The present study will cover two key areas, covering different parts of the Kuch area in the Blue Nile Basin: Bokotabo and Daguja area.

The present study focused on the petrographic and geochemical characterization of the upper Paleozoic sandstone around the Kuch area, in the Blue Nile Basin, intending to provide insight into the provenance, paleoclimate, and tectonic setting. Petrographic and geochemical characterization of sediments is important for the implication of provenance, tectonic, and paleoclimate conditions. Thin sections were prepared at Geological Survey of Ethiopia, Addis Ababa and then petrographic studies have been conducted using transmitted light microscopes in the petrology laboratory of the Department of Earth Science at Bahir Dar University. The analytical techniques for major, trace, and rare earth elements have been performed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) techniques at the laboratory of the ALS in Ireland. Other aspects such as textures are studied to the additional fulfillment of the aim of the study.

1.2. Location and accessibility

The study area lies in the Northwestern plateau of Central Ethiopia and Southern parts of Kuch area, bounded by $9^{\circ}08,09'N$ to $10^{\circ}24,45'N$ latitudes and between $37^{\circ}00,44'E$ to $37^{\circ}04,40'E$ longitudes covering a total area of 390 km^2 . It is about 500 km far from Addis Ababa and is reached through two main routes. The first route is from Addis Ababa to Debre Markos, Bure-Bokotabo road. The road from Addis Ababa to Bure is asphalted whereas a road from Bure to the study area is a gravel road. The other one is through Addis Ababa to Nekemte, Agemsa - Bokotabo road. The road from Addis Ababa to Nekemte is asphalted and the remaining route from Nekemte to the study area is a gravel road. It is also accessed along with Bahir Dar Debre Markos, Bure - Bokotabo road. The study area is accessible by a field car and motorcycle during all seasons.

Figure 1(A) The geological map of Ethiopia after (Billi, 2015); (B) Location Map of the study area, western Blue Nile basin modified after (EMA, 1987)

1.2.1. Physiography

The physiography of the study area is characterized by subdued and rolling terrain dissected by streams which are tributaries of the Blue Nile River cross the area in a general west direction in the central part of the area. The altitude within the study area ranges from about 1079 m to 2044m in the Bokotabo-Sentom area and 1200 to 1666 in the Daguja area. The study area, topographically, is characterized by valleys, flat areas and cliff with slope gradient varying from gentle to a steep slope.

Figure 2 Physiographic map of the study area including both areas (Bokotabentom and Daguja area)

1.3. Previous work

The recent works that have been studied in the study area include Assefa (1991), Russo et al. (1994), Wolela (2007), Tsigaye (2008), Gani et al. (2009), Enkurie (2010) and Lewin et al. (2018). Assefa (1991) studied the lithostratigraphy and environment of deposition of the Late Jurassic Early Cretaceous sequence of the central part of Northwestern Plateau, Ethiopia. Assefa studied lithostratigraphy and the depositional environment of the Muger Mudstone and the Debre Libanos Sandstone of Northwestern Plateau. Russo et al. (1994) studied the sedimentary evolution of the Abay River (Blue Nile) Basin, Ethiopia. They gave a detailed explanation about the formation and evolutions of every succession in the Blue Nile basin which includes sandstone (Adigrat sandstone), Gohatsion formation, Antalestone, Muger sandstone (muddy sandstone), and Debre Libanos sandstone (upper sandstone). Wolela (2007) studied the source rock potential of the Blue Nile (Abay) basin, Ethiopia. According to his study, Permian Karroo Group shale was found to be over-maturing for oil generation; whereas algal laminated gypsum from the Middle Hamanlei Limestone Formation is organic lean and had

little source potential. Tsigie (2008) studied and mapped the general Geological map and major structures of the Bure area. Garret al. (2009) studied Stratigraphic and structural evolution of the Blue Nile Basin, Northwestern Ethiopian Plateau. They outlined the stratigraphic and structural evolution of the Blue Nile Basin based on field and remote sensing studies. Eskurie (2010) studied Stratigraphy, Facies, Depositional environments and palynology of Adigrat sandstone in Northern and Central Ethiopia. He gave a detailed investigation of the stratigraphy, sedimentary facies, depositional environments and palynology of the Adigrat Sandstone, succession in the Mekelle and Blue Nile basins. Lewin et al. (2018) studied the Provenance of Paleozoic sandstones in Ethiopia, including the study area. They used petrographic and geochemistry (X ray fluorescence) analysis to determine the provenance of the sandstone. According to Lewin et al. (2018), the upper Paleozoic sandstone is less mature with a geochemical signature of juvenile source material, most likely the Arabian, Nubian Shield. However, they only studied one sample from the upper Paleozoic sandstones of the Blue Nile basin.

1.4. Statement of the Problem

Even though the petrography and geochemistry of all sedimentary successions in the Blue Nile basin are well studied by the above authors, detailed work has been done on the Paleozoic sandstone. General geology and major structures of the sandstone were investigated by the Geological Survey of Ethiopia. Besides, Lewin et al. (2018) studied the Provenance of the upper Paleozoic sandstones in Ethiopia, but their study more focused on Northern Ethiopia. Only one sample was prepared in the Blue Nile basin. Hence, its geochemistry and petrography that reveal the provenance, paleoclimate and tectonic setting of this sandstone have not been well studied yet.

Therefore, petrographical and geochemical studies are required to address the provenance, Paleoclimate, tectonic setting of the upper Paleozoic sandstone. Furthermore, structures and textures will provide adequate information about the depositional environments of the upper Paleozoic sandstones.

1.5.Objectives

1.5.1. General Objective

The general objective of the present study is to conduct petrographical and geochemical investigation on the upper Paleozoic sandstone around the Kuch area, the Blue Nile basin, Central Ethiopia, to evaluate the provenance, tectonic setting, paleoclimate during the upper Carboniferous to Early Permian glaciation.

1.5.2 Specific Objectives

The specific objectives of the present study include:

- conducting a detailed petrographical investigation to determine the provenance of upper Paleozoic sandstone;
- conducting detailed geochemical analysis (major, rare and trace element analysis) to calculate geochemical proxies, such as Chemical Index of Alteration (CIA), Plagioclase Index of Alteration (PIA) and Chemical Index of Weathering (CIW);
- assessing the paleoclimate and tectonic setting during the upper Carboniferous to lower Permian glaciations by using the calculated geochemical proxies;
- Attempting to conduct regional correlation with coeval deposits in Mekelle basin, in Ethiopia.

1.6. Methodology

Based on the availability and relevance, different methods and techniques are employed to accomplish the above-mentioned objectives.

1.6.1 Field methods

Forty-eight samples were collected from each lithological unit for petrographical and geochemical investigations. Two field trips were carried out during this study to examine the upper Paleozoic sandstone succession in the study area. The first field trip was conducted on December 25th, 2019 for 6 days to observe and select well-exposed lithology and stratigraphic sections around the Bokotab-Sentom area. The second field trip was conducted on January 14th, 2020 for 4 days around the Daguja area to observe and select well-exposed lithology and stratigraphic sections. Geological traverses and orientations in the field were carried out by Bure topographic maps of 1:50,000 scales produced by the Ethiopian Mapping Agency. During the fieldwork, various sedimentary structures and textures; grain and color variations; mineral composition were examined. At the field, grain size was determined by hand lenses, and locations and thicknesses of each lithologic section were measured by GPS instrument.

Sample collection techniques

Forty-eight representative samples were collected based on sampling intervals from 1 m to 15 m for each succession with little or no lithologic changes. Sampling intervals were selected for lithology that rapidly changed. 25 (twenty-five) sandstones, 9 (nine) mudstones, 6 (six) siltstones and 5 (five) tillites were collected from various sections for petrographic and geochemical analysis. These samples were labeled as SST for sandstone; SIT for siltstone; MUD for mudstone; TIL for tillites; and Gr for granitoid. Field photographs and sketches were employed to document and illustrate key geological features such as sedimentary lithologies, structures, textures, and changes in exposure.

1.6.2. Laboratory methods

The analyses were done emphasizing the petrographical and geochemical aspects of the observed rocks. The collected fresh samples were placed into zip lock polythene bags marked with sample number and location and sent to the Geological Survey of Ethiopia, Addis Ababa for thin section preparation and the laboratory of ALS for Geochemistry.

1.6.2.1 Petrographic analysis

The petrographic analysis is used for the determination of modal composition and textures of sandstones and it gives insight into the source material and the processes involved in the formation of the rock (Aleali et al., 2013). 17 (seventeen) samples which include; 11 (eleven) sandstones, 4 (four) siltstones, 1 (one) mudstone and one tillite are prepared for thin section. The selected samples were sent for thin section preparation to the Geological Survey of Ethiopia, Addis Ababa. They were evenly cut into rectangular slabs and either side being polished for soft, flat surface then adherence to glass specimen plates. Later than, the samples were trimmed and polished to get an even surface (~0.03mm thickness) that allowing maximum light distribution through the specimen plates. 17 (seventeen) sections were prepared and analyzed by using a petrographic microscope. Then petrographic studies were conducted using polarized transmitted light microscopes in the mineralogy and petrology laboratory of the Department of Earth Science at Bahir Dar University. Rock compositions, size, degree of sorting and roundness, and other features were studied. The modal analyses were carried out by counting more than 300 points per thin section, using the Dickinson point counting method (Gazzi, 1966; Dickinson, 1970). After that, rooted in the modal composition, sandstone classification was made using the McBride scheme (McBride, 1963). Sandstone composition and tectonic discrimination were recognized by QFL and QmFLt plots proposed by Dickinson and Suczek (1979).

1.6.2.2 Geochemical analysis

Out of the 17 (seventeen) rock samples, 8 (eight) representative samples were selected for geochemical analysis. These samples are 3 (three) sandstones, 3 (three) siltstones, 1 (one) mudstone and one tillite. The analytical techniques for major, trace and rare earth elements has been performed by inductively coupled plasma mass spectrometry (ICPMS) and inductively coupled plasma atomic emission spectroscopy (ICPES) techniques. Before, weathered part of the samples removed; split into significant sizes, and the samples have been carefully crushed to chips of micron size particles. They were crushed to 76.9% less than 2mm, ruffle split off 0.75g and then pulverized split to 91.4% passing 75µm before analysis. This preparation is done in ALS services plc, Nifas silk city. These pulp samples were analyzed by AFS for major oxides together with trace elements analyzed by AFB and ICPMS. These analyses

were performed at the laboratory of the ALS Loughrea located at Dublin Road, Loughrea, Co. Galway, Ireland. The process was accomplished by dissolution of the pulp sample in lithium metaborate or tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) fusion method. This mixing lithium metaborate or tetraborate fusion with a prepared sample (0.75g) was fused in a furnace at 1000°C. After that, an acid mixture (nitric, hydrochloric and hydrofluoric acids) was used to cool and dissolve the mixture. The solution was then analyzed by ICP-AES and ICP-MS. For samples that are high in sulfides, a Na_2O_2 fusion may be substituted to obtain a better result. Loss of ignition (LOI) represents the total volatile content of the rock that is determined by igniting the rock was measured after heating the samples overnight at 100°C to remove water, at 550°C for four hours to remove organic matter, and at 1000°C for two hours to remove carbonates. The major and trace element concentrations were recalculated to 100% volatile free.

After geochemical analysis, the AN-K diagram, the CIA, CIW, and PIA and elemental ratios were calculated to quantitatively measure the source rock composition and degree of weathering. The relative mobility of certain oxides has helped many researchers in developing some paleoclimate proxies such as the Chemical Index of Alteration (CIA), Plagioclase Index of Alteration (PIA), Chemical Index of Weathering (CIW), AN-K ternary diagram and elemental ratios. In this study, these paleoclimate proxies were applied. Besides, the pattern of REE may give some indication of the weathering intensity. Correspondingly, the pattern of REE, major and minor element abundance and their ratios have been used for the interpretation of the provenance. Bivariate, ternary and multiple plots have been created by using the Chemical Data toolkit (GCDkit) (Janoušek et al., 2006).

1.6.2.3 Summary of petrographic and geochemical methods

No	Analysis methods	No of samples	Examination
1	Petrographic analysis	17	Modal and source rock composition and texture
2	Geochemical analysis (ICP-AES and ICP-MS)	8	trace and major element for discrimination tectonic setting and provenance

Figure 3- The flow chart showing the methodology of this thesis work

1.7. Expected Outcome and Significance of the Study

The outcome of this thesis work will contribute to the understanding of the provenance, tectonic setting and paleoclimate of the upper Paleozoic sandstone in the Bure area, Western part of Blue Nile basin, Central Ethiopia. Additionally, the output will be;

- a detailed petrographical investigation that determines the provenance of the upper Paleozoic sandstone;
- detailed geochemical analysis (i.e., major and trace element analysis) that calculate geochemical proxies;
- a detailed evaluation of the paleoclimate and tectonic setting during the upper Carboniferous, lower Permian glaciations by using the calculated geochemical proxies;
- Regional correlation with coeval deposits in the Mekele basin, in Ethiopia.

The Significance of this research is to give comprehensive information on the provenance, tectonic setting, paleoclimate and depositional condition of the upper Paleozoic sandstone around the Kuch area, western Blue Nile Basin

2. REGIONAL GEOLOGICAL SETTING

2.1. Introduction

The final assemblage of Gondwana was an extended process during the Neoproterozoic between 650 Ma to 600 Ma. During this time, the East African Orogen was formed which is one of the largest accretionary orogens in Earth's history (Collins and Pisarevsky, 2005; Abate et al., 2015). At the end of the Precambrian time the accretion and dismantling of the East African Orogen occurred, which was followed by a long period of erosion (Mogessie et al., 2002; Dawit, 2014). In Northern Africa, a vast peneplain developed after the consolidation of the newly formed continent, on which a blanket of Paleozoic sandstone was deposited (Asrat et al., 2005). Between Paleozoic and Triassic, the Precambrian tectonic structures reactivated as extensional faults that guide the deposition of eolian and glacial deposits (Edaga Arbi Glacials and Enticho Sandstones), and successively of alluvial plain sediments (Adigrand Sandstones) (Dawit, 2014; Abate et al., 2015 and Sembroni et al., 2016). From three major transgression and regression cycles, the first cycle was responsible for the formation of the majority of Mesozoic sediments in Ethiopia (Kazmin, 1972; Mogesse et al., 2002). In Cenozoic, around Eocene, the impingement of the Afar plume starts to deform the lithosphere causing a regional broad uplift and the emplacement of the flood basalts on the Paleozoic sandstone (Dawit, 2014; Sembroni et al., 2016).

2.2. Stratigraphy of the Blue Nile Basin

The Blue Nile Basin is situated in the northwestern Ethiopian plateau, between latitudes 08°45' to 10°30' N and longitudes 36°30' to 39°00' E and covers an area of 55,000 square kilometers (Enkurie, 2010). It is one of a series of NE and NW trending intracontinental rifts and extensional basins, which were subsequently filled with about 2000 meter section of Paleozoic Mesozoic sediments (Mogessie et al., 2002; Gani et al., 2009). The stratigraphy of the Blue Nile Basin is characterized by the Precambrian crystalline basement, Palaeozoic and Mesozoic sedimentary successions and the Tertiary continental flood basalts (Trap series). Paleozoic Mesozoic sedimentary rocks unconformably overlying on the Neoproterozoic basement rocks and unconformably overlain by Early, Late Oligocene and Quaternary volcanic rocks (Gani et al., 2009).

2.2.1. The Precambrian basement

The Neoproterozoic basement rock, ranging from 850 to 550 Ma, lies on the base of the Paleozoic Mesozoic sedimentary succession in the Blue Nile Basin (Sami et al, 2009; Enkurie, 2010). It consists of low-grade meta-volcano-sedimentary succession and mafic-ultramafic complexes of the Arabian Nubian Shield (ANS) and the high-grade metamorphosed and deformed Mozambique Belt (MB), produced between West and East Gondwana by the closure of the Mozambique Ocean (Tadesse et al. 2000; Stern et al. 2004). These are overlain unconformably by a Permian-Triassic Karroo succession around 450 m thick (Wibléla, 1997).

2.2.2. Paleozoic sedimentary successions (Pre-Adigrat sandstone)

The Palaeozoic units comprise sediments of one of the two major Gondwana glaciations, Late Carboniferous to Early Permian glacial/lacustrine deposits (Bussert and Schrank, 2007; Bussert, 2010). According to (Russo et al., 1994), Pre-Adigrat sediments are considered as a single unit but after (Enkurie, 2010), Paleozoic sedimentary rocks are classified into three sections: Pre-Adigrat I, Pre-Adigrat II, and Pre-Adigrat III sediments

2.2.2.1. Pre-Adigrat I

Pre-Adigrat I sediments are the oldest sedimentary succession in the Blue Nile basin with thickness of up to 50 m (Enkurie, 2010). This rock is composed of poorly sorted, massive to crossbedded medium to coarse grained white sandstones and conglomerates (Enkurie, 2010). Different structures such as ductile sediment deformation structures, large scale trough crossbedding, crude horizontal bedding and channel type cut and fill structures have been found (Enkurie, 2010). These structures lead to correlate this succession with the lower glaciogenic part of the Enticho Sandstone in the northern Ethiopia. It overlies the crystalline basement and is exposed in small isolated outcrops (Enkurie, 2010).

2.2.2.2. Pre-Adigrat II

Pre-Adigrat II sediments are extensively exposed in the Blue Nile basin and reach a maximum thickness of 400 m in the Finchale area of central Ethiopia and it reaches up to 200 m in the northwest of Blue Nile basin (in Bokotabo area, which is the parts of the basin) (Enkurie, 2010). These successions are composed of lateral accretion deposits, floodplain fines, crevasse splays, playa-lake, and eolian dune sediments (Sawit and Bussert, 2009; Enkurie, 2010). Based on the

age of the overlying unit, the age of these successions considered to be late carboniferous. It is unconformably overlain either pre-Adigrat I or the Precambrian basement (Enkurie, 2010).

2.2.2.3. Pre-Adigrat III

Pre-Adigrat III sediments have a thickness of 350 m in Fincha and Dedu areas and 100 m in Fuliya and Dejen areas (Enkurie, 2010). It consists of three successive cycles of stacked, multi-story sheet sandstone bodies that are capped by overbank fines and crevasse splay deposits. These successions can be interrelated with Karoo sediments (fluvial and lacustrine syn sediments) which are widespread in eastern and southern Africa (Enkurie, 2010). Based on palynological dating, the lower part of these successions are late Carboniferous to Early Permian age (which is also the parts of the study) (Price, 1983; Stephenson et al., 2006) and the top of the succession indicate a Middle Triassic age (Geletu & Wille 1998). These successions are underlain by Pre-Adigrat sediments and overlain by Adigrat sandstone (Enkurie, 2010).

2.2.3. Mesozoic sedimentary successions

2.2.3.1. Adigrat sandstone

Adigrat Sandstones have a thickness of ~300 m and deposited above the partially peneplain Triassic surface that is unconformably developed above the Permian Triassic sediments as well as of the basement and overlain by Early, Middle Jurassic Lower Limestone unit (Gani et al, 2009; Abbate et al., 2015). Based on some biostratigraphic data and correlation with adjacent areas that providing fossil ages, this succession is assigned as Early Jurassic in age (Russo et al., 1994).

2.2.3.2. Gohatsion formation

The succession has a thickness of 450 m and It is assigned as Early Middle Jurassic age (Toarciano Bathonian) (Assefa, 1981). It consists of a cyclic repetition of facies successions that are composed of alternating dolostones, marlstones and shales, bioturbated mudstones with thin siltstone intercalations, fine-grained coquinoid cross-laminated sandstones and thick beds of gypsum (Assefa, 1981; Russo et al., 1994) is underlain by the Adigrat sandstone unit and overlain by a Middle-Late Jurassic Antalo Limestone unit (Gani et al., 2009).

2.2.3.3. Antalo Limestone

This unit is a carbonate succession of Middle-Late Jurassic age, based on the Callovian to Kimmeridgian benthic foraminifers and macrofauna (Russo et al. 1994 and Atnafu, 2008) is found in the SW..owing segment of the Blue Nile basin, which comprises thinly bedded to massive limestone with a thickness of ~400 m (Gani et al., 2009). This unit is sandwiched between the Gohatsion Formation and either the Muger mudstone unit or the Debre Libanos Sandstone unit or the volcanic rocks (Gani et al., 2009; Enkurie, 2010)

2.2.3.4. Muger Mudstone

This unit is named by Assefa (1991) after the unit was found alongside the Muger River in the eastern part of the Blue Nile basin. It is believed to be Kimmeridgian to pre-Middle Eocene age based on stratigraphic position (Assefa, 1991). This unit is dominantly exposed in the canyons of Muger, Ega, Wodem, Dersena, Beressa, Adabai, Zhema, Wancha and Ghennli rivers (Mogessie et al., 2002). It is conformably underlain by the Antalo Limestone and overlain by either the Debre Libanos Sandstone unit or the volcanic rocks (Enkurie, 2010)

2.2.3.5. Debre Libanos Sandstone

Its thickness varies from west to east; from ~200 up to ~500 m with an average thickness of 280 m (Gani et al., 2009; Enkurie, 2010). Based on its stratigraphic relationship with overlying and underlying units, its age is assigned to be of Late Jurassic to Early Cretaceous age (Assefa, 1991; Russo et al., 1994). It is underlain by Muger mudstones and unconformably overlain by the Early, Late Oligocene volcanic rocks (Assefa, 1991; Gani et al., 2009 and Enkurie, 2010)

2.2.3.6. Trap series

The basalt series with subordinate trachytes and rhyolites envelop most of the Northwestern Ethiopian Plateau and overly the Debre Libanos sandstone or Antalo limestone, (Gani et al., 2009; Enkurie, 2010). Based on Arage dating and magnetostratigraphy, these units are assigned as Lower, Upper Oligocene age (26, 29.4 Ma) and vary in thickness from 500 to 2000 m (Hofmann et al., 1997)

3. GEOLOGY OF THE STUDY AREA

The studied area is bounded between $11^{\circ}09'N$ to $10^{\circ}24,45'N$ and $37^{\circ}00,44'E$ to $37^{\circ}04,40'E$ and are grouped into two sections; the Bokotabo area and the Daguja area (fig

3.1. The Bokotabo-Sentom area

The upper Paleozoic sandstone sections are located from the northeast of the Bokotabo village to the southeast of the Sentom village. It covers $10^{\circ}22,55'N$ to $10^{\circ}24,45'N$ and $37^{\circ}00,44'E$ to $37^{\circ}04,40'E$. The upper Paleozoic sandstone sections in this area reach about 150m. It is unconformably underlain by the Neoproterozoic basement and unconformably overlain by Adigrat sandstone. This work categorizes the studied upper Paleozoic sandstone into three units based on lithology and mineralogical composition. This succession is composed of sandstone, siltstone and mudstone unit.

The sandstone units

This sandstone unit is found at the bottom of the formation and exposed in the northeast of Bokotabo area. This unit is unconformably underlain by Neoproterozoic granitoid rocks. It is approximately, 6m in thickness. This massive sandstone formation is fine to medium grained, subangular to sub-round in shape, and moderately sorted with variable color (pale purple, white and red). This unit is mostly composed of quartz and feldspar minerals. At the bottom, this unit contains soft sandstone with sized clasts (fig-4-E). The white sandstone is spotted by red color minerals which may indicate Fe oxide minerals such as hematite. The pale purple sandstone is relatively fine-grained in size. Some structures are observed in this section such that: graded bedding and trough cross bedding (fig-4-B & C) which are also the characteristics of glacial sandstone. This sandstone unit is overlain by laminated siltstones.

The siltstone units

This laminated siltstones unit is approximately 04m in thickness. It has a white and red color (fig-4-D). The white siltstone intercalated with mudstone is mainly composed of fine quartz with some pinkish minerals which may be feldspar minerals. The colored siltstone may be due to Fe oxide minerals. This formation is fine to medium grained and moderately sorted. It is overlain by laminated mudstone in the Sentom area and overlain by Adigrat sandstone in the Bokotabo area.

The mudstone unit

This mudstone unit is only exposed in the Sentom area and has roughly 50m thickness. It is entirely reddish which may indicate the composition is dominated by Fe-oxide minerals such as hematite, as cementing materials. Two types of mudstone are observed in this area. The upper part is highly laminated and friable, while the bottom one is hard and massive mudstone. This hard and massive mudstone overlies the siltstone in the Sentom area.

Adigrat sandstone

This sandstone is fine to coarse grained, medium sorted with variable color (yellow, white and red sandstones). Its thickness reaches about 100m. Different structures are observed in this section; graded bedding, herringbone cross bedding trough and planar tabular cross bedding and hummocky cross bedding (fig 4F&G). Tabular and herringbone cross bedding are common in this unit. It overlies the siltstone units in the Bokotabo area and mudstones in the Sentom area.

A

B

C

D

E

F

G

Figure 4- The outcrops view of sandstone units and show (A) partial view of siltstone and mudstone units overlying by Adigrat sandstone, (B) and (C) the sandstone unit showing rough cross bedding, (D) thin white and dark red laminated siltstone, (E) outsized clasts in sandstone, (F) herringbone bedding, (G) hummocky cross bedding.

3.2. The Daguja area

This area is bounded between $9^{\circ}08,09'N$ to $10^{\circ}19,49'N$ and $37^{\circ}01,00'E$ to $37^{\circ}03,10'E$. The thickness of this section is approximately reached to 130 meters. It consists of two sections; the tillite and sandstone and siltstone section (Fig. 5A).

The tillite unit

The tillite unit is unconformably underlain by Neoproterozoic granitoid rocks. Its thickness reaches up to 50m. It consists of rounded clasts with white and pinkish color (Fig. 5-D). The grain size of these clasts ranges from fine rocks to boulder size. Most of these clasts are granitoids. The matrixes in this unit have whitish yellow color and medium to coarse grain size and sub angular shape. This tillite is overlain by pale yellow sandstone-siltstone unit.

The sandstone-siltstone unit

This massive sandstone-siltstone unit has a thickness reaches up to 60m. It has yellow and pale yellow color (fig-5-B). The siltstone unit is hard and composed of fine yellowish grains. The sandstone unit is both soft and hard massive sandstone. It consists of fine to medium grains, sub angular to sub-round in shape, and moderately sorted grains. Only normal graded bedding structure is observed in this unit (Fig. 5C).

A

B

C

D

Figure 5- Field photographs of the outcrops from Daguja are (A) a partial view of tillite and sandstone in the study area, (B) a cliff showing massive yellow sandstone, (C) normal graded bedding in sandstone (D) tillite boulder outcrop that composed of medium to coarse grained clasts

A geological map was prepared at a scale of 1:50,000, based on their lithologic change. The vertical exaggeration between the geological map and the section is 1:1. A normal fault is found in the northwestern parts of the Bokotabo area. This fault dissects all sedimentary units (including Adigrat sandstone) except the upper Paleozoic sandstone which underlain the siltstone unit. A-B cross section was chosen to show all lithological units. The upper Paleozoic sandstones in both areas are underlain by the Neoproterozoic granitic basement and overlain by Adigrat sandstone and tuff basalt.

Figure 6 (A) Geological map and lithostratigraphic column of Bokotabo Sentom and Daguja area with samples for petrography and geochemistry analyses; LP (late Paleozoic), M (Mesozoic). (B) Geologic cross section of Bokotabo Sentom and Daguja area.

4. PETROGRAPHIC AND GEOCHEMICAL RESULTS

4.1 Petrography

The mineralogical composition of the upper Paleozoic sandstones was determined by using Gazzi, Dickinson's point counting method and plotted in a Q₁-F₁-L₁ ternary diagram for sandstone classification and tectonic setting discrimination (fig-18 & 19). Petrographic descriptions are presented in (Table 8). According to the classification scheme of McBride (1963), based on the modal composition the upper Paleozoic sandstone in both areas is dominated by arkose (fig

4.1.1 Bokotabo-Sentom area

17 (seventeen) thin sections were prepared and analyzed under a polarized microscope. The major constituent minerals in these samples are quartz, plagioclase, feldspar, the mica minerals (muscovite and biotite), carbonate (calcite) and accessory minerals (zircon, tourmaline, garnet and FeTi oxide), respectively. Framework grain components dominate 87.1% of the rock samples with matrix and cement constitute about 1.1%. Based on the overall analysis, the upper Paleozoic sandstone has an average modal composition of 65.6 vol. % quartz, 30.1 vol. % feldspar, 3.7 vol. % lithic fragments and 0.5 vol. % accessory minerals. The sample ranges from fine to coarse grained, subangular to subrounded, and moderately to poorly sorted sandstones (table 8). In the sampled thin section, the rock (lithic) fragments are composed of metamorphic, sedimentary, and plutonic rocks (fig 7). In thin sections heavy minerals are dominated by zircon, tourmaline, rutile, garnet, iron oxides (magnetite, and hematite), few opaque phases and minor orthopyroxene, while most of them have occurred as inclusions (fig 7 E & F). Grains of heavy minerals are very fine and rounded to well rounded grains. All analyzed samples contain cement such as silica, calcite, and mica (fig 7). Sandstone samples for instance Sst3bok and Sst8bok are strongly cemented with silica; Sst4bok and Sst9bok are strongly cemented with calcite and Sst12bok is strongly cemented with hematite. In some samples, quartz, plagioclase and some lithic fragments altered to hematite and calcite. Sandstone samples (Sst5bok, Sst6sen and Sst10bok) are different from their compositions from the rest samples; they are related to Adigrat sandstones.

Quartz is the principal constituent mineral in the studied samples in three varieties; monocrystalline (Q_m), polycrystalline (Q_p), and stretched quartz (Q_s). The quartz grains

are generally subangular to sub-round in shape. Along with quartz grains, monocrystalline quartz is leading over polycrystalline quartz with an average modal volume percentage of 43.3 vol. % and 21.2 vol. %, respectively. The majority of the Qm grains show straight to slightly undulatory extinction and some quartz grains contain inclusions such as quartz, zircon, tourmaline and garnet (fig 7-A & H). Feldspar is the second most dominant constituent minerals with subangular shapes. Plagioclase, orthoclase, microcline, and perthite are the major common varieties, respectively (fig 7-A&K). Plagioclase dominates over feldspar with the average modal composition of 23.4 vol. % and 4.1 vol. % respectively. Among feldspar, microcline is dominant over orthoclase and microperthite. Rock (lithic) fragments are the least framework grain with an average modal composition of 7.9 vol. %. In general, the fragments are subangular in shape. They are abundant with siltstone, metamorphic lithoclasts, plutonic lithoclasts, respectively. Metamorphic lithoclasts are slates, schists, and metamorphic sedimentary rocks which show foliation (fig 7-E&I). The sedimentary lithoclasts are the sandstone and siltstones. Cementing materials occurring as pore fillings are composed of silica, carbonate (calcite), iron oxides (hematite), and mica (muscovite and biotite) minerals, respectively (fig 7-J). Fluid, lithic fragment and heavy mineral inclusions are observed in the analyzed thin sections (fig 7-A, E & H).

4.1.2. The Daguja area

The analyzed samples in this section have the major components of quartz (64.0 vol. %), feldspar (30.7 vol. %), lithic fragments (4.3 vol. %), and accessory minerals (0.5 vol. %). The samples vary from fine- to coarse-grained, subangular, and moderately to poorly sorted sandstones (Table 3). The lithic fragments are metamorphic, sedimentary, and plutonic in origin. Framework grain components account for 6 vol. % of the rock samples with matrix and cement constitute about 4 vol. %. Accessory minerals are zircon, tourmaline, rutile, garnet, oxides, and minor orthopyroxene (Table 3). Types of cement are silica, calcite, and mica (muscovite and biotite). Siltstone sample (Sst1dag) is strongly cemented with calcite followed by muscovite, Sst1dag strongly cemented with hematite and muscovite without calcite cement Sst2dag and Sst3dag are moderately cemented with silica, hematite with calcite (fig 7- I, J & K). The quartz grains are generally subangular to sub-round, monocrystalline (Qm) is dominated over polycrystalline (Qp) with an average of 40.5 vol. % and 23.5 vol. %, respectively (Table 3).

The majority of the Qm grains are undulatory extinction and some quartz grains contain mineral inclusions such as rutile, zircon, tourmaline and garnet.

Feldspar is the second dominant constituent with angular grains. Plagioclase, orthoclase, microcline, and microperthite are the major constituent minerals. Plagioclase dominates over K feldspar (22.9 vol. % and 7.8 vol. %, respectively) (Table 3). Among K feldspar, microcline is dominant over orthoclase minerals.

Rock (lithic) fragments are the least framework grain with an average of 4.9 vol. %. In general, the fragments are subangular in shape. They are abundant with plutonic lithoclasts, sandstone, claystone, and metamorphic lithoclasts respectively. Metamorphic lithoclasts are composed of slates, micaceous schist, and meta-sedimentary rocks. The sedimentary lithoclasts are sandstone and siltstones.

A

B

C

D

E

F

Figure 7- Photomicrographs of the upper Paleozoic sandstones showing (A) and (B) monocrystalline and polycrystalline quartz (Qm and Qp), plagioclase and microcline (xpl and ppl, 4x); (C) and (D) mudstone, monocrystalline quartz and microcline (xpl and ppl, 4x); and (F) mineral inclusion in kyanite (red, blue and black arrow), pore space (green arrow) (xpl and ppl, 10x)

G

H

I

J

K

L

(G) monocrystalline and polycrystalline quartz with stretched grains cemented by silicas with hematite micro-crack on the quartz crystal (xpl, 10x); (H) monocrystalline quartz with inclusion (Qin) and undulatory extinction (Qu) (xpl, 10x); (I) cements such as calcite (yellow arrow), muscovite flakes (green arrow), biotite (red arrow) and hematite (blue arrow) (xpl, 4x); (J) cements hematite (green arrow), calcite (red arrow), and siltstone rock fragment (blue arrow), muscovite (yellow arrow) (xpl, 4x); (K) micro-perthite grains (xpl 10x); (L) fluid inclusion in quartz (xpl, 4x).

4.2. Geochemistry

4.2.1. Source rock compositions

The major and trace element concentration and their ratios of all analyzed samples are given in (Table 4&5). The sandstones were measured up to the average composition of the upper continental crust (UCC) (McLennan, 2001) and PAAS (Taylor and McLennan, 1985). The selected major and trace elements normalized to primitive mantle (Sun & McDonough, 1989) are plotted in (fig 9&11). Besides, REE data were plotted on REE primitive mantle spider plots (McDonough & Sun, 1995). The entire samples show comparable patterns with upper continental crust and Proterozoic sediments that display LREE enrichment and moderately HREE pattern (fig 9& 11).

4.2.1.1 Bokotabo-Sentomarea sandstone

8 (eight) samples were prepared and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for trace and rare earth elements and inductively coupled plasma emission spectroscopy (ICP-AES) techniques for major, trace and rare earth elements. The SiO₂ content in this sample is an indicator of the abundance of all silicate minerals present in the sandstone mainly quartz, feldspars, and clay minerals, while quartz is the important mineral. It accounts the highest concentrations in all samples (74.96 wt. %). Other major elements are relatively have low concentration: Al₂O₃ (3- 14.05 wt. %, mean 8.50 wt. %), Na₂O (0.01- 4.14 wt. %, mean 1.62 wt. %), Fe₂O₃ (0.41- 4.37 wt. %, mean 1.73 wt. %), K₂O (0.04- 2.01 wt. %, mean 0.93 wt. %), TiO₂ (0.11- 0.75 wt. %, mean 0.30 wt. %), CaO (0.02- 0.67 wt. %, mean 0.23 wt. %), MgO (0.04- 0.49 wt. %, mean 0.18 wt. %), ZrO₂ (0.01- 0.18 wt. %, mean 0.05 wt. %), and MnO (0.01- 0.05 wt. %, mean 0.02 wt. %). Some samples from this area show nearly negligible concentrations of some major elements such as CaO, MnO, MgO, and TiO₂. The ratios of SiO₂/ Al₂O₃ values are range from 5.31 to 32.00. All the studied samples show low CaO/ Al values (0.007 to 0.06). Moreover, the low concentrations of TiO₂ (<1wt. %) that show low abundances of Ti-bearing opaque minerals such as rutile. When compared with UCC (McLennan, 2001) PAAS (Taylor and McLennan, 1985) the studied samples are characterized by high SiO₂ contents and low in Al₂O₃, Fe₂O₃, CaO, Na₂O, MgO, K₂O. However, siltstones (SIT5 & SIT6) have a higher value of Na₂O than the UCC and PAAS. The depletion of Na₂O < 1 wt.

%) in mudstone can be attributed to a relatively smaller amount of Na plagioclase in them (Table 4). According to K_2O and Na_2O contents and their ratios, the mudstone sample has the highest ratio ($K_2O/Na_2O = 18$). Al_2O_3 content is relatively high in all samples except sandstones sample # SST5 (3 wt. %). The sandstone sample (SST5) has the highest value of SiO_2 (96 wt. %), and it has the lowest value of other major oxides such as CaO , MgO , Fe_2O_3 , CaO , MgO , Na_2O . Depend on all geochemical values, the sandstone sample (SST5) might be different from other samples during their formation, it is possibly from an alkali sandstone.

The correlation between SiO_2 and other major elements is negative for the studied samples that indicate much of the SiO_2 is present as quartz grains. The SiO_2 content of the studied samples shows a strong negative correlation with Al_2O_3 , TiO_2 , Fe_2O_3 and P_2O_5 , and a weak negative correlation with MgO , Na_2O , and CaO (Table 6). Except for SiO_2 , all major elements have a positive correlation with Al_2O_3 (fig-8); P_2O_5 , Fe_2O_3 , TiO_2 , and K_2O strongly correlated while Na_2O , MgO , and CaO weakly correlated and MnO exhibit no correlation. Mudstone has a relatively high concentration of TiO_2 that indicates rich opaque minerals such as rutile. Additionally, it has increased trace element concentrations (Th, Y, Zr, and REEs like Ce, Dy, Gd, La, Sm and Tb), that indicate heavy minerals such as zircon (Table 6).

Figure 8 - Multiple plots of all major elements against Al₂O₃; (A) Al₂O₃ vs SiO₂, (B) Al₂O₃ vs CaO, (C) Al₂O₃ vs MgO, (D) Al₂O₃ vs Na₂O, (E) Al₂O₃ vs K₂O, (F) Al₂O₃ vs TiO₂, (G) Al₂O₃ vs P₂O₅, and (H) Al₂O₃ vs Fe₂O₃; all major elements are measured by w. %

Large-ion lithophile elements (Rb, Ba, Pb, Cs, and Sr) are relatively mobile and incompatible elements. Ba, Rb, Pb, Sr, Cs concentrations in all samples are well below the values for the UCC, except siltstone sample that are enriched in Ba compared to the UCC (fig-9). These mobile elements are enriched in mudstone and siltstone than the sandstones. Cs, Rb, and Sr show a strong positive correlation with Al_2O_3 (Table- 9). All studied samples are enriched in Pb that indicates arkosic sandstone, except sandstones (SST3 and SST5) which have negligible amount of Pb (< 2 for both samples).

High field strength elements (Th, U, Ti, Hf, Zr, Nb, and Ta) are incompatible and immobile elements that are enriched in felsic rather than mafic rocks (Bauluz et al., 2000). They are used as an indicator of provenance due to their immobility (Taylor and McLennan, 1985). All HFSE in the studied sample, except mudstone, are well below the values for the UCC (fig-A). The studied mudstone shows higher concentrations of high strength elements (HFSE) such as Zr, and Hf compared to UCC. The lower sandstone (SST3) shows depletion in high field strength elements such as Ga, Ta, Hf, Nb, Sr, Th, U, Zn and Zr. The depletion of Hf (2.1-4.5 ppm) in all samples except mudstone (9.1 ppm) is due to the depletion of mafic minerals in the (Table 5). Th shows weak positive correlation with Al_2O_3 ($r = 0.64471$) and strong positive correlations with elements, such as Ti and Nb ($r = 0.985788$ and $r = 0.998344$, respectively) (Table 6).

Transition trace elements (Sc, Cu and Ni): All transition trace elements are depleted compared to the UCC (fig-A). Mudstone is relatively enriched by Cu and Sc, while is Ni enriched in siltstone. Medium correlations between Cu and Ni and selected major elements have been observed (Table 6). The depletion of Sc and Ni in all studied samples indicates the depletion of mafic rocks in these formations. Sc correlates strongly positive with Al_2O_3 ($r=0.879816$), Ti ($r=0.934036$), Zr ($r=0.884455$) and the REEs ($r=0.859301$; $r=0.915178$ for HREEs) (Table 7&9).

Rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu) are the least concentration, insoluble and relatively immobile element during weathering, and have the most important application for provenance in sedimentary rocks (McLennan, 1989; Rollinson, 1993). The presence of heavy minerals such as zircon, monazite possibly has a considerable effect on the REE pattern of individual samples (Rollinson, 1993). The total REE concentration of the

studied samples (REE) is 103.88 ppm, which is lower than the average PAAS (183 ppm) and UCC (145.72 ppm) concentrations (Table 8). The CI-normalized REE patterns are similar to the PAAS and UCC with slightly enriched LREEs, flat HREEs and a slight negative Eu anomaly (fig-9-B). The Eu anomaly factor was calculated according to (McLennan, 1989):

Where N = chondrite normalized values.

The Eu anomaly values of greater than 1.0 indicate a positive anomaly while values of less than 1.0 indicate the negative anomaly.

Similar to other LREE, Eu is an incompatible element, however is specially incorporated into plagioclase. Accordingly, the average UCC exhibits Eu depletion through fractionation effects (McLennan, 1989). In all studied samples, the Eu shows a negative anomaly ($Eu/Eu^* < 1$) with an average of 0.82, except sample SIT6 (1.03). The mean and median Eu/Eu^* is slightly lower than the PAAS and UCC (Table 8). The $(La/Yb)_N$ value, which describes the total slope of the CI normalized REE trend, is higher than the PAAS (Taylor & McLennan, 1985) in all samples. The chondrite normalized $(La/Sm)_N$ ratios which indicate the LREE enrichment in this sample ranges from 3.5-4.0 and have an average of 3.7. The $(Gd/Yb)_N$ values range from 1.2-2.1 with average ratios of 1.8 (Table 8), that indicate a flat HREE pattern (fig-9-B).

LOI values for all samples are range from 0.9% (SST3) to 5.15% (MST1). Mudstone sample (MST1) has the highest value of LOI which is expected in felsic rocks. Sandstone sample (SST3) from Bokotabentom area has the lowest value of LOI that indicates it is enriched in mafic minerals rather than felsic.

A

B

Figure 9 - (A) The selected major and trace element concentrations normalized to the primitive mantle after (McDonough and Sun, 1989) (B) Rare earth element concentrations, chondrite normalized after (McDonough and Sun, 1995) patterns for PAAS from (Taylor and McLennan, 1985) and UCC from (McLennan, 2001) have been plotted for comparison.

4.2.1.2. The Daguja area sandstone

The selected major and trace elements normalized to upper continental crust and shale, and chondritenormalized REE are plotted in (fig1). SiO_2 concentrations in the Daguja area range from 65.3, 76.5 wt. %. The relative enrichment of Al_2O_3 (12.2, 13.95 wt. %, mean 12.97 wt. %), Na_2O (1.96-4.81 wt. %, mean 3.7 wt. %), and K_2O (1.01-4.1 wt. %, mean 2.28 wt. %) in this area, is possibly due to elevated levels of feldspar. It is also, relatively, enriched in CaO (0.42-5.94 wt. %, mean 2.34 wt. %), Fe_2O_3 (1.27-3.09 wt. %, mean 1.91 wt. %), MgO (0-12 1.85 wt. %, mean 1.03 wt. %), TiO_2 (0.15-0.47 wt. %, mean 0.32 wt. %), P_2O_5 (0.04-0.17 wt. %, mean 0.09 wt. %), and MnO (0.02-0.11 wt. %, mean 0.05 wt. %) when compared with Bokotabo-Sentom area. The siltstone samples in this area are relatively enriched in CaO . $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio values of the studied samples range from 5.12 to 6.32. All samples show low $\text{CaO}/\text{Al}_2\text{O}_3$ values (0.034 to 0.466), but relatively high when compared with Bokotabo-Sentom area sandstones. All samples generally have low concentrations of TiO_2 (0.15-0.47 wt. %) which indicates low abundances of Ti-bearing opaque minerals such as rutile (Table 6). The studied samples show high contents of SiO_2 and Na_2O and low in Fe_2O_3 , Al_2O_3 , MgO , and TiO_2 contents, when compared with UCC (McLennan, 2001) and PAAS (Taylor and McLennan, 1985). Siltstone (sampled as SIT1) has a higher value of CaO (5.94%) and enriched in Fe_2O_3 content. The tillite (TIL1) has a higher value of K_2O (4.1%) than the UCC and PAAS which is mainly controlled by the presence of feldspar (K mica) (Wedepohl, 1978). The SiO_2 concentration shows a strong negative correlation with Fe_2O_3 , MnO , CaO and P_2O_5 , while Al_2O_3 and K_2O exhibit no correlation with SiO_2 (Table 6). Al_2O_3 shows a strong negative correlation with MgO and TiO_2 , a strong positive correlation with K_2O , and weak positive correlation with Na_2O , and no correlation with CaO , P_2O_5 , Fe_2O_3 , and SiO_2 (fig-10). The enrichment of Na_2O (1.96-4.81 wt. %, average 3.7%) in these samples can be attributed to a relatively higher amount of Na-rich plagioclase in them. The K_2O and Na_2O contents and their ratios ($\text{K}_2\text{O}/\text{Na}_2\text{O}$) in all samples are <1 . The tillite samples are relatively enriched in Al_2O_3 and K_2O content. All samples have correspondingly increased concentrations of trace elements (Zr, Th, Y, and REEs like La, Ce, Sm, Gd, and Dy) (Table 5). All sandstone and siltstone samples have higher LOI values (4.04%-4.95%), which is expected in felsic sediments, while the tillite has a lesser value (0.67%).

Figure 10 - Multiple plots of Al_2O_3 against all major elements the Daguja area (A) Al_2O_3 vs SiO_2 , (B) Al_2O_3 vs CaO , (C) Al_2O_3 vs MgO , (D) Al_2O_3 vs Na_2O , (E) Al_2O_3 vs K_2O , (F) Al_2O_3 vs TiO_2 , (G) Al_2O_3 vs P_2O_5 , and (H) Al_2O_3 vs Fe_2O_3 ; all major elements are measured by (w.%).

Large-ion lithophile elements: Rb, Sr and Cs concentrations in all samples are well below the UCC values, while all samples are enriched in Ba compared to the UCC except sandstone samples (SST1). Rb, Cs and Ba concentrations are relatively enriched in the tillite unit while Sr is enriched in siltstone samples. Cs, Rb and Ba show a strong positive correlation with Al_2O_3 (Table 9).

High field strength elements: Th, U, Y, Hf, Nb and Ta in all studied samples are well below UCC (fig-11-A). Sandstone sample (SST1) is relatively enriched in elements such as Hf, Sm, and Zr, and depleted in Ga and V (Table 5). Siltstone (SIT1) is relatively enriched in Y, V, Zr and Ta, while depleted in Th. And the tillite is relatively enriched in Ga, and depleted in Zr, Sm, Y. This shows a strong positive correlation with Al_2O_3 ($r=0.852818$) and strong negative correlations with elements, such as TiO₂ and Nb ($r=-0.97709$ and $r=-0.99785$, respectively) (Table 9).

Transition trace elements: All transition trace elements are depleted in the studied samples as compared to the UCC value. Sample SIT1 is enriched in Sc and Ni while the tillite is enriched in Cu (Table 5). Strong negative correlations between Cu and Ni ($r=-0.74543$) have been observed. Sc correlates strongly positive with TiO₂ ($r=0.827788$) and correlates weakly with Al_2O_3 ($r=-0.20968$), Zr ($r=0.13618$) and the REEs ($r=0.140108$) (Table 9).

Rare earth elements: The average total REE concentration (ΣREE) is 87.34667 ppm, much lower than the average PAAS and UCC concentrations (Table 6). Chondrite-normalized REE patterns are similar to the PAAS and UCC with enriched LREEs, flat HREEs (Fig. 11-B). In all Daguja samples, Eu is well above the UCC values, except the tillite unit sample which indicates Na₂O enrichment (Fig. 11-B).

The $(La/Yb)_N$ value, which describes the total slope of the chondrite-normalized REE trend, is higher than the PAAS (Taylor & McLennan, 1985) in all samples. The chondrite-normalized $(La/Sm)_N$ ratios which indicate the LREE enrichment in this sample range from 2.53 to 3.1 and have an average of 2.9. The $(Gd/Yb)_N$ values range from 0.52 to 0.73 with average ratios of 1.0, which indicate...at HREE pattern (Table 6).

A

B

Figure 11- (A) selected major and trace element concentrations normalized to the primitive mantle after (McDonough and Sun, 1989)(B) Rareearth element concentrations, chondrite normalized after (McDonough and Sun, 1995). Patterns for PAAS from (Taylor and McLennan, 1985) and UCC from (McLennan, 2001) have been plotted for comparison.

Classification of the upper Paleozoic sandstones

The chemical classification of sandstone was proposed by (Lindsey 1999) based on major elements (Table 1). Though, it is controversial to differentiate arkose and lithicarenite.

Using the geochemical classification diagram (Pettijohn et al., 1972) the log (SiO₂/Al₂O₃) vs. log (Na₂O/ K₂O), all siltstones and mudstone from Bokota Sentom area and tillite unit from Daguja area are classified as arkose, while sandstone and siltstone from Daguja area are classified as lithicarenite and sandstone from Bokota Sentom area is classified as sub lithicarenite (fig-12). Based on the classification diagram of (Herron, 1988) the log (SiO₂/Al₂O₃) vs. log (Fe₂O₃/K₂O), mudstone and sandstone from Bokota Sentom area fall on Fesand field, while sandstone and siltstone from the Daguja area fall on lithicarenite field, and siltstones and tillite unit from Daguja area fall on arkose field

Table 1 Chemical classification of the upper Paleozoic sandstone based on (Lindesy, 1999)

Classes	log (SiO ₂ /Al ₂ O ₃)	log (K ₂ O/Na ₂ O)	log ((Fe ₂ O ₃ +MgO)/(K ₂ O+ Na ₂ O))
quartzarenite	>= 1.5	-	-
greywacke	> 1	< 0	-
Arkose(sub arkose)	< 1.5	>= 0	< 0
Lithic-arenite (subgraywack and protoquartzite)	>1.5	< 0	>0

Samples	Log (SiO ₂ /Al ₂ O ₃)	Log (K ₂ O/Na ₂ O)	Log ((Fe ₂ O ₃ +MgO)/(K ₂ O+Na ₂ O))	Chemical classification
SIT5(BOK)	0.86	-0.37	0.77	Arkose
SIT6(BOK)	0.84	-0.31	1.50	Arkose/Lithicarenite
SST5(BOK)	1.51	0.60	0.41	Quartzarenite
SST3(BOK)	1.49	-0.14	1.02	Arkose/Lithicarenite
SIT1(DAG)	0.71	-0.44	0.89	Arkose
SST1(DAG)	0.80	-0.29	0.16	Arkose

A

B

Figure 12- Geochemical classification of (A) the $\log (\text{SiO}_2/\text{Al}_2\text{O}_3)$ vs. $\log (\text{Na}_2\text{O}/\text{K}_2\text{O})$ (Pettijohn et al., 1972), (B) the $\log (\text{SiO}_2/\text{Al}_2\text{O}_3)$ vs. $\log (\text{FeO}_3/\text{K}_2\text{O})$ (Herron, 1988) for upper Paleozoic sandstone, in both Bokdabo Sentom and Daguja area.

The Al_2O_3/TiO_2 vs. (SiO_2) plot of (Le Bas et al., 1986) was used to determine the sample whether is felsic or mafic in composition (fig-3A). The geochemical differences between elements such as Th and La (felsic igneous source indicator) and V, Sc and Cr (mafic igneous sources indicator) are used as an indicator of contrasting felsic and mafic provenance using ternary plots such as Ni-V-Th*10 plots (fig-13B) (Condie and Wronkiewicz, 1990; McLennan and Taylor, 1991 and Racciali et al., 2007). Based on both diagrams, the upper Paleozoic sandstone in both sections is felsic in composition. But sandstone from the Daguja area is close to the mafic field because it has a higher amount of V. The granitoid boulders sampled from tillite have similar compositions to those in the granitoid which underline the tillite

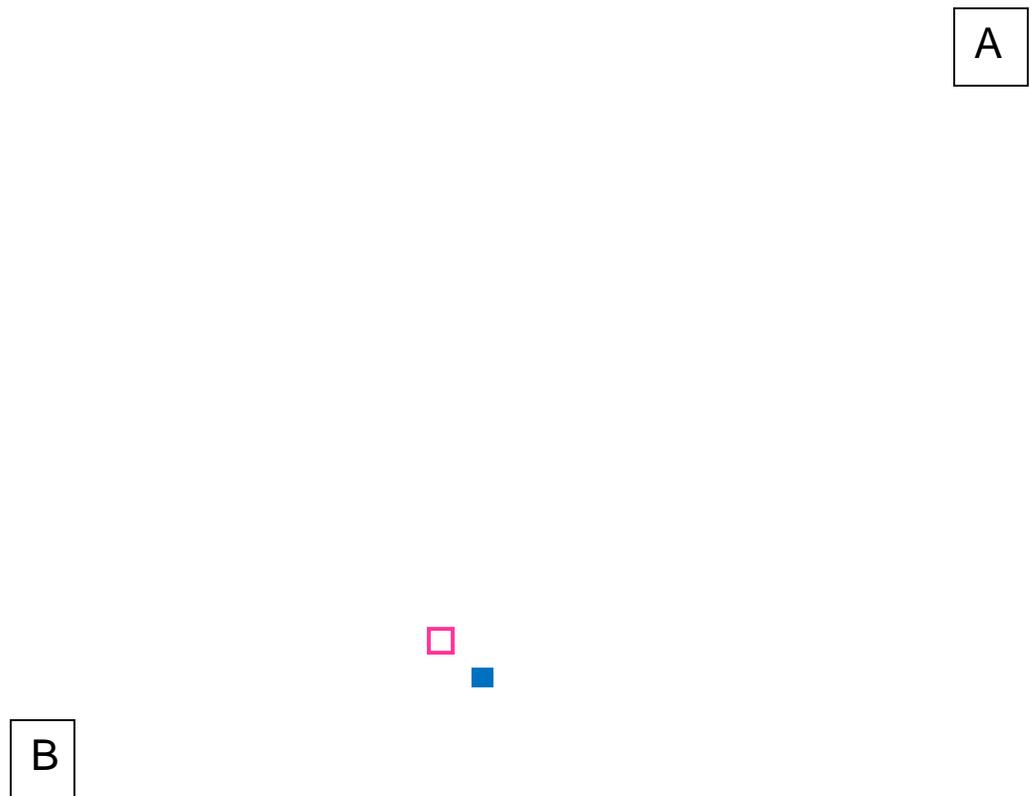


Figure 13,, (A) The Al_2O_3/TiO_2 vs. (SiO_2) relationship to determine whether upper Paleozoic sandstone is felsic or mafic (Le Bas et al., 1986)(B) Ternary Ni, V,, Th*10 diagrams for source rock discrimination after (Bracciali et al., 2007)

4.2.2. Paleoclimate condition

4.2.2.1. Major Oxides climate proxies

4.2.2.1.1. CIA, CIW, and PIA

Chemical weathering affects the mineralogy of rocks and sediments that leads to affecting their major element composition. The degree of chemical weathering possibly acquired by chemical index of alteration (CIA), plagioclase index of alteration (PIA), and chemical index of weathering (CIW) on a molecular basis of the major element oxides to evaluating how these processes have affected the rocks and sediments, proposed by Nesbitt and Young, 1982).

$$CIA = \frac{Al_2O_3}{(Al_2O_3 + CaO + Na_2O)} \times 100 \text{ Equation (1)}$$

$$PIA = \frac{Al_2O_3}{(Al_2O_3 + CaO)} \times 100 \text{ Equation (2)}$$

$$CIW = \frac{Al_2O_3}{(Al_2O_3 + CaO + Na_2O)} \times 100 \text{ Equation (3)}$$

CaO* represents CaO incorporated in silicate minerals and accepted when CaO/Na₂O (Fedo et al., 1995) CaO was low in all measured samples. Therefore, CaO* was considered as equal to CaO. High CIA, PIA, and CIW values (75-100) shows intensive weathering history in the source area, while low values (60 or less) indicate low weathering in the source area. The CIA, CIW and PIA were calculated and presented in (Table 4.1).

Bokotabo-Sentom area

The calculated CIA values for studied Bokotabo-Sentom samples range from 63.4 (sample SIT6) to 94.5 (sample MST1), with an average of 73.9. The PIA values range from 52.1 (sample SIT6) to 89.7 (sample MST1), with an average of 64.8. The CIW values range from 71.5 (sample SIT6) to 99.4 (sample MST1) with an average of 81.0. The mudstone sample (MST1) has relatively the highest value of CIA, PIA, and CIW that shows the highest chemical weathering history. While the siltstone sample SIT6 has the lowest value that indicates the lowest weathering history.

Daguja area

The CIA values for these samples are range from 60.5 (for tillite) to 78.3 (sample SST1), with an average value of 68.3. The PIA values range from 42.8 (for tillite unit) to 71.8 (sample SST1), with an average of 57.2. The CIW values range from 54.3 (sample SIT1) to 83.7 (sample SST1) with an average of 70.5. The tillite sample (TIL 1) has the lowest value of CIA and PIA and CIW while the sandstone sample (SST1) has the highest value of CIA, CIW and PIA.

4.2.2.1.2. The A CN K diagram

Paleoweathering conditions can also be identified using the $\text{Al}_2\text{O}_3(\text{CaO}^* + \text{Na}_2\text{O}) - \text{K}_2\text{O}$ (A-CN-K) ternary diagram of Nesbitt and Young (1984), where unweathered rocks are crowded together alongside the feldspar-plagioclase join (Nesbitt and Young, 1984; Holail and Moghazi, 1998). All the studied samples examined here in both area plot parallel to the A line (Fig-14). The Bokoto-Sentom sections show medium-high weathering conditions, while the Daguja section shows low to medium weathering conditions.

A bivariate plot of SiO₂ against total $\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{NaO}$ as proposed by Suttner and Dutta (1986) was used to classify the maturity of sandstone (Zaid and Al Gahtani, 2015), and all samples in both areas lie on semi-arid fields, except sandstone (SST3) which lies on semi-humid fields (fig 15).



Figure 14 - A,, CN,, K ternary diagram [Al₂O₃- (CaO*+Na₂O) ,, K₂O] ; for both study area Bokotabe Sentom area Daguja area after (Lesbitt and Young, 1984).

Figure 15 Chemical maturity of the upper Paleozoic sandstone stated by bivariate plots of SiO₂ / (Al₂O₃+K₂O+Na₂O) after (Suttner and Dutta, 1986)

4.2.3 Tectonic setting

Based on the Petrographic approach Dickinson and Suczek (1979), and Dickinson et al. (1983) worked on the relationship between sandstone compositions and tectonic setting. Dickinson and Suczek (1979) proposed that tectonic settings of depositional basins are recognized by plotting the detrital framework modes of sandstone suites on the QFL and QmFLt ternary diagrams (Dickinson and Suczek, 1979; Dickinson et al., 1983). The QFL (Quartz-Feldspar, Lithics) diagram is grouped into three main fields that are representative of three different tectonic regimes, named: continental block, magmatic arcs, and recycled orogens (Dickinson et al., 1983), and plotted on (fig 9-A). The QmFLt diagram is comparable to the QFL diagram, except that it plots exclusively monocrystalline quartz (Qm), and total lithics (L) (Dickinson et al., 1983) and plotted on (fig 9-B).

For selected major elements, trace elements and REEs, valuable comparison can be made with sandstones derived from known tectonic settings. Various authors have depicted that the effectiveness of major element geochemistry of sedimentary rocks to identify tectonic settings based on discrimination diagrams (Shah, 1983; Roser and Korsch, 1986). Armstrong and Verma (2013) proposed two new discrimination function based diagrams for siliciclastic sediments from 3 main tectonic settings; continental rift, arc, and collision. These diagrams were used to distinguish the tectonic setting of siliciclastic sediments by employing major elements and optimized for both low silica (35% to 63% SiO₂) and high silica rocks (63% to 95% SiO₂). They are tested on Neogene-Quaternary as well as Precambrian sediments with success rates of 75% to 100% (Verma and Armstrong, 2013; Bassis, 2017). In these diagrams, three different tectonic settings were considered: (1) Arc field (Continental and ocean island arcs), (2) Collision field (continental collision) and (3) Rift field (continental rifting leading to the development of passive margins and intracratonic basins) (Verma and Armstrong, 2013). The equations for the Discrimination function (DF1 and DF2) were programmed for the high silica ((SiO₂) = > 63 % to <=95 %) sediments and low silica (SiO₂adj =>35%- <=63 %) sediments (Verma and Armstrong, 2013). It excludes all samples with (SiO₂adj)>95% and (SiO₂)<35% as suggested by the original authors (Verma and Armstrong, 2013). Since the silica content in the upper Paleozoic sandstones is >= 65, high silica sediment equations were used for this thesis. Samples with (SiO₂adj) > 95 % are excluded, for the reason that they possibly characterize

relatively high analytical errors in the determination of the major elements (Verma and Armstrong, 2013).

$$DF1_{(Arc-Rift-Col) ml} = (-0.263 * \ln (TiO_2/SiO_2)_{adj}) + (0.604 * \ln (Al_2O_3 / SiO_2)_{adj}) + (-1.725 * \ln (Fe_2O_3 / SiO_2)_{adj}) + (0.660 * \ln (MnO / SiO_2)_{adj}) + (2.191 * \ln (MgO / SiO_2)_{adj}) + (0.144 * \ln (CaO / SiO_2)_{adj}) + (-1.304 * \ln (Na_2O / SiO_2)_{adj}) + (0.054 * \ln (K_2O / SiO_2)_{adj}) + (-0.330 * \ln (P_2O_5 / SiO_2)_{adj}) + 1.588$$

$$DF2_{(Arc-Rift-Col) ml} = (-1.196 * \ln (TiO_2/SiO_2)_{adj}) + (1.064 * \ln (Al_2O_3 / SiO_2)_{adj}) + (0.303 * \ln (Fe_2O_3 / SiO_2)_{adj}) + (0.436 * \ln (MnO / SiO_2)_{adj}) + (0.838 * \ln (MgO / SiO_2)_{adj}) + (-0.407 * \ln (CaO / SiO_2)_{adj}) + (1.021 * \ln (Na_2O / SiO_2)_{adj}) + (-1.706 * \ln (K_2O / SiO_2)_{adj}) + (-0.126 * \ln (P_2O_5 / SiO_2)_{adj}) - 1.068$$

The subscript adj in $(SiO_2)_{adj}$ refers to the SiO_2 value obtained after volatile free adjustment of the ten major elements to 100 wt.%.

The tectonic setting discrimination diagram of Verma and Armstrong (2013) based on major oxide concentrations are plotted on (fig 16). All samples from the Daguja area and SIT5 from the BokotabøSentom area plotted in the €continental rift• and all samples from BokotabøSentom area, except SIT5, plotted in the €arc. In the tectonic discrimination diagram of (Roser and Korsch, 1986) based on major oxides, all samples except mudstone, are allocated to an active margin setting (fig 17). A passive margin setting is distinct by silica rich sands ($SiO_2=70\%$) with (K_2O / Na_2O) ratio of more than unity (Bhatia, 1983) and $FeO + MgO$ content of less than 5% (Taylor and McLennan, 1985). Depend on these; mudstone from the Sentom area is correlated with passive margin setting.

Figure 16 Tectonic discriminant function diagrams for the upper Paleozoic Sandstone proposed by (Verma and Armstrong, 2013).

Figure 17 Tectonic setting discrimination diagrams based on major elements, ARC- Oceanic island arc, AM- active continental margin, PM- passive margin, after Roser and Korsch, 1986.

5. DISCUSSION

5.1. Implications for provenance

The most relevant features that are used to interpret the provenance of sandstone are the chemical composition of the rocks, which helps to interpret source rock lithology and the direct observation of features (sedimentary structures and grain size and shape) in thin sections (Boggs, 2009)

Sandstones with less abundant quartz and enriched in unstable minerals (lithics, feldspar) have resulted from short transport distances that will allow less stable materials (such as lithic fragments) to survive and get deposited (Dickinson et al., 1983; Johnsson, 1993). Slight to slightly undulatory extinction of monocryalline quartz grains in the sampled thin sections point toward the granitic source (Pettijohn et al., 1987). Inclusions of heavy minerals like zircon and tourmaline in monocrystalline quartz in the studied samples direct evidence of the granitic source. However, some monocrystalline quartz is excluded from these heavy mineral inclusions and shows slight undulatory extinction indicates that the source might be older gneiss or schist rocks (Pettijohn, 1975). Polycrystalline quartz with stretched grains and subboundaries are derived from metamorphic source, apparently schistose (Dietz, 1967; Folk, 1980). Therefore, the whole quartz analysis in the studied samples points toward granitic and schistose provenance. Feldspar is more significant to offer information about primary source rocks composition than quartz because they are chemically and mechanically less stable and less likely to be recycled (Boggs, 2009). A high abundance of feldspars in the sampled thin sections proposed the origin from crystalline rocks (Folk, 1980). Microcline, in the studied samples, indicates the origin of felsic igneous or metamorphic rock (Boggs, 2009). According to Pittman (1963), unzoned plagioclase is to be likely from a metamorphic origin (Krainer & Spotl, 1989). Unzoned plagioclase in the sampled thin sections probably is sourced from low grade metamorphic rocks, such as slate. The presence of micropertitic intergrowths in the sampled thin sections suggest it is sourced from an igneous rock granites (Folk 1980). The presence of zircon and rutile in the sampled thin section indicate an acid igneous source (Pettijohn, et al., 1987). Based on feldspar in the studied samples, the upper Paleozoic sandstone is feldspar rich arkosic lithology which indicates that local deposits derived from low to medium grade metamorphic rocks (slate and schistose) and granitic basement rocks (Pettijohn et al., 1972; Miall, 1984). Based on feldspar

content, the upper Paleozoic sandstone is compositionally immature (the Daguja area) to sub mature (in the Bokotabo Sentom area).

Rock fragments are also giving the best clue to the provenance of rocks. The presence of siltstone and sandstone rock fragments in the sampled thin section indicates sedimentary origin, while, plutonic lithic fragment include clasts of quartz and feldspar are granitoid in origin.

Clay minerals are excellent for provenance studies because individual clay minerals are typically formed by the weathering of particular bedrock types (Blatt, 1985; Nichols, 2009). The presence of mica (muscovite and biotite) in the sampled thin section, probably indicates low grade metamorphic rocks origins like schist, gneiss and granite (Ghazi, 2009).

According to the QFL triangular diagram (McBride, 1963), the classification of the upper Paleozoic sandstones is arkosic.

Figure 18 The QFL triangular diagram shows the classification of the upper Paleozoic sandstones after (McBride, 1963).

The SiO_2 contents and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) are the most used geochemical criteria for sedimentary maturity. They are reflecting the quantity of silica (quartz), clay, and feldspar content (Potter, 1978 and Rollinson, 1993). The negative correlation between SiO_2 and Al_2O_3 , indicating that much of the SiO_2 is present as quartz grains (Akarish and El Gohary, 2008; Ahmad and Chandra, 2013). enrichment signifies the abundance of feldspar and clay minerals which is related to lower maturity. A positive correlation of Al_2O_3 with K_2O and Na_2O indicates that Al distribution considerably influenced by the concentrations of the feldspars and suggests that the abundance of these elements is mostly controlled by plagioclase and Feldspare bearing minerals such as clay mineral (mica and muscovite) concentrations (McLennan et al., 1983; Akarish and El Gohary, 2008). Al_2O_3 and K_2O concentration in the studied samples possibly associated with the presence of feldspars (orthoclase and microcline), and mica. The relative enrichment of Na over K_2O in all samples can be attributed to a relatively higher amount of Na rich plagioclase in them, while depleted in mudstone due to a relatively small amount of Na rich plagioclase. The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios ($\text{K}_2\text{O}/\text{Na}_2\text{O}$) in all samples (except mudstone) are $<1\%$ that perhaps according to plagioclase feldspar dominates over feldspar. Some samples (typically, siltstone in the Daguja area) are relatively enriched in CaO which possibly due to the presence of diagenetic calcite cement. Some samples (typically, mudstone and siltstone) are enriched in Fe_2O_3 content that is possibly related to the abundance of Fe oxide heavy minerals. The geochemical classification diagram proposed by (Herron 1988) and (Pettijohn et al., 1972) shows that the upper Paleozoic sandstones are arkosid Lithicarenite. Based on the $\text{Ca}-\text{Na}-\text{K}$ ternary diagram, all Formation in both areas was derived from plagioclase smectite source terrain. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ vs. (SiO_2) ratios proposed by Le Bas et al., 1986 and Ternary $\text{Ni}, \text{V}, \text{Th} \times 10$ diagrams (Bracciali et al., 2007) implies the whole the upper Paleozoic sandstone is felsic in composition.

The tillite unit is enriched in Al that signifies the abundances of feldspar and clay minerals which is related to lower maturity. It has a slightly higher amount of Na than the K_2O indicates controlled by the presence of plagioclase than feldspar (K mica) (Wedepohl, 1978)

The most important elements for provenance indicators are REE, Sc, Th, and lesser Cr, Co. These elements are unaffected by diagenesis and metamorphism due to their low concentration in sea and river, and low residence time in the ocean and element ratios. Accordingly

reflect their source rock chemistry (Rollinson, 1993). Immobile elements such as Zr, Hf and Sc are possibly controlled by the distribution of heavy minerals and dispersed according to grain size. Co, Cr, Fe, Sr and Ta that controlled by ferromagnesian minerals are low concentrations in the studied samples (Culler, 1988). Most formations (on average, mudstone in Sentom and sandstones in the Daguja area) have correspondingly increased concentrations of trace elements (Zr, Th, Y, and REEs like La, Ce, Sm, Gd and Dy), which are indicative of heavy minerals like zircon.

The concentrations of Ba, Rb, and Cs are controlled by feldspar. The enrichment of Ba and Rb in mudstone and siltstone is strongly influenced by the presence of feldspar and mica (biotite and muscovite). Strong positive correlation of Cs, Rb, Sr and Ba with Al_2O_3 in the studied samples show phyllosilicate (clay minerals and mica) as a controlling factor of LILE concentrations (Etemad Saeed et al., 2011). The enrichment of LILEs in the upper Paleozoic sandstones is possibly as a result of less weathering and metamorphic processes and controlled by K-feldspar and mica. As high field strength elements are incompatible and immobile elements, they are a good indicator of provenance (Taylor and McLennan, 1985). Y, Pb, Ti and Zr enriched in most sandstones and mudstones that indicates felsic source rather than mafic rocks. Th shows strong positive correlations with elements, such as Ta and Nb, which indicates that it is possibly controlled by clays or Ta and Nb bearing phases associated with clay minerals. Sc correlates strongly positive with TiO_2 . This may indicate heavy minerals as controlling factors for Sc concentrations (Etemad Saeed et al., 2011). The depletion of Sc, V, Co, Ni and Cr in most samples is due to the depletion of mafic minerals in them, the low concentration of these elements in the studied samples related to felsic provenance rather than mafic composition. Although rare earth elements are the least concentrated, they are an excellent indicator of provenance due to their immobility during weathering (McLennan, 1989; Rollinson, 1993). Chondrite-normalized patterns show moderate LREE enrichment and HREE segments. LREE enrichment indicates the source of felsic crust. Eu which is mostly incorporated in plagioclase is relatively enriched in siltstones in both areas.

5.2. Implications for paleoclimate

Climate is one of the factors that has an intense impact on the composition and maturity of siliciclastic sediments and the climatic signatures are well preserved in the deposited sediments (Suttner and Dutta, 1986)

Based on Petrographic evidence, paleoclimatic conditions of the upper Paleozoic sandstone can be determined. For instance, less abundance of rounded quartz, grained feldspars, and sub-angular grain sizes are related to a low/moderate degree of chemical weathering. Besides angularities of quartz grains and detrital components, textural immaturity indicates the first cycle of erosion sediments or short distance of transportation before deposition. These sediments which have a high amount of feldspar are immature (Osea et al., 2006). The high proportion of feldspar and the dominance of chemically unstable plagioclase over feldspar in the upper Paleozoic sandstones suggest that the source was exposed to low to moderate weathering. An abundance of unaltered feldspars and lithics in these sandstones suggested that it is sourced from moderate to high relief and rapid erosion and deposition in nearby basins with insignificant alteration. Color also can give helpful information on lithology, depositional environment. For instance, ferric iron frequently occurs as the mineral hematite and provides a red color to the rock. Hematite formed under oxidizing conditions and these are often found within sediments originated under semi-arid environments. Mudrocks formed under these environments (e.g., deserts, lakes, and rivers) are repeatedly reddened through hematite pigmentation. The dominance of unstable grains (feldspar and other rock fragments), a low percentage of monocrystalline quartz (especially in the Daguja area), and the lesser alteration of feldspar grains implied that the source area experienced a short to moderate period of chemical weathering (Pettijohn et al., 1987; Amireh, 1991).

The degree of chemical weathering can be achieved by calculation of the chemical index of alteration (CIA), plagioclase index of alteration (PIA), and chemical index of weathering (CIW) (Nesbitt and Young, 1982). These CIA and PIA values indicate moderate degrees of weathering of the source, or during transport before deposition, which may reflect stage recycling in semi-arid and semi-humid climate conditions in the source area (McLennan et al., 1993; Osea et al., 2006; Bakkiaraj et al., 2010). The studied samples (MST1 in Sentom and SST1 in the Daguja area) have the highest value of CIA, CIW and PIA which may indicate higher

weathering history. The highest values of chemical proxies in the mudstone are due to high chemical weathering such as oxidizing. The rest studied samples values indicate low to moderate degrees of weathering of the source. Generally chemical weathering values of the upper Paleozoic sandstone shows moderate to high weathering history in the Bokotabə Sentom area, and low to moderate degrees of weathering in the Daguja area, that reflect moderate recycling in semi-arid and semi-humid climate conditions in the source area or during transport (McLennan et al., 1993; Osea et al., 2006)

A, CN, K ternary diagram of molecular proportions of $\frac{Al_2O_3}{(CaO+Na_2O)}$, K_2O proposed by Nesbitt and Young, (1984) to determine the paleo-weathering of the upper Paleozoic sandstone falls between plagioclase and smectite fields. ACN-K- diagram shows low medium to high chemical weathering conditions in both areas. A bivariate plot of $\frac{SiO_2}{total\ Al_2O_3+K_2O+Na_2O}$ as proposed by Suttner and Dutta., (1986) was used to identify the maturity of the upper Paleozoic sandstone as a role of climate. This plot shows that the upper Paleozoic sandstones fall in the semi-arid climatic conditions except for sandstone from the Bokotabə Sentom area which falls on a semi-humid field.

The tillite unit has the lowest value of CIA and PIA that indicates low weathering history, or direct input of immature continent detrital minerals into the depositional system (Bakri et al., 2010).

5.3. Implications for tectonic setting

A variety of ternary diagrams (Dickinson and Suczek, 1979; Ingersoll and Suczek, 1979; Dickinson, 1985) were applied to construct the relationship between detrital mineralogy and tectonic setting. Sandstone compositions are related to major provenance types such as stable cratons, basement uplifts, magmatic arcs, and recycled orogens (Dickinson et al., 1983). Sandstones enriched in lithics and less abundant in quartz resulted from short transport distances that decrease physical sediment sorting and chemical weathering and characterized by magmatic arc depositional systems (Dickinson et al., 1983; Johnsson, 1993).

The upper Paleozoic sandstone was plotted on the QFL and QmFLt ternary diagrams (Dickinson et al., 1983) to interpret the tectonic discrimination source field (fig-19). In the QFL plot (Dickinson, 1985) the selected samples are plotted in transitional continental region of continental block provenance field. This indicates the detritus derived from transitional areas between craton interiors and basement uplift masses. The detritus sediments derived from this field have intermediate compositions between craton (pure quartzose sand) and uplifted basement (arkosic sands). In the QmFLt plot (Dickinson, 1985) most of the samples from the Daguja area, fall in basement uplift fields while most of the samples from the Bokotabe-Sentom area plotted in the transitional continental region.

Figure 19 The QFL and QmFLt ternary diagram for tectonic discrimination of the upper Paleozoic sandstone after (Dickinson et al., 1985).

Different tectonic environments do have distinctive geochemical signature, therefore, geochemical data can be used to extract important environmental information from source that assign tectonic environment (McLennan et al., 1990; Rollinson, 1993). Fe, Mg, Ti, and Al are more abundant in Arc-derived sediments rather than cratonic and recycled sediments. Most of the studied samples from both areas are enriched in Al. Sediments derived from transitional recycled sources are moderately enriched in the light rare earth elements (REE) and flat HREE slopes, without the pronounced flattening seen in other cratonic sediments. All studied samples from both areas show moderate enrichment in the light rare earth elements (REE) and flat HREE slopes.

The discriminant function diagram which is used to evaluate the tectonic setting of upper Paleozoic sandstones suggests that the upper Paleozoic sandstone possibly derived from the continental arc and continental rift. Based on major oxides, on active versus passive margin diagram of (Roser and Korsch, 1986) all samples, except mudstone are derived from active margin setting. Mudstone is derived from passive margin setting.

Comparison of the upper Paleozoic sandstone in Blue Nile Basin and Mekele Basin

The upper Paleozoic sandstones in the Blue Nile Basin consist of tillite sandstone and siltstone, around the Daguja area and sandstone, siltstone and mudstone around the Bokota-Sentom area. In Mekele basin, it consists of tillite at the base overlain by laminated siltstones (Edaga Arbi Glacials) and basal tillite, a lower glaciogenic sandstone unit and an upper shallow marine sandstone unit (Enticho Sandstone) (Lewin et al., 2013).

The upper Paleozoic sandstone in Blue Nile Basin and Edaga Arbi Glacials in Mekele Basin has similarity in source composition and provenance, based on petrographic and geochemical results. Both show juvenile, crustal sources such as the Arabian-Nubian Shield. The upper Paleozoic sandstones in the Blue Nile Basin are arkose lithicarenite, while subarkose to arkose in the Mekele Basin. Accessory minerals such as zircon, tourmaline, rutile, garnet and opaque minerals are observed in both formations. Both formations show Al, Na, and K enrichment that indicates a low maturity of the rock. However, there is a slight difference between their CIA values which indicates paleoweathering and tectonic setting discrimination. Based on CIA value, the upper Paleozoic sandstones in the Blue Nile Basin show low to medium weathering history while the Mekele Basin has low weathering history. In the tectonic setting discrimination diagram of Verma and Armstrong (2013) based on major oxide concentrations, the upper Paleozoic sandstones in the Blue Nile Basin show continental rift and arc, while in the Mekele Basin it shows continental rift and collision. In the active versus passive margin discrimination, the upper Paleozoic sandstones in the Blue Nile Basin are assigned in the passive margin setting while the Mekele Basin are assigned in the active and passive margin setting.

6. CONCLUSIONS AND RECOMMENDATION

Based on the petrological and geochemical analysis of the upper Paleozoic sandstones (Permian to Carboniferous), the following conclusions can be drawn:

- The upper Paleozoic sandstone has a provenance transitional continental and basement uplift with a mixture of acid igneous, meta-sedimentary and low-grade metamorphic rocks. It is compositionally immature to sub-mature and has been classified as arkosic and lithicarenitic in composition. Additionally, some euhedral heavy minerals (zircon and tourmaline grains) show short transport distances. Therefore, it was derived from basement rocks nearby, possibly Neo-Proterozoic granitoid rocks and low-grade metamorphic rock (slate and schist). Based on the above statement and trace element geochemistry, the Neoproterozoic basement of the nearby ANS is almost certainly the source.
- The upper Paleozoic sandstone has moderate to high weathering history in the Bokotabo-Sentom area, and low to moderate weathering history in the Daguja area. Paleoclimate data for the upper Paleozoic sandstone suggests semi-arid climate conditions for all sandstones in both areas and semi-humid climate conditions for sandstone from the Bokotabo-Sentom area.
- The tectonic setting discriminant diagram suggests that deposition of the sediments is in the continental arc and continental rift fields. Based on the active and passive diagrams, sediments are derived from the active margin, and mudstone is derived from the passive margin.

Recommendation

Isotopic analysis (that reduces the influence of sedimentary sorting on provenance studies) is required to have a better understanding of the provenance, tectonic setting, and paleo-weathering history.

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Appendix

Table 2- Locations of the upper Paleozoic sandstones sampling sites and outcrops with GPS coordinate.

Sample	Location	Northing	Easting	Position	Lithology	color	size	considerable features
Mst1-se	Sentom	10°23.65	37°01.72	top	mudstone	red	-	Laminated silty mudstone
SST2-b	Boko Ta	10°22.16	37°00.82	bottom	sandstone	brown	medium	Soft, friable sandstone
SST3-b	Boko Ta	10°22.23	37°00.95	bottom	sandstone	white	coarse	Hard, massive Sandstone with
SST4-b	Boko Ta	10°22.03	37°01.19	bottom	sandstone	pinkish white	medium	Sandstone with muds
SST5-b	Boko Ta	10°23.03	37°01.38	top	sandstone	white	medium	Massive, hard sandstone
SST6-s	Sentom	10°23.88	37°02.55	top	sandstone	white	fine	Slightly crumbled sandstone
SST8-b	Boko Ta	10°22.23	37°00.96	bottom	sandstone	Pale green	medium	Hard Sandstone with speckle
SST9-b	Boko Ta	10°22.23	37°00.97	bottom	sandstone	white	coarse	Oxidized sandstone
SST10-	Sentom	10°24.38	37°00.77	top	sandstone	red	coarse	Massive sandstone with sec
Sit2-bo	Boko Ta	10°22.53	37°00.99	middle	siltstone	Dark red	fine	laminated Silty mudstone
Sit5-bo	Boko Ta	10°22.73	37°00.91	middle	siltstone	white	coarse	Black and white lamination
Sit6-bo	Boko Ta	10°22.83	37°01.02	middle	siltstone	red	medium	laminated siltstone
SST1-d	Daguja	10°18.92	37°02.92	top	sandstone	Pale pink	coarse	Massive, crumbled (soft) sa
SST2-d	Daguja	10°18.93	37°02.93	top	sandstone	yellow	fine	Massive hard
SST3-d	Daguja	10°18.63	37°03.13	top	sandstone	brown	medium	Soft sandstone
Sit1-d	Daguja	10°18.53	37°03.07	top	siltstone	Pale yellow	medium	Hard sandstone
till1-d	Daguja	10°18.54	37°03.17	middle	tillite	pink	-	

Table 3 Point-counted data and the derived QFL indices of the upper Paleozoic sandstone: zi (zirconium), tou (tourmaline), ru (rutile), gar (garnet), opx (orthopyroxene), hem (hematite), cal (calcite), mosc (muscovite), bio (biotite), sit (siltstone), sst (sandstone), FS (fine size), MS (medium size), CS (coarse size), PS (poorly sorted), MS (moderately sorted), WS (well sorted).

Sample	Quartz (%)			Feldspar (%)				Rock Fragment (%)				total cc	HM	Opq	cement	Roundn	Grain : Sorti
	MQ	PQ	Q-total	M	O	Plg	F-total	SRF	MRF	PIRF	RF-total						
SST2-bo	26.4	44.3	70.7	8.8		19.5	28.3	0.3		0.7	1	307	2zi,1tou,1ru	2	hem,musc,cal	subangular	MS PS
SST3-bo	42.9	27.2	70.1	6.4	1.9	19.1	27.4	0.8	0.3		1.1	357	2tou,1ru	2	qrtz,hem,cal	subangular	CS WS
SST4-bo	39.9	23.5	63.4	6.4	0.77	25.6	32.77	0.26	2.8		3.06	391	3zi,2tou	3	cal,hem	angular	MS PS
SST5-bo	70.8	28.6	99.4	0.3		0.3	0.6					339	2zi,1tou,2ru	2	sit,sst	subround	MS MS
SST6-se	10.7	15.6	96.3	0.3	0.3		0.6			1.3	1.3	301	5zi,3tou,1ru	2	sit	subround	FS PS
SST8-bo	41.7	23.4	65.1	7.4	0.5	23.7	31.6	0.5			0.5	393	3zi,1ru,1tou,1opx,2gar	qr,hem,cal	sub angular	MS PS	
SST9-bo	47.3	20.4	67.7	7.5	0.3	23.2	31	0.3	0.6		0.9	319	3zi,2tou,1ru,1gar	cal,musc,hem	subangular	CS MS	
SST10-b	76.1	23.3	99.4	0.3		0.3	0.6					305	4zi,3tou,1ru	1	qr,sit,hem,cal	subround	CS MS
Sit2-bok	50.7	11.1	61.8	3.7	3.4	24.4	31.5	2.3	3.4		5.7	353	6tou,1ru	1	cal,hem,bio,musc	angular	FS PS
Sit5-bok	36.8	20.2	57	5	3	29.5	37.5		2.7		2.7	302	5zi,2tou	1	musc,he,cal	angular	CS PS
Sit6-bok	42.5	17.5	60	5.3	1	22	28.3	9.6	1.5		11.1	395	5zi,1tou	3	hem,musc,cal	angular	MS PS
SST1-dag	7.6	31.1	48.7	15.4		26.7	42.1	5.3	3.8		9.1	318	1zi		hem,musc	subangular	CS MS
SST2-dag	1.9	35.3	57.2	11	3.5	22.2	36.7	2.1	4		6.1	374	5zi,3tou,1ru	2	cal,hem	subangular	FS MS
SST3-dag	9.5	30.7	60.2	14.2	1.8	21.1	37.1		2.7		2.7	332	1zi,4tou		cal,musc,	subangular	MS MS
Sit1-dag	24.8	42.6	67.4	6.1	2.9	21.6	30.6		1.9		1.9	310	2zi,3tou,1ru,1opx		musc,cal	subangular	MS PS

Table 4- Major element composition with CIA, CIW and PIA values of Late Palaeozoic sandstones. Element concentrations were measured with ICP-AES are given in weight%.

SAMPLE	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	Sum %	%LOI	CIA	CIW	PIA
SIT1(DAG)	65.3	12.75	3.09	5.94	1.11	4.81	1.73	0.47	0.11	0.17	95.488	4.94	66.1	54.26	57.1
SIT5(BOK)	80	11.1	1.22	0.67	0.49	3.19	1.35	0.22	0.01	0.02	98.272	2.84	68.06	74.2	59.7
MST1(74.6	14.05	4.37	0.05	0.14	0.04	0.72	0.75	0.01	0.18	94.918	5.15	94.55	99.36	89.1
SIT6(BOK)	78.7	11.25	1.98	0.34	0.13	4.14	2.01	0.26	0.05	0.05	98.915	1.22	63.42	71.52	52.1
SST1(DAG)	76.5	12.2	1.38	0.42	1.85	1.96	1.01	0.33	0.03	0.04	95.723	4.95	78.26	83.68	71.1
SST5(BOK)	96	3	0.41	0.02	0.04	0.01	0.04	0.15	0.01	0.01	99.68	1.23	97.72	99.01	96.1
SST3(BOK)	95.1	3.09	0.68	0.09	0.09	0.74	0.53	0.11	0.03	0.01	100.473	0.9	69.44	78.83	57.1
TIL1(DAG)	74.8	13.95	1.27	0.66	0.12	4.33	4.1	0.15	0.02	0.05	99.453	0.67	60.55	73.65	42.1

Table 5- Trace elements composition of Late Palaeozoic sandstones. Element concentrations were measured with ICP-MS and ICP-AES are given in ppm.

SAMPLE	Ba	Ce	Cr	Cs	Dy	Er	Eu	Ga	Gd	Hf
SIT1(DAG)	608	34.3	40	0.24	4.07	2.8	1.42	11.7	4.64	4.1
SIT5(BOK)	727	20.7	10	0.89	1.2	0.77	0.49	9.6	1.47	4.1
MST1(536	104	50	1.17	6.73	3.58	1.96	15.6	8.82	9.1
SIT6(BOK)	607	19.5	30	0.31	1.65	1.11	0.68	10.5	2.01	3.1
SST1(DAG)	298	47.1	10	0.64	3.1	1.61	1.36	11.4	4.33	6.1
SST5(BOK)	22.6	24.5	10	0.09	1.29	0.64	0.44	2.4	1.78	3.1
SST3(BOK)	88.5	18.2	10	0.21	0.81	0.51	0.34	2.3	1.16	2.1
TIL1(DAG)	914	14.7	10	2.46	1.36	0.88	0.33	13.9	1.24	2.1

SAMPLE	Ho	La	Lu	Nb	Nd	Pr	Rb	Sm	Sn	Sr
SIT1(DAG)	0.81	17.7	0.34	5.9	19.6	4.68	34.9	4.37	3	31
SIT5(BOK)	0.24	10.4	0.12	3.4	9.5	2.47	34.2	1.64	2	110
MST1(1.24	57.2	0.48	15.9	54.9	13.8	28.4	9.81	5	29
SIT6(BOK)	0.36	11.3	0.2	3.5	11.2	2.78	39.6	2.01	2	14
SST1(DAG)	0.6	28.5	0.23	5.7	28.1	7.05	25.5	5.59	2	53
SST5(BOK)	0.24	12.3	0.12	2.9	11.3	3.06	1.5	2.06	2	6.1
SST3(BOK)	0.16	9	0.06	1.8	8.6	2.13	11.6	1.63	1	27
TIL1(DAG)	0.28	7.4	0.14	4.8	6.5	1.64	132.5	1.52	1	22

SAMPLE	Ea	Tb	Th	Tm	U	V	W	Y	Yb	Zr
SIT1(DAG)	0.6	0.66	2.28	0.39	1.01	75	2	26.8	2.36	15
SIT5(BOK)	0.3	0.16	2.42	0.12	0.43	13<1		6.3	0.85	17
MST1(1.1	1.2	12.7	0.51	2.2	67	3	30.2	3.4	33
SIT6(BOK)	0.4	0.25	2.1	0.18	0.65	38	1	9.8	3.4	12
SST1(DAG)	0.4	0.57	3.35	0.24	0.74	17	1	15.7	3.4	28
SST5(BOK)	0.2	0.22	2.64	0.12	0.6	6	1	6.8	3.4	13
SST3(BOK)	0.3	0.14	1.46	0.08	0.2	12	1	4.1	3.4	8.1
TIL1(DAG)	0.4	0.18	6.65	0.15	1.52	19	2	8.2	3.4	7.1

Table 6 -Values of Pearson,s coefficient of correlation of major elements of studied samples(A) for BokotabøSentom area, (B) for Daguja area.

	SiO2	TiO2	Al2O3	P2O5	Fe2O3	K2O	Na2O	CaO	MgO	MnO	Eu/Eu*	(La/Yb) _N	(Gd/Yb) _N	(La/Sm) _N
SiO2	1													
TiO2	-0.73627	1												
Al2O3	-0.9984	0.17599	1											
P2O5	-0.71020	0.99350	0.7299	1										
Fe2O3	-0.8147	0.197865	0.6827	0.58498	0.4261	1								
K2O	-0.6750	0.10481	0.16363	0.50528	0.22251	0.22	1							
Na2O	-0.44460	0.26601	0.40465	0.27600	0.10598	0.38276	1							
CaO	-0.43390	0.21901	0.14199	0.28540	0.14107	0.76955	0.58142	1						
MgO	-0.45950	0.01466	0.46564	0.50101	0.00270	0.44483	0.65317	0.76191	0.7079	1				
MnO	-0.06013	0.28405	0.00524	0.20090	0.09762	0.43303	0.36052	0.10692	0.28763	1				
Eu/Eu*	-0.3220	0.39369	0.28249	0.40530	0.24194	0.83002	0.69903	0.84816	0.50152	0.45973	1			
(La/Yb) _N	0.58270	0.30603	0.55067	0.78443	0.07609	0.21209	0.93780	0.71796	0.44330	0.51966	0.90782	1		
(Gd/Yb) _N	0.39036	0.43302	0.22035	0.40353	0.18962	0.88746	0.98959	0.85758	0.58600	0.51706	0.99305	0.93216	1	
(La/Sm) _N	0.25000	0.03701	0.12571	0.25097	0.30025	0.92109	0.32627	0.16956	0.88656	0.70309	0.50257	0.41986	0.24	1

	SiO2	TiO2	Al2O3	P2O5	Fe2O3	K2O	Na2O	CaO	MgO	MnO		
SiO2	1											
TiO2	-0.74053	1										
Al2O3	0.06980	0.72214	1									
P2O5	-0.9970	0.47870	0.31014	1								
Fe2O3	-0.9810	0.18568	0.20262	0.7992	0.434	1						
K2O	0.15709	0.07780	0.2996	0.14822	0.27863	0.34569	1					
Na2O	-0.73308	0.80857	0.36272	0.40682	0.16587	0.22556	0.533	1				
CaO	-0.9940	0.28055	0.07171	0.29995	0.9995	0.73625	0.76465	0.9394	1			
MgO	0.05800	0.06627	0.2099	0.18201	0.40671	0.3673	0.10976	0.80721	0.63044	0.753	1	
MnO	-0.9706	0.68803	0.39203	0.7079	0.85465	0.9988	0.60738	0.90654	0.9990	0.20518	0.3725	1

Table 7 - Values of Pearson's coefficient of correlation between selected trace element of the studied samples

	Cs	Rb	Ba	Sr	Th	U	Y	Zr	Hf	Nb	Ta	Sc	Cu	Ni	SREE	SLREE	SHREE
Cs	1																
Rb	0.563737	1															
Ba	0.70190	0.1964581	1														
Sr	0.84670	0.664310	0.4644501	1													
Th	0.76620	0.118440	0.323100	0.5868211	1												
U	0.72100	0.423770	0.3253560	0.88904986112	0.88904986112	1											
Y	0.74230	0.92260	0.830160	0.491836	0.4985180	0.99531	1										
Zr	0.86740	0.931730	0.639880	0.389380	0.396490	0.395850	0.6951539	1									
Hf	0.86700	0.731040	0.539140	0.889430	0.296920	0.796060	0.795460	0.6999787	1								
Nb	0.78780	0.526050	0.629820	0.390510	0.499670	0.898930	0.799320	0.896930	0.1973096	1							
Ta	0.77420	0.434650	0.835540	0.293500	0.996880	0.396090	0.498230	0.792020	0.692600	0.7981513	1						
Sc	0.76530	0.366320	0.162960	0.998780	0.583100	0.787640	0.5903150	0.853208	0.852307	0.787250	0.8905855	1					
Cu	0.850	0.50560	0.854270	0.395910	0.891790	0.194310	0.194570	0.5969200	0.966705	0.940607	0.891600	0.2945984	1				
Ni	0.08300	0.685770	0.976310	0.8196130	0.30960	0.22240	0.17690	0.17340	0.18380	0.23310	0.142022	0.61890	0.05324	1			
SREE	0.74620	0.218180	0.221730	0.786920	0.199850	0.998560	0.8987690	0.95100	0.95660	0.399600	0.497620	0.5834700	0.90810	0.30895	1		
SLREE	0.74490	0.17420	0.2821110	0.2865270	0.99800	0.198450	0.298620	0.695070	0.695590	0.499540	0.597490	0.1829920	0.90510	0.31690	0.99996	1	
SHREE	0.75840	0.229050	0.930640	0.191910	0.298900	0.499290	0.599920	0.695490	0.295850	0.199640	0.298680	0.889810	0.9943520	0.1880	0.199130	0.5990154	1

Table 8- Selected ratios for the upper Paleozoic sandstones

SAMPLE	SREE	SLREE	SHREE	SLREE/SHREE	SREE/SLREE	Eu/Eu* (La/Yb)	Na/Sm	Cl/Y
SIT5 (BOK)	50.1	46.7	3.5	13.5	1.0	8.3	4.0	1.
MST1 (267.6	250.5	17.1	14.6	0.6	11.4	3.7	2.
SIT6 (BOK)	54.5	49.5	5.0	9.9	1.0	6.2	3.5	1.
SST3 (BOK)	43.3	41.1	2.2	18.3	0.8	12.7	3.5	2.
SST5 (BOK)	58.8	55.4	3.4	16.5	0.7	11.5	3.8	2.
SIT1 (DAG)	94.9	83.5	11.4	7.3	1.7	5.1	2.5	0.
SST1 (DAG)	29.9	122.0	7.9	15.5	0.8	12.6	3.2	2.
TIL1 (DAG)	37.2	33.3	3.9	8.6	0.7	5.6	3.1	1.

Table 9 - Linear correlation coefficients for selected element distribution in the analyzed samples (A) for Bolotabo, Sentom area, (B) for Daguja area

Selected element	correlation coefficient	Selected element	correlation coefficient
TiO ₂ - Zr	0.972	TiO ₂ - Zr	0.44308
TiO ₂ -Th	0.985	TiO ₂ -Th	-0.977
TiO ₂ -Sc	0.934	TiO ₂ -Sc	0.827
TiO ₂ -REE	0.925	TiO ₂ -REE	0.67148
Al ₂ O ₃ -V	0.575	Al ₂ O ₃ -V	-0.17988
Al ₂ O ₃ - La	0.419	Al ₂ O ₃ - La	-0.9748
Al ₂ O ₃ - Yb	-0.17	Al ₂ O ₃ - Yb	0.03759
Al ₂ O ₃ -REE	0.43	Al ₂ O ₃ -REE	-0.99750
Al ₂ O ₃ -Th	0.64	Al ₂ O ₃ -Th	0.85
Al ₂ O ₃ -Sc	0.879	Al ₂ O ₃ -Sc	-0.209
Al ₂ O ₃ -Cs	0.763	Al ₂ O ₃ -Cs	0.885
Al ₂ O ₃ -Rb	0.794	Al ₂ O ₃ -Rb	0.972
Al ₂ O ₃ -Sr	0.870	Al ₂ O ₃ -Sr	0.482
Al ₂ O ₃ -Ba	0.821	Al ₂ O ₃ -Ba	0.976
P ₂ O ₅ -REE	0.73	P ₂ O ₅ -REE	0.07133
Zr- La	0.908	Zr- La	0.99245
Zr- Yb	0.024	Zr- Yb	0.13618
Cr- V	0.954	Cr- V	0.99953
Th-Nb	0.918	Th-Nb	-0.997

