UNIVERSITY OF GHANA

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PROVENANCE OF PALEOPROTEROZOIC BIRIMIAN METASEDIMENTARY ROCKS IN PARTS OF THE WA-LAWRA BELT, NORTHWESTERN GHANA

BY

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DECLARATION

This is to certify that, with the exception of referenced research work which have been duly cited, this thesis is as a result of research undertaken by Magdalene Agoe for the award of a Master of Philosophy degree in Geology. This thesis has neither in whole nor in part been submitted for a degree either in this university or any other.

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ABSTRACT

Shales from the Paleoproterozoic Birimian Supergroup in parts of the Wa-Lawra Belt, Northwestern Ghana, were analyzed for their major and trace element contents using ICP-MS and ICP-AES with the main aim of establishing the geochemical characteristics of the shales and inferring their provenance. On the whole twenty-two (22) samples of the shale was collected for analysis. The studied shales were compared to Early Proterozoic crust (EPC) and Post Archean Australian Shales (PAAS), and the various models proposed suggest that the studied shales show enrichment in the transition metals (TM) and depletion in the High field strength elements (HFSE) but shows resemblance in REE patterns with characteristics to their Archean equivalence. The geochemical data also suggests that the studied shales may have been derived from a confined source of mixed felsic and mafic compositions, with the mafic dominating. A model of 60% basalts, 20%TTG and 20%UCC explains this derivative. Hence, the source rock composition within the study area is more of andesitic to basaltic volcanic rocks and this may be suggested to have been derived from the mafic volcanic rocks and their associated granitoids in the Birimian greenstone belts. The corrected CIA values of the studied shales ranges from 70 to 85, suggesting intermediate intensity of weathering at the source area under semi-arid to arid conditions and are deposited in a tectonic setting comparable to modern Island arcs, with minor contribution from the older upper crust (i.e., Pre-Birimian sources). Geochemical features of the studied shales in parts of the Wa-Lawra Belt show trace element variations which suggest a significant compositional variation through time.

DEDICATION

This research is dedicated to the Almighty God for His presence throughout my life.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Current research into crustal growth and accretion tends to restore contributions from different regions of the crust and the mantle and this generates materials for crustal growth (Rollinson, 2007).There are several processes involved in the crustal growth of Birimian rocks and these processes have essentially been defined from petrological, geochemical and isotopic data on the volcanic sequences and on the suites of granitoids as well as sedimentary rocks over the years (Leube et al., 1990, Asiedu et al., 2003).

It is widely accepted that plume and arc type magmatism are the largest producers of magma for crustal growth. The two main components which contribute to arc magmatism is the mantle beneath the arc which consistently supplies arc material and the subduction slab with its sedimentary cover which reworks the mantle compositions as proposed by Rollinson, (2007). Therefore, to know the source or provenance of the arc lavas, the mantle component would have to be determined in relation to its enrichment and depletion history (Taylor and McLennan, 1985).

The Paleoproterozoic Birimian Supergroup (Junner, 1940) forms the northern and eastern portions of the Leo-Man Shield, which occupies the southern segment of the West African Craton (Fig. 1.1). It is composed of two major units: dominant volcano-detrital rocks and the other mostly represented by bimodal although largely tholeiitic volcanics (Abouchami et al., 1990). Geochronological studies on the Birimian rocks suggest they were formed during the time interval ~2.3 to 2.0 Ga (Abouchami et al., 1990; Liégeois et al., 1991; Boher et al., 1992; Taylor et al., 1992 Leube et al., 1990).

The rocks were deposited on deformed and metamorphosed basement rocks of no more than 50 m.y. older (Abouchami et al., 1990), as sediments and volcanics in an extensive geosyncline. They were later folded, metamorphosed under mostly greenschist-facies conditions and invaded by various generations of granitoids during the Eburnean event at 2.1 Ga (Leube et al., 1990; Hirdes et al., 1992). There is controversy regarding the lithostratigraphic successions of the main units (i.e., the volcano-sedimentary and bimodal volcanics). Some workers (e.g., Junner, 1940; Milési et al., 1992) have proposed that the volcano-sedimentary unit is older whereas others (e.g., Tagini, 1971; Hottin and Quedraogo, 1975) hold a contrary opinion, that the volcanic unit is older. However, Leube et al. (1990) have proposed that the two units formed quasicontemporaneously as lateral facies equivalent.

Also various alternative models have been proposed with respect to the tectonic setting of the Birimian rocks in West Africa: intraplate oceanic plateaus (Abouchami et al., 1990); from intra-cratonic rift to oceanic-spreading and finally to an accretion-related setting (Leube et al., 1990); immature island arcs built on oceanic crust (Sylvester and Attoh, 1992); and back-arc basin (e.g., Vidal and Alric, 1994).

Geochemical studies tend to become valuable for source rock characterization and an extrapolation of geological processes. Chemical composition of fine-grained sedimentary rocks is particularly valuable for provenance studies as they provide a representative view of the average crust in the region due to their grain size homogeneity and post-depositional impermeability (Taylor and McLennan, 1985; Cox and Lowe, 1995). It has been particularly employed to obtain information on the depositional setting and provenance in the case of Archean and Proterozoic sediments as noted by Cullers, (2000), Condie et al. (2001) and Hofmann, (2005) among many others.

Most geochemical studies on the Birimian have concentrated on the metavolcanic rocks within the greenstone belts (e.g., Abouchami et al., 1990; Leube et al., 1990; Sylvester and Attoh, 1992; Béziat et al., 2000) and to a lesser degree, the granitoids (e.g., Leube et al., 1990; Doumbia et al., 1998; Loh and Hirdes, 1999). In comparison to the volcanic rocks, the Birimian sedimentary rocks have received very little attention in geochemical studies even though sedimentary rocks contain substantial information about provenance and crustal evolution (e.g., McLennan et al., 1990, 1995). It is now well established that part of a record of geologic history is retained in detrital sediments. Petrographic examination has frequently been an important method in extracting this information (e.g., Dickinson and Suczek, 1979; Dickinson et al., 1983), but has generally not proved very useful in the examination of mudstones and metamorphosed sediments (Asiedu et al., 2003). Geochemical examination, particularly REE has no such restrictions however, and can be used effectively for all types of clastic sediments to evaluate the nature and evolution of the provenance and of sedimentary history (McLennan et al., 1995). The geochemical approach is, therefore, more appropriate to this study of metamorphosed sedimentary rocks. Acquiring geochemical data from the metasedimentary rocks in some areas within the Wa Lawra greenstone belt can aid in interpretations on provenance which includes the tectonic setting, source rock composition and weathering conditions at source, to improve the understanding of the geology of this area.

Although the Birimian terrane is relatively larger compared to the study area, research on the metasedimentary rocks such as the shales from well-defined prospects as Atikpi, Basabli, Bepkong, and Kunche within parts of the Wa–Lawra belt, would help provide a localized provenance model which may be applicable to some other areas (Figure 1.2).

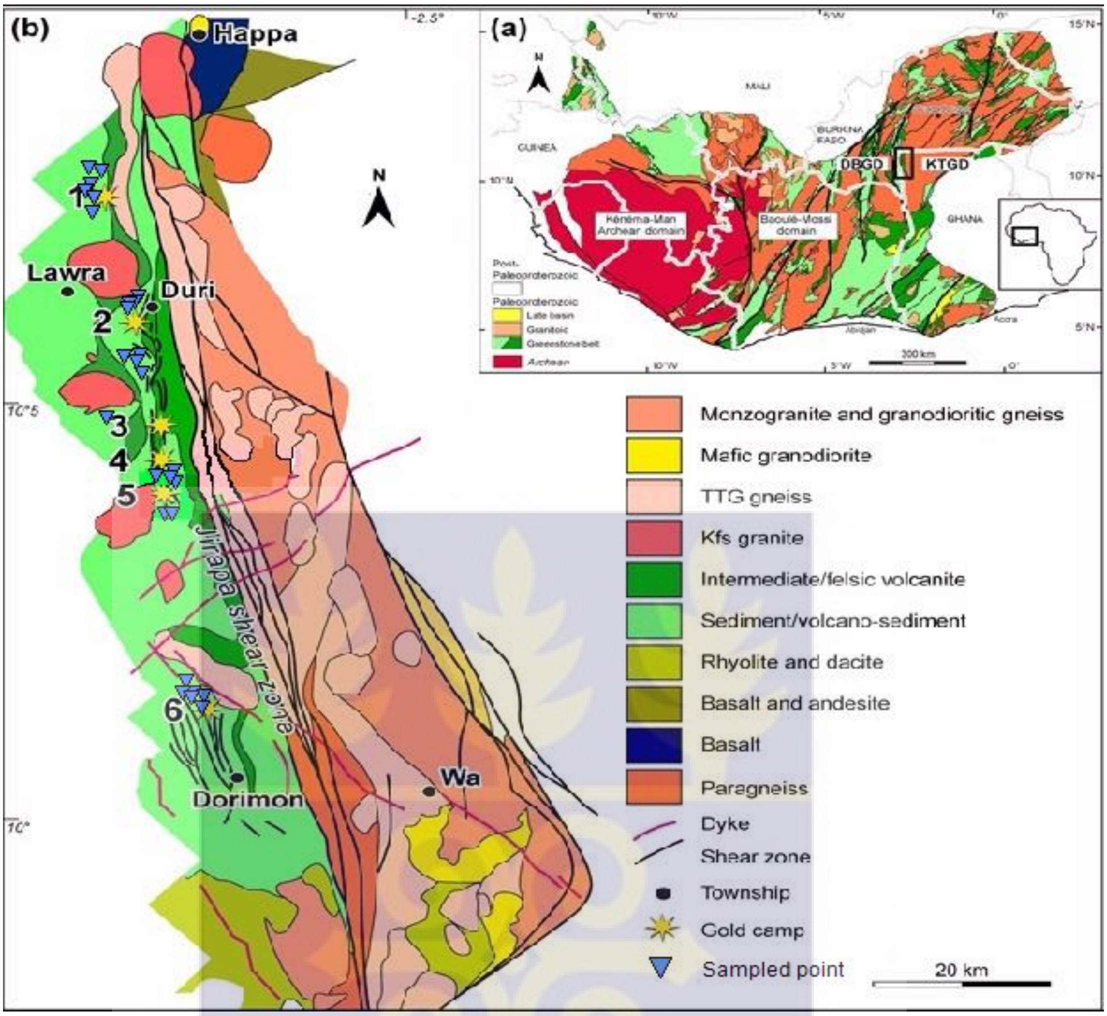

Figure 1.1a Geological map showing the study area and sample locations in parts of the Wa-Lawra belt. Figure 1.1b showing the West African Craton (After Amponsah et al., 2015).

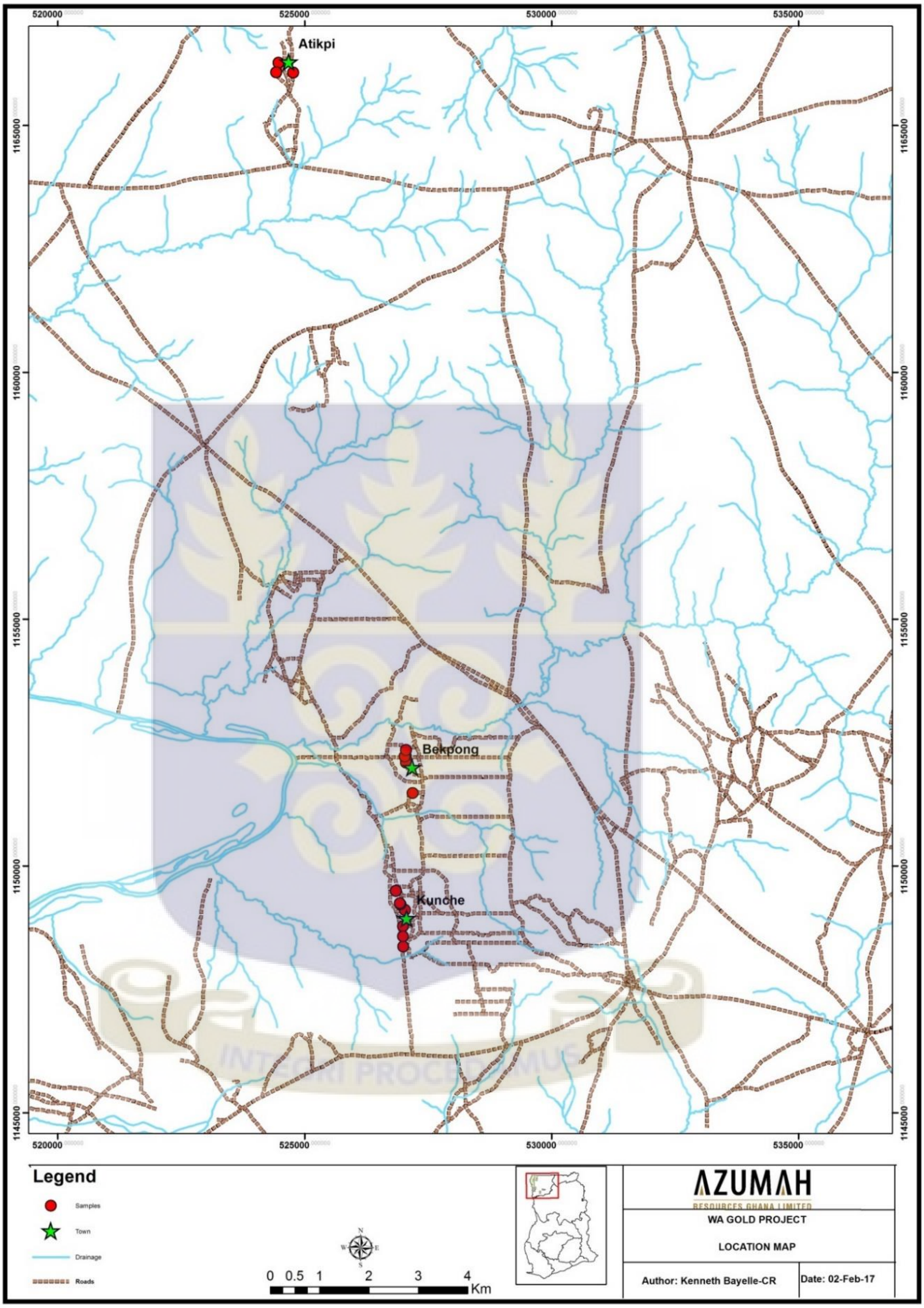

Figure1.2 Map of study area showing sample locations and prominent study areas in parts of the Wa-Lawra Belt. (After Amponsah et al., 2015).

1.2 Aims and Objectives

The main aim of this project is to study and interpret the provenance of the metasedimentary rocks in parts of the Wa-Lawra Belt.

The study was carried out with the Objective to investigate the following:

- Generate a geochemical database for the metasedimentary rocks.
- Source area lithology.
- Infer the source area weathering conditions.
- Constrain the source rock composition and tectonic setting at time of deposition.

1.3 Study Area

1.3.1 Location

The study area is located in the northwestern part of Ghana and lies between latitudes 10˚ 00' 30" N and 11˚ 00' 00" N and longitudes 02˚30' 00" W and 00˚14' 00" W (Figure 1.2). Notable towns in the study area include: Atikpi, Basabli, Bekpong, Dorimon, Duri and Kunche (Sakyi et al., 2014).

1.3.2 Accessibility

The study area occupies an area of about 8800 km2, it constitutes 12.7% of the total land area of Ghana. It is easily accessed by the Most of the study area are linked by footpaths. However, accessibility to some parts of the study area is difficult due to the relief and the nature of settlement within the study area (Sakyi et al., 2014).

1.4 Climate

The study area is characterized by brief but extreme rainfall season which starts in July and peaks in August with prolonged dry season from October to the end of April.

During dry seasons, the area is under the influence of the North Eastern trade winds; Harmattan (Dickson and Benneh, 1988).

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

This research mainly focuses on the provenance studies of fine - grained sedimentary rocks from parts of the Wa-Lawra belt, areas which include Atikpi, Basabli, Bekpong, and Kunche. It also focuses on factors that contribute to a more resolute composition of clastic sedimentary rocks, their tectonic settings as well as the weathering at source regions and how their geochemical characteristics significantly impart the geology of the study.

2.1.1 Provenance of Fine - Grained Sedimentary Rocks

Provenance studies generally describes the interpretation and reconstruction of history of sediments from their parent source to their burial place. This basically reveals the source region of the sediments (where the sediments are coming from) and where they have been deposited and in detail the geological processes involved during their transportation as well as the weathering conditions in every stage and how these processes affect the sediments (McLennan et al., 1993; Johnsson, 1993). Chemical and physical conditions in post-depositional environments are also taken into consideration as well as diagenetic occurrences during provenance studies (McLennan and Taylor, 1991; McLennan et al., 1993; Johnsson, 1993).

Although previous provenance studies primarily relied on proportions of detrital fragments, further studies employ the use of various experimental, geophysical and isotopic methods to explore sedimentary rocks as well. (E.g. Dickinson et al., 1983). Numerous research over the years proposed various methods in studying fine-grained siliciclastic sedimentary rocks.

This approach mainly focuses on detrital heavy assemblages for quantitative provenance studies. However, Other researchers such as Nesbitt and Young, (1984); Bhatia, (1985); Asiedu et al., (2004), also used whole-rock geochemistry to reveal geochemical signatures of sedimentary rocks and this has proved very useful in further understanding of various geological provinces. This method is commonly used and it involves determining major, trace elements as well as rare earth element abundances in sediments. These elements provide important information about the rock composition, weathering conditions and tectonic setting at source (Nesbitt and Young, (1984), Bhatia, (1985) and McLennan et al., 1993). These findings coupled with isotope geochemistry or zircon dating, in recent studies help determine provenance of sediments (e.g., Kalsbeek et al., 2008; Chen et al., 2014; De et al., 2015).

2.1.2 Source Rock Composition

Studies have shown that source rock composition of clastic sedimentary rocks may be determined from their chemical elemental compositions (McLennan et al., 1993). Mostly the tectonic setting is believed to immensely control the composition of clastic sedimentary rocks (Dickinson and Suczek, 1979; Bhatia, 1983; Chamley, 1990). Work done by Bhatia, (1983), Dickinson et al., (1983) and McLennan et al., (1993) describes plate tectonic processes which reveal distinctive petrological and geochemical characteristics of sedimentary rocks. Sedimentary rocks within different tectonic settings may have distinctive provenance characteristics recognized by different sedimentary processes McLennan et al., (1993). Asiedu et al. (2004), Armstrong - Altrin et al. (2004) and Osae et al. (2006) support this fact as well.

The application of elemental geochemistry to identify source rocks of clastic sedimentary rocks is based on the relationship in the characteristics of immobile elements such as rare earth elements (REEs), high field strength elements (HFSE) and the various minerals that host these elements, despite weathering, diagenesis, hydrothermal imprint and metamorphism that took place at source region (Taylor and McLennan, 1985; Bhatia and Crook, 1986).

Thorough research that the elements when transported in quantified proportions, unfractionated within the minerals will exhibit concentrations and elemental ratios distinct for different rock types within their respective tectonic environments, thus reflecting their source compositions (Cullers and Stone, 1991; Bhatia and Crook, 1986 and Getaneh, 2002).

A complementary relationship between sediment composition and tectonic setting is mostly established by plotting the rock suites on discrimination diagrams using elemental composition of the sediments as proposed by Roser and Korsch, (1986, 1988). The cluster of rock suites that emerges is mutually compared to the tectonic environment of the inferred source terrains. Several discrimination diagrams have been presented by previous workers such as Dickinson et al. (1983), Bhatia, (1983), Bhatia and Crook, (1986) and Roser and Korsch, (1986, 1988) to verify these outcomes. Even though most of the inferred tectonic terranes proposed by these workers were mainly used for sedimentary rocks, the introduction of bulk - rock geochemical analyses permit them to be applied to metasedimentary rocks as well (e.g., Bhatia and Crook, 1986; Asiedu et al., 2004; Armstrong - Altrin et al., 2004; Osae et al., 2006).

2.1.3 Chemical Weathering

The degree and duration of weathering solely depends on the climatic conditions as well as the relief (Johnsson, 1993). Generally, chemical weathering is more intense in the tropics relative to the temperate and arid regions (Krynine, 1936; Mann and Caravoc, 1973; Basu, 1976; Suttner and Basu, 1981; Girty et al., 1988).

Chemical weathering is supported by factors such as low relief and gentle slopes as well as high relief with steep slopes. This supports erosion as well as rapid removal of minerals from weathering environments before they become severely altered by weathering processes (Johnsson, 1993). During chemical weathering conditions, there's destruction and depletion of less stable minerals such as olivine, pyroxenes, amphiboles, calcium plagioclase. More stable minerals such as sodium plagioclase, potassium feldspars, muscovite, and quartz are enriched. This is because common rock-forming minerals have different stabilities with respect to chemical weathering processes (Goldich, 1938) or the climatic conditions within the region. Thus, the principal effect of weathering on silicilastic sedimentary rocks is very important in the evaluation of provenance of sedimentary and metasedimentary rocks (Johnsson, 1993; Goldich, 1938).

Chemical weathering can be measured by the compositional changes resulting from mineralogical alteration and chemical changes (Folk, 1974; Nesbitt and Young, 1984). The effect of weathering on the composition of sediments has been studied by numerous workers (Nesbitt et al., 1980; Knoll and James, 1987; Hansley, 1987; Bennet and Siegel, 1987; Johnsson et al., 1988). Nesbitt and Young (1982, 1984) from several examinations drew conclusions and quantified the intensity of chemical weathering as the chemical index of alteration (CIA). The chemical index of alteration (CIA) is interpreted as a measure of the extent of conversion of feldspars (which dominate the upper crust) to clays such as kaolinite (Nesbitt and Young, 1982, 1984; Fedo et al., 1995; Maynard et al., 1995).

2.1.4 Abrasion and Mechanical Breakdown

Transport of sediments serves as an important link between source and depositional areas (Johnsson, 1993). However, various sedimentary processes occur prior to the deposition of sediments which affect the composition of these sediments (Johnsson, 1993). These sedimentary processes may include chemical weathering, abrasion, mechanical breakdown, hydrodynamic sorting and mixing which occur before deposition of sediments (McLennan et al., 1993). During the transportation of sediments, abrasion and mechanical breakdown are the most important processes involved as they lead to the removal of mechanically less stable components especially lithic fragments and exposure of freshly unreacted mineral surfaces to chemical weathering (Dutta and Wheat, 1993). Highly weathered particles are susceptible to abrasion and mechanical breakdown during transport (Bradely, 1970).

In general, abrasion and mechanical breakdown increase the concentration of mechanically stable minerals as well as heavy minerals including zircon and destroy less mechanically stable minerals such as plagioclase in sediments (Dutta and Wheat, 1993). Thus, geochemical characteristics of clastic sediments may be used to infer the effect of abrasion and mechanical breakdown in sedimentary and metasedimentary rocks by evaluating the quartz/feldspar ratio and the heavy mineral (e.g. zircon) composition of clastic sediments (McLennan et al., 1993).

2.1.5 Sorting and mixing

Sorting and mixing of clastic sediments during transport affects the composition of these sediments (Johnsson et al., 1991). Hydrodynamic sorting controls the grain size composition and it is responsible for the differences in composition of the suspended load and bed load of most rivers during transport of clastic sediments.

An example is the separation of most clay minerals and other fine materials from coarser-grained minerals (Garvanti, 1986; Koehnken, 1990; Johnsson et al., 1991).

The degree of sorting may be deduced by evaluating the quartz/feldspar ratio (SiO_2/Al_2O_3) and the accumulation of heavy minerals such as zircon in siliciclastic sedimentary rocks (Armstrong - Altrin, 2004). According to Mielke (1979), the geochemical characteristics of zirconium, Zr a predominant constituent of zircon ($ZrSiO2$) can be used to evaluate the degree of sorting in clastic sediments.

2.1.6 Diagenesis

Burial of sediments when deposited alters the geochemical characteristics of the rocks within the burial environment and this can result to intense post - depositional modifications in composition (Scholle and Schluger, 1979; McDonald and Surdam, 1984). Even though the chemistry of diagenetic processes is not established, most of the reactions involved in this process may be very important in the studies of sedimentary and metasedimentary rocks (Morad et al., 1990). Diagenesis may result in alterations of sedimentary materials producing different geochemical signatures relative to the protolith and thus significant loss in provenance information (McLennan et al., 1993; Johnsson et al., 1991).

2.2. The Paleoproterozoic Birimian Terrane

The Proterozoic Birimian terrane occupies the southern third of the West African craton also known as the Baoulé-Mossi Domain (Fig. 2.1). This covers areas in Ghana, Burkina Faso, Ivory Coast, Mali, eastern Mauritania and Senegal (Taylor et al., 1992). The Birimian consists of rocks of Paleoproterozoic age which have been affected by a major 2.1 Ga tectono-thermal event referred to as the Eburnean event (Taylor et al., 1992).

Additionally, the terrane is characterized by, parallel and evenly spaced volcanic belts and intervening sedimentary basins trending towards northeast. The volcanic belts comprise low metamorphic grade lavas of prevalently tholeiitic composition, minor felsic volcaniclastics, as well as 'belt type' tonalite-granodiorite intrusions (Hirdes et al., 1992). The sedimentary basins consist of isoclinally folded, mostly dacitic volcaniclastics, wackes and argillites (Leube et al., 1990) intruded by extensive, late-kinematic 'basin type' granitoid plutons which vary from tonalite to peraluminous granite (Hirdes et al., 1992; Davis et al., 1994). The main Paleoproterozoic crustal growth events in the West African craton is characterized by the formation of huge volumes of juvenile material with the involvement of significantly small Archean crust component (Abouchami et al., 1990; Taylor et al., 1992)

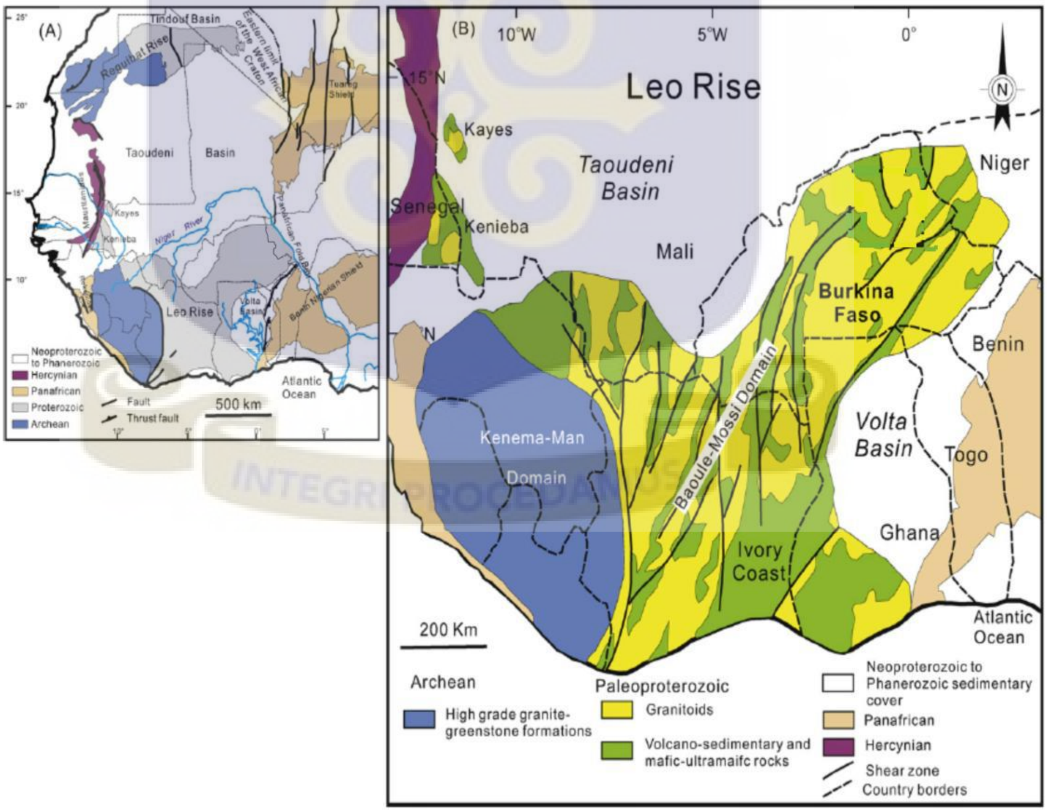

Figure 2.1 Simplified geological map of the West African Craton (A) with emphasis on the Leo-Man shield (B) showing the major geological units. After Tapsoba et al. (2013).

2.2.1 The Birimian Province of Ghana

The Birimian terrane in Ghana covers over two-thirds of the western part of Ghana. The volcanic belts are typically 15–40 km wide, and about 60 and 90 km apart (Taylor et al., 1992) (Fig. 2.2). The total thickness of the Birimian succession could be in the order of 10,000 to 15,000 meters (Wright et al., 1985).

According to Leube and Hirdes, (1986); in Taylor et al., (1992), the sedimentary basins show extensive isoclinal folding which indicate a major post-Birimian crustal shortening and this may have resulted in the shortening of the spacing between the volcanic belts to less than one-third of the original spacing. The Birimian volcanic belts consists of basaltic flows, andesitic to dacitic pyroclastic rocks and lavas, volcanogenic turbidites, and manganeferous cherts which have been metamorphosed to greenschist facies, and form synclinal structures cored by late orogenic, alluvial, molasse-type sedimentary rocks (Kesse,1985; Wright 1985; Leube et al., 1990). The metasedimentary belts are composed of fragmental felsic rocks, flysch-type turbidites (Trashliev, 1974 in Sylvester and Attoh, 1992) and large concordant peraluminous granitic plutons (Leube et al., 1990). These have been metamorphosed to amphibolite facies. Overlying the Birimian volcanics is the Tarkwaian Group. Eisenlohr (1992). They also proposed that the rocks of the Birimian have U– Pb zircon dating of extrusive volcanism in a rhyolite flow in Ghana by Hirdes and Davis (1998), this gave an age of 2189 ± 1 Ma. Even though the lithology gives Proterozoic ages, the lithological associations and trace element characteristics and signatures resemble that of an Archean greenstone belt (e.g., Leube et al., 1990; Sylvester & Attoh 1992).

2.2.2 Metamorphism and Tectonic Evolution

The Birimian terrane is characterized by low-medium grade metamorphism which generally ranges between pumpellyite-prehnite facies and almandine-amphibolite subfacies. However, metamorphism of most of the rocks is confined to the chlorite zone of the greenschist facies (Leube et al., 1990). Amphibolite-facies assemblages occur intermittently but especially around the margins of granitoid bodies. (Gueye et al., 2008). The general trend of the Birimian belts and basins is north-northeastern–south-southwestern (NNE–SSW). However, some of the belts and basins are oriented north (N) and north-northwest (NNW). A few of such belts which differ in orientation are the volcano-sedimentary sequences north of the Massigui pluton, west of the Kekoro-Bougouni unit in Mali (Liégeois et al., 1991), and the Lawra belt in northwestern Ghana.

The structural evolution of Birimian terrane has been interpreted by some authors as monocyclic (Leube et al., 1990; Abouchami et al., 1990) and others as polycylic (Milési et al., 1992). The tectonic setting of emplacement of the Birimian volcanics is a subject of much debate. Various interpretations of the geodynamic context proposed are based on the source variation of the tholeiitic and calc-alkaline, that is whether these suites originated from a single geotectonic setting or as different processes in a distinct geotectonic setting (Pouclet et al., 2006). Earlier authors (Lemoine, 1988; Milési et al., 1989; Vidal et al., 1992 in Pouclet et al., 2006) have suggested that the Birimian volcanics may have been emplaced in an intracontinental rifting environment. Other authors (Abouchami et al., 1990; Boher et al., 1992) discounted that claim on the basis that the Birimian terrane is juvenile in nature and the possibility of a pre-Birimian basement was unlikely. The mafic lavas of the Birimian greenstone belts are suspected to belong to large ocean plateaus by one school of thought (Abouchami et al., 1990; Lompo, 2009) while others have suggested modern plate tectonic models such as oceanic ridges, subduction-related oceanic or continental volcanic arcs and back-arc basins (Sylvester and Attoh, 1992; Vidal and Alric, 1994; Béziat et al., 2000; Asiedu et al., 2004; Dampare et al., 2008).

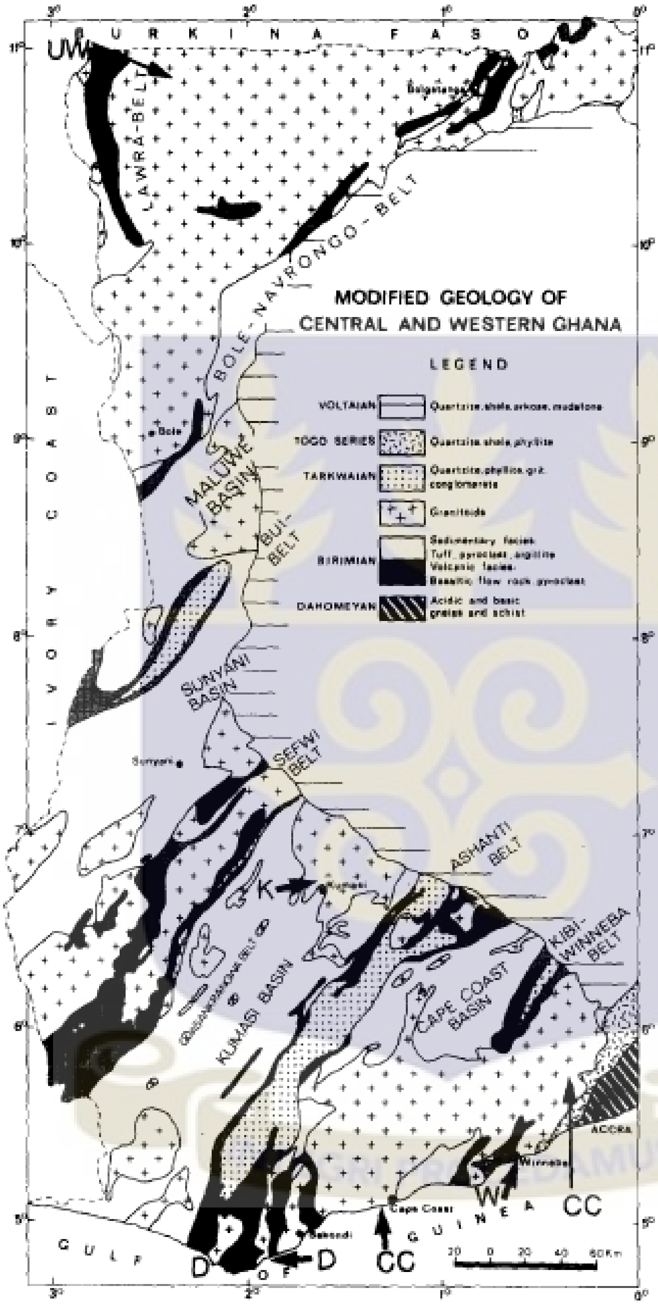

Figure 2.2 Simplified geological map of western and central Ghana showing the major geological units. After Taylor et al. (1992).

2.2.3 Metavolcanic Belts

According Leube et al. (1990), the volcaniclastic sediments are interbedded with the basaltic flows in all the Birimian volcanic belts in Ghana.

Investigation of the these metalavas also showed that the sample suite of volcanic rocks used by Leube et al. (1990), classified the Birimian rocks from all the belts as having 81 % basaltic compositions and only 16 % possessing andesitic compositions. Interpretation of the stratigraphical succession in the Birimian terranes was a matter subject to debate due to contrasting views on the relative stratigraphical positions of the volcanic and sedimentary suites. Earlier authors (references in Taylor et al., 1992) suggested that the sedimentary rocks underlay the volcanic rocks and hence pre-date the volcanic rocks (Junner, 1940, Milesi et al., 1992). The opposite relationship has also been proposed by (Tagini, 1971; Papon, 1973; Hottin & Ouedraogo, 1975), where the Birimian Supergroup was divided into two: The Lower Birimian and the Upper Birimian (Roddaz et al., 2007). More recent studies in Ghana (Leube et al., 1990) have suggested that the volcanic belts and sedimentary basins are lateral equivalent facies.

2.2.4 Metasedimentary Rocks

The metasedimentary rocks of the Birimian in Ghana are mostly located within the sedimentary basins with minor occurrences in the belts (Aseidu et al., 2009). Early authors (e.g., Milési et al., 1992) categorized the sedimentary basins as the Lower Birimian in terms of stratigraphical order from the bottom. These basins have been separated by a series of fairly evenly spaced, sub-parallel NE-SW trending volcanic belts. Pohl and Carlson (1993) described the Birimian sedimentary basins as " linear to equant flysch basins filled with volcanoclastic detrital rocks, as well as minor amounts of manganeferous and siliceous chemical sediments, and carbonates". According to Aseidu et al. (2009), metagraywackes from the Konongo area in southern were derived from mafic rocks, andesitic rocks and TTG's of the adjacent penecontemporaneous Birimian metavolcanic belts. This could also apply to the other sedimentary deposits in the basins.

The metasedimentary succession can be divided into four main groups which are: 1) volcaniclastic rocks; (2) turbidite-related wackes; (3) argillitic rocks; and (4) chemical sediments (Leube et al., 1990). These comprise various lithologies such as pyroclastics, volcanogenic epiclastics, chert, graphitic schist, phyllites, and carbonates, tuffaceous and schists. The metasedimentary rocks have also been intruded by 'basin-type' granitoids (Junner, 1940 in Asiedu et al., 2009).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The field work carried out was basically reconnaissance survey of the study area. The purpose for this activity was to get the sense of available outcrops and their distribution throughout the study area and to learn as much as possible the geology of this area. This activity did not yield much, as the outcrops are few and scattered. Most of the outcrops observed were very weathered. Therefore, the shale samples used for this work were obtained from diamond drill core from Azumah Resource Limited. Sampling for this study was carried out on the basis of the distribution and occurrence of the shales within the drill cores or boreholes.

3.1.1 Drill Core Sampling

From the drill cores, the least altered samples were meticulously selected for analysis. Altered drill core samples show prominent quartz veins as a result of remobilization (Fig. 3.1a). Sample documentation include identification number, location details and other geological details. The samples were properly labeled and placed in sample bags. Prominent structural features observed were foliations, crenulations, veins, faulting and folding (Fig. 3.2 and 3.3). The rocks which were sampled were photographed with a digital camera for easy identification and description. The samples brought from the field where regrouped and selection of the best representative samples for geochemical analysis was done. The resampling was undertaken to ensure the uniformity and homogeneity of the physical characteristics of the rocks before sent to the Lab. This activity was also carried out to ensure that the samples selected for further studies covered the study area as much as possible.

Forty-one (41) samples were collected from about 30 drill holes across the Azumah Resource Limited concession within parts of the Wa-Lawra belt. The samples were described and characterized on the basis of textures and mineralogical compositions. From hand specimen description the samples were classified as metamorphosed shales. The shales are locally interlayered with volcanoclastic units (Fig. 3.1b).

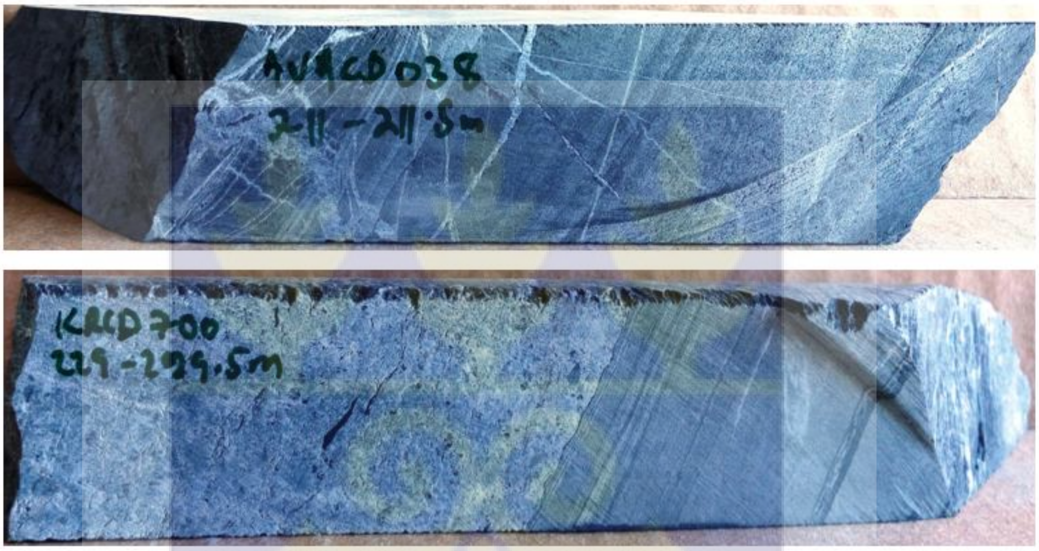

Fig 3.1 Core sample of metasedimentary rocks showing A. veinlets B. intercalation

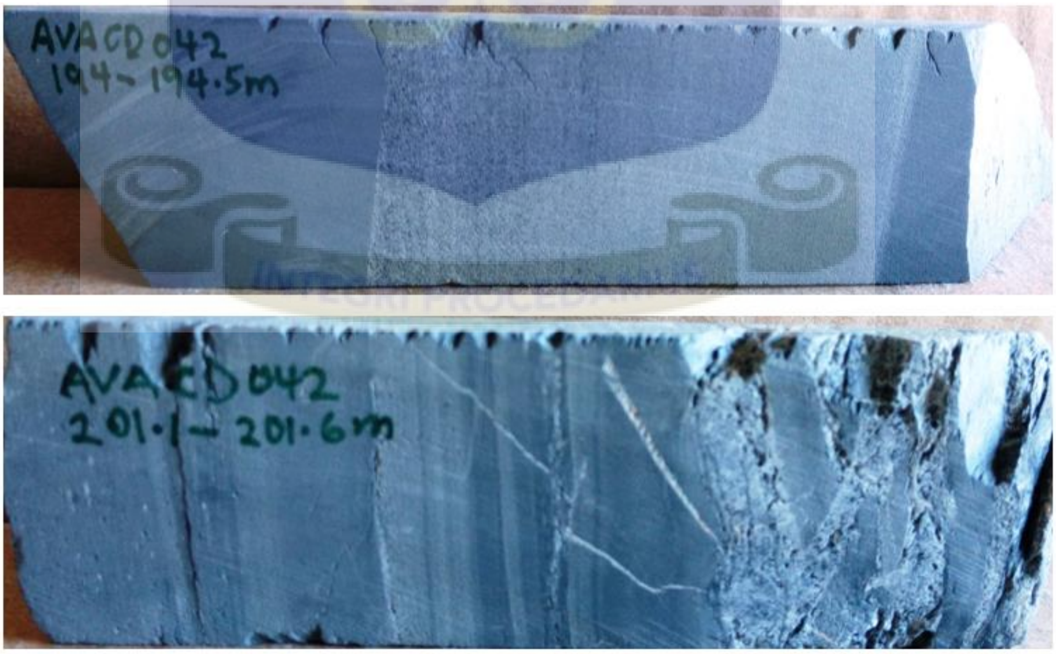

Fig 3.2. Core sample of metasedimentary rocks showing A. contact and B. micro fault.

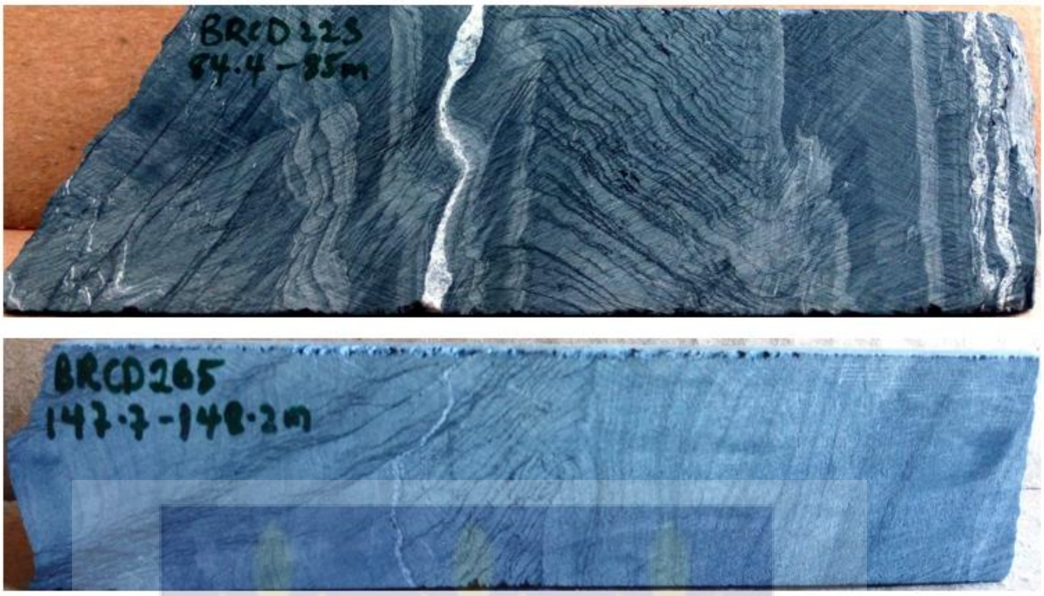

Fig 3.3. Core sample of metasedimentary rocks showing micro fold and foliations.

3.1.2 Thin Section Studies

Thin sections were prepared at the Petrographical Laboratory, Department of Earth Science, University of Ghana. Selected samples were cut with a diamond blade rock saw to small, thin rectangular billets with dimensions which could fit on a glass slide (46 by 26 millimeters). Twenty-two (22) samples were prepared into thin sections for petrographical and microstructural studies. During this activity, the physical and optical properties of minerals were studied using the Leica DM750P polarising microscope. Some of these properties included grain form/shape, colour, relief, pleochroism, interference colours etc. In recognizing the various rock types, the textures and mineral associations were employed. The minerals were examined under plane and crossed polarised light to highlight the mineralogical and textural features of the samples. Various magnifications (25, 40 μm) were used in investigating the samples in the thin sections.

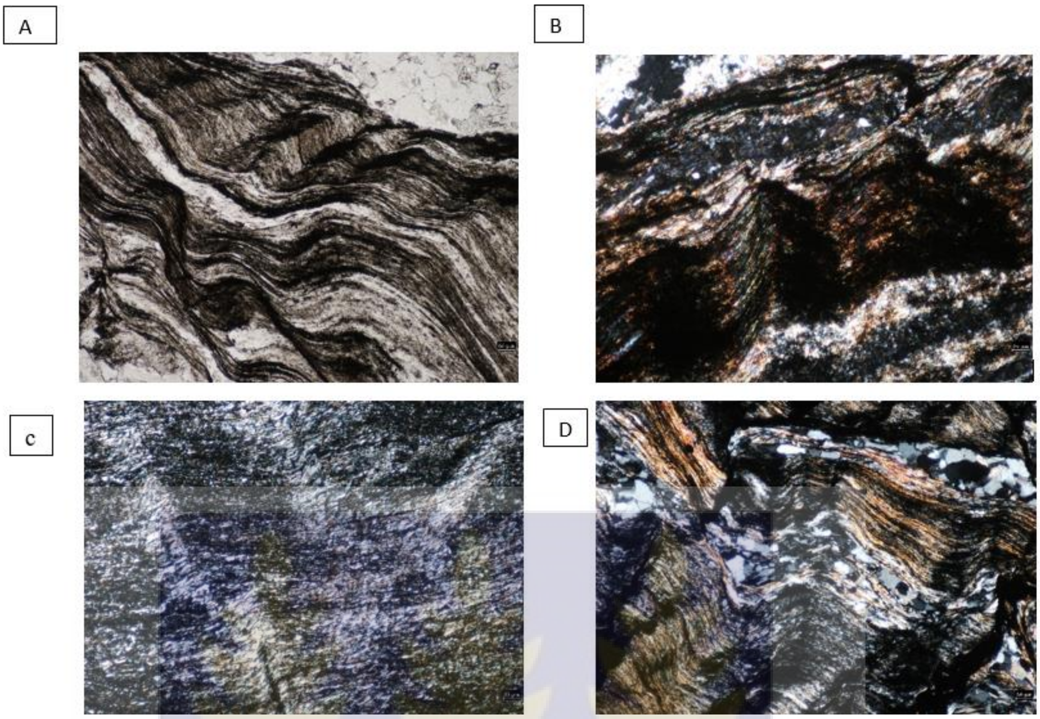

Fig.3.4 A. plane polarized view of shale showing two foliation directions. B. thin section showing ductily deformed metapelite black shales. C. fine-grained ductily deformed metasedimentary rock. D. deformed quartz and mica minerals in shale.

3.2. Whole Rock Geochemistry

Rock samples selected for whole - rock geochemical analysis, were cut into sizeable blocks with dimensions of about 2 centimeters in thickness using a rock saw with a diamond blade, it was packaged in a box and sent to the ALS laboratory in Vancouver, Canada through ALS laboratory at New Brofoyedru in Ashanti region of Ghana for geochemical analysis. Twenty - two (22) selected samples were sent to the ALS laboratory for their whole rock major and trace elements (including REEs) analysis. Sample preparation was done by placing sample (1.0 g) in an oven at 1000 °C for one hour, cooled and then weighed. The percent loss on ignition was calculated from the difference in weight. The major elements were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

This was first achieved by decomposition of samples by lithium metaborate/lithium tetraborate (LiBO2/Li2B4O7) fusion method. This involved mixing a prepared sample (0.200 g) with lithium metaborate/- lithium tetraborate flux and fused in a furnace at 1025 °C. The mixture was then cooled and dissolved in an acid mixture containing nitric, hydrochloric and hydrofluoric acids. The solution was then analyzed by ICP-AES. The results were corrected for spectral inter-element interferences. The trace element analyses were performed observing the protocols as for the major element analyses. However, here the prepared sample weighed 0.100g and the analysis was done by the Inductively Coupled Plasma - Mass Spectroscopy (ICP - MS). The base metals were analyzed using the ICP - AES. A 0.25g prepared sample was digested with perchloric, nitric, hydrochloric and hydrofluoric acids. Dilute hydrochloric acid was then added to the residue and the solution was analyzed by the ICP - AES. Results obtained were corrected for spectral inter-element interferences (ALS laboratory).

3.3 Data Interpretation and Analysis

The results from both the field work and laboratory work were compiled into tables, diagrams, graphs and maps using computer software such as Microsoft excel, Corel draw version x4, Geochemical Data Toolkits (GCD kit) version 2.3, Delta software version 5.6.5, ArcGIS and MapInfo professional. Delta software version 5.6.5 was used to plot variation diagrams, ternary diagrams and discrimination diagrams. Corel draw version X4 was then used the draw the fields and the domains on the plots. Statistical analysis, mainly the calculation of correlation coefficient for the various elements was also carried out using the Microsoft excel. MapInfo professional and ArcGIS were used to develop the geological and topographic maps.

CHAPTER 4

RESULTS

4.1 GEOCHEMISTRY

Table 1 shows the results of the geochemical data of major and trace elements (including REEs) of twenty-two (22) rock samples, from the Paleoproterozoic Birimian metasedimentary rocks in parts of Wa-Lawra greenstone belt.

4.2 Major Elements

The studied shales parts of the Wa-Lawra belt generally show significant variation in their major elemental compositions. For example, SiO_2 ranges from (53.9 to 68.6 wt %) with an average of 59.72, TiO_2 (0.55-0.81) wt% average of 0.69, Al_2O_3 (14.5 to 20.5) wt% average of 17.33, Fe_2O_3 (6.39 to 10.15) wt% average of 8.44, MgO, (2.43 to 4.47) wt% average of 3.62, CaO (0.24-2.21 wt%) average of 0.14, Na_2O (0.94 to 3.63 wt%) average of 2.63wt%, K_2O (1.17 to 3.18 wt%) average of 2.20, P_2O_5 (0.11-0.21) with an average of 0.16 and MnO (0.05-0.1) with an average of 0.08 wt%. On the whole the average compositions of major elemental data reveal few geochemical differences relative to Early Proterozoic Crust (EPC) and Post Archean Australian Shales (PAAS). With the exception of Na_2O all the major oxides are relatively lower in concentration as compared to that of PAAS (Table 4.1; Fig. 4.1). However, when compared to EPC, the studied shales show high concentrations in Fe_2O_3, MgO and TiO_2 and lower concentration of SiO_2 (Figure 4.2).

Al_2O_3/SiO_2 (0.21-0.38 wt % average of 0.29) and Al_2O_3/TiO_2 (22.63-28.93 wt % average of 25.27) of the studied shales are moderately higher than EPC (Al_2O_3/SiO_2 = 0.22; Al_2O_3/TiO_2 = 0.97; Condie, 1993) whereas K_2O/Na_2O values (0.31-2.63 wt %

average of 1.05) are relatively lower in the studied shales than EPC (25.69; Condie, 1993).

From the calculation of the elemental compositions, the studied shales have low Chemical Index of Alteration CIA (59.71 to 73.67 %) with an average of 66.75 %. They show moderately low plagioclase index of alteration (PIA) 62.08 to 86.84% with an average of 73.14 % but high chemical index of weathering (CIW) 66.22 to 89.83 % with an average of 77.09 %. Additionally, the studied shales have index of compositional variability (ICV) of 1.24-1.60 with an average of 1.44 (Table 4.1).

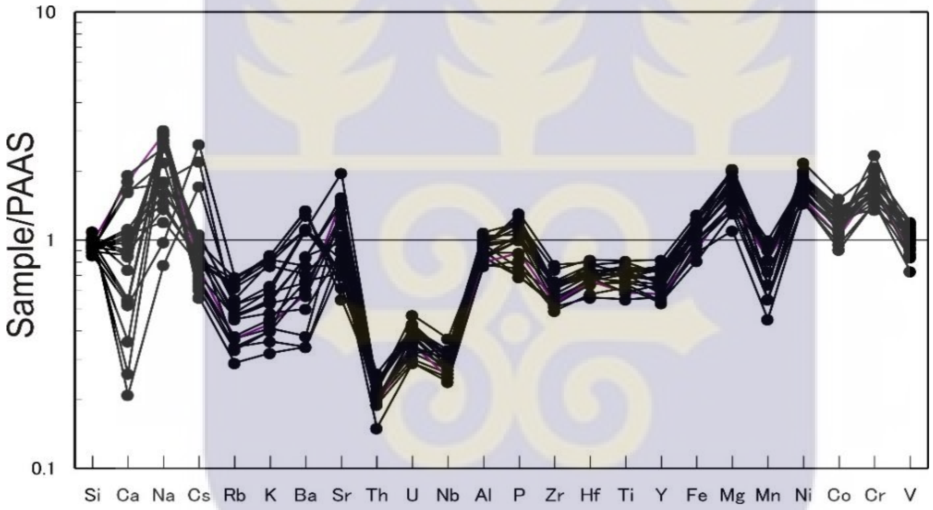

Figure 4.1.Major and trace elements plot of the studied shales normalized against the Post-Archean Australian Shales (PAAS, Taylor and McLennan, 1985).

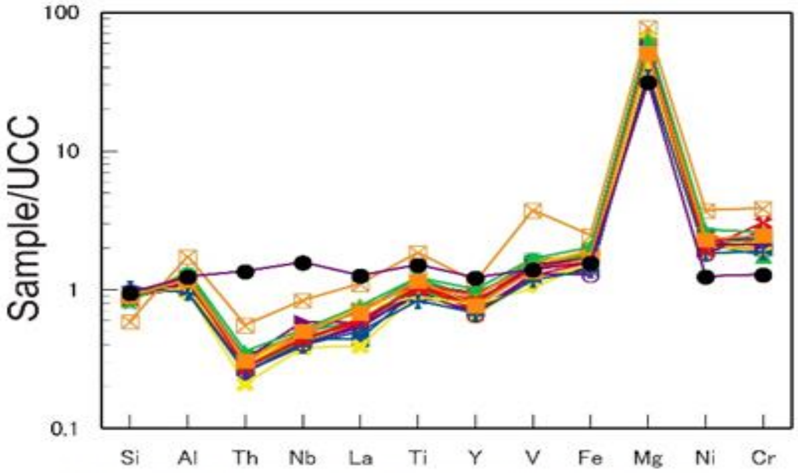

Figure 4.2: A diagram of the studied shale sediments and PAAS (Post Archean Australian Shales) normalized to average continental Crust (UCC). Data for post - Archean Australian average shale (PAAS) and upper continental crust (UCC) are from Taylor and McLennan (1985).

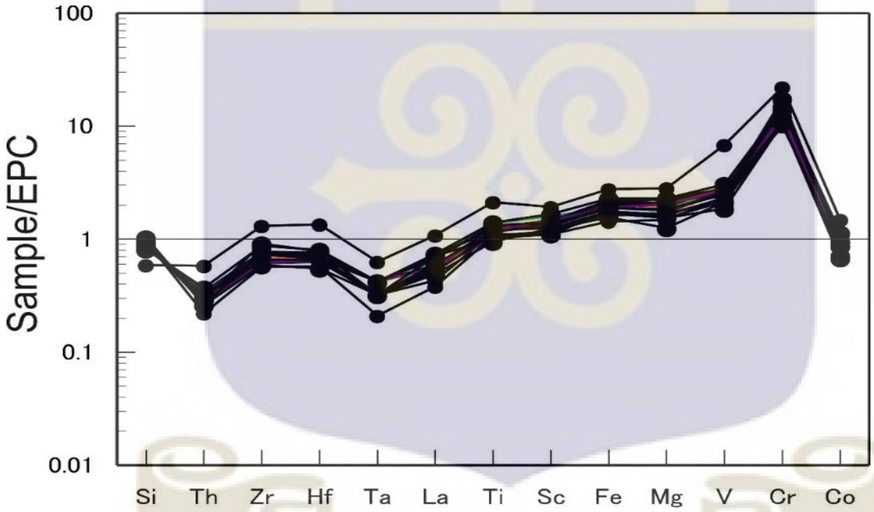

Figure 4.3 The average multi-element pattern of the studied shales plotted against Average Early Proterozoic Crust (EPC). EPC values reported by Condie (1993).

4.3 Trace Elements (Including Rees)

The trace elements include large ion lithophile elements (LILE) (e.g. Cs, Rb, Ba, Sr, Eu, K), transition metals (e.g., Mg, Fe, Ni, Cr, Co, V, Sc), high field strength elements (HFSE) (e.g., Zr, Hf, Nb, Ta, Ti, Y, Ti, Al), and rare - earth elements (REE) (e.g. La - Lu).

4.3.1 Large Ion Lithophile Elements (LILE)

The concentrations of the LILE are variable, Cs (2.59-12.1 ppm) average of 4.67 ppm, Rb (45.8-110 ppm) average of 78.05 ppm, Ba (218-879 ppm) average of 532.73 ppm, Sr (110-394 ppm) average of 213.48 ppm and Eu (0.68-1.25) average of 0.98. The concentrations of these elements are lower relative to PAAS with the exception of Sr which is higher.

The diagram of the studied shales samples normalized to PAAS (Figure 4.1) show slight to strong depletion in the LILEs with the exception of Sr which s enriched. However, when compared to EPC the LILE show general depletions (Table 4.1, Fig.4.3).

4.3.2 Transition Metals

Prevalently, the shales show very high concentrations in Ni (73 to 120ppm) average of 94.5pm, Co (21 to 35) average of 27.41, Cr (150 to 260ppm) with an average of 190 ppm and V (110 to 180) with average of 151 relatives to PAAS as well as EPC. Generally, the studied shales are enriched in the, Co, Cr, V including Fe and Mg with the exception of Mn which is depleted relative to PAAS and EPC (Table 4.1; Fig. 4.1 and Fig. 4.3).

4.3.3 High Field Strength Elements (HFSE)

The studied shales have moderately low concentrations of Zr ranging from (103-163 ppm) with an average of 127.68 ppm, Hf (2.8-4.1ppm) an average of 3.49, with Th and U ranging from (2.26-3.86ppm) an average of 3.12 and (0.91-1.34) with an average of 1.15 relative to PAAS and EPC. However, the concentration Sc (16-24) an average of 19.77 is slightly high relative to PAAS and EPC. Hence, the HFSE are general depleted in PAAS and EPC but slightly enriched in Sc with the exception of P which show slightly similar compositions (Table 4.1 and Fig.4.1 and Fig.4.3).

4.3.4 Rare Earth Elements (REEs)

The REE data for the studied shales are somewhat variable with total REE (ΣREE) values of 61.42-118.7ppm with an average of 90.56 ppm which is relatively lower than that of the post- Archean Australian average shale (PAAS; ΣREE, average = 184.8 ppm; Taylor and McLennan, 1985). Generally, the shales exhibit similar REE patterns when normalized to PAAS (Fig. 4.4) with Light REE (LREE) slightly depleted over Heavy Rare Earth Elements (HREE). HREE in the shales, although similar in pattern are slightly lower in concentration than PAAS (Fig. 4.4).

The studied shales have variable negative Eu anomalies with Eu/Eu* ranging from 0.62 to 0.98 with average of 0.8 higher than PAAS (~0.65) and Gd_N/Yb_N values of 1.13-1.65 with an average of 1.50. However, on the normalized chondrite diagram, the shale samples show general enrichment of LREE relative to HREE (average La_N/Yb_N = 6.78) characteristic of sediments derived from upper continental crust (Fig. 4.5).

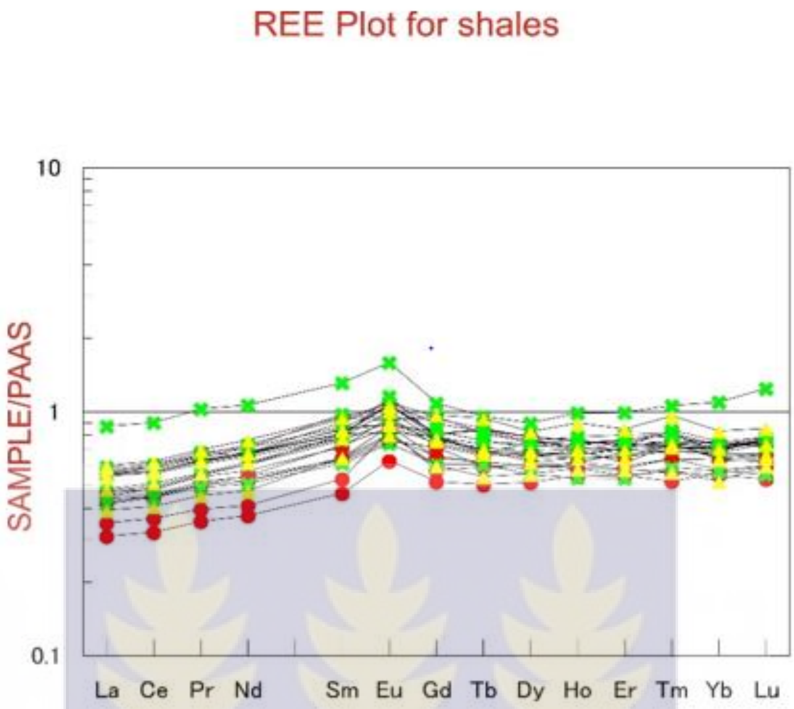
REE Plot for shales

Figure 4.4. Plot of the Rare Earth Elements (REE) of the studied shales normalized against the PAAS

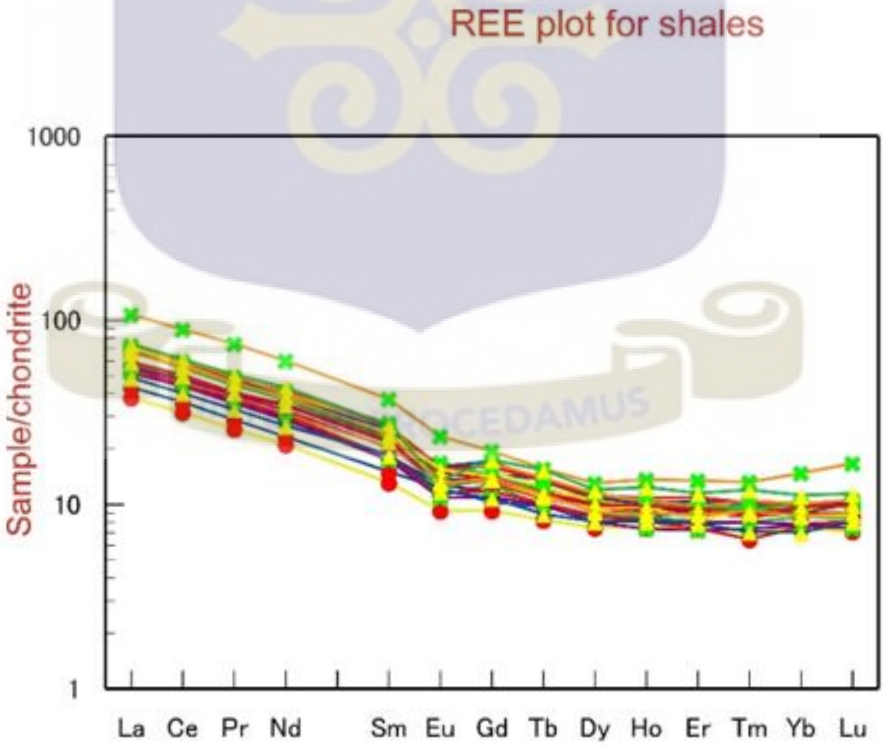
REE plot for shales

Figure 4.5. Chondrite - normalized REE patterns in Paleoproterozoic shales Normalizing values are from Boynton (1984).

Table 4.1 Chemical compositions of the Paleoproterozoic Birimian metasediments, Northwestern Ghana.

Sample	BRCD 223	BRCD 258	BRCD 302	BRCD 203	BRCD 263	BRCD 450	BRCD 450	BRCD 265	KRCD 699	KRCD 695	KRCD 700
major oxides in wt%											
SiO2	59.60	58.10	61.90	57.70	61.40	64.30	55.60	62.10	56.10	60.60	64.20
TiO2	0.66	0.66	0.65	0.76	0.59	0.62	0.73	0.71	0.80	0.61	0.64
Al2O3	16.95	16.15	15.95	18.15	15.15	14.70	18.70	16.10	19.60	17.65	16.55
Fe2O3	9.08	8.81	8.59	9.08	7.18	7.53	9.79	7.91	8.44	6.70	6.39
MnO	0.11	0.09	0.09	0.06	0.09	0.08	0.10	0.06	0.07	0.07	0.06
MgO	3.68	3.80	3.43	3.70	3.31	2.98	3.87	3.17	3.47	3.21	2.89
CaO	1.11	1.92	0.63	0.62	2.07	0.97	0.99	1.03	2.21	2.07	0.85
Na2O	3.22	2.12	3.45	3.20	3.52	3.29	3.56	3.48	3.05	3.11	3.63
K2O	1.53	2.18	1.33	1.97	1.59	1.17	1.76	1.48	2.95	2.39	2.24
P2O5	0.11	0.16	0.11	0.12	0.14	0.12	0.19	0.17	0.17	0.11	0.14
LOI	4.51	5.33	4.19	4.35	5.49	3.68	4.66	3.80	3.78	2.94	2.82
Total	100.64	99.42	100.39	99.81	100.63	99.52	100.04	100.11	100.80	99.60	100.54
CIA	66.83	64.26	67.23	68.33	59.71	65.46	67.30	65.21	62.25	61.81	62.93
PIA	70.76	69.59	70.91	73.89	62.08	68.48	71.58	68.73	67.35	66.02	67.64
CIW	73.82	74.37	73.72	77.32	66.22	71.28	74.72	71.98	72.97	71.16	72.63
ICV	1.51	1.60	1.50	1.41	1.60	1.49	1.47	1.46	1.43	1.37	1.35
AL2O3/SIO2	0.28	0.28	0.26	0.31	0.25	0.23	0.34	0.26	0.35	0.29	0.26
K2O/NA2O	0.48	1.03	0.39	0.62	0.45	0.36	0.49	0.43	0.97	0.77	0.62
AL2O3/TIO2	25.68	24.47	24.54	23.88	25.68	23.71	25.62	22.68	24.50	28.93	25.86
K2O/AL2O3	0.09	0.13	0.08	0.11	0.10	0.08	0.09	0.09	0.15	0.14	0.14
Trace Element (ppm)											
Ba	246.00	422.00	222.00	373.00	376.00	218.00	324.00	395.00	720.00	653.00	714.00
Co	30.00	26.00	29.00	31.00	24.00	26.00	32.00	25.00	29.00	22.00	24.00
Cr	170.00	170.00	150.00	190.00	190.00	180.00	180.00	190.00	200.00	210.00	230.00
Cu	64.00	107.00	51.00	83.00	54.00	60.00	72.00	57.00	86.00	45.00	51.00
Ga	20.00	20.40	18.80	22.40	18.90	15.50	22.00	19.30	27.00	21.40	18.40
Hf	3.40	3.20	3.20	3.50	3.30	2.90	3.70	3.30	3.90	3.30	3.50
Nb	5.20	5.20	5.00	5.70	4.70	4.60	5.60	5.40	6.00	4.80	4.90
Ni	100.00	110.00	94.00	102.00	83.00	85.00	105.00	90.00	101.00	73.00	80.00
Pb	5.00	7.00	5.00	3.00	1.90	7.00	11.00	8.00	6.00	6.00	7.00
Rb	58.90	83.20	53.60	72.90	59.60	45.80	71.30	53.10	87.70	80.30	76.00
Sc	22.00	20.00	22.00	21.00	17.00	17.00	21.00	18.00	23.00	16.00	16.00
Sr	282.00	233.00	182.00	241.00	297.00	153.50	177.50	261.00	394.00	355.00	141.00
Th	2.96	2.97	2.95	2.97	2.76	2.26	3.49	2.91	3.43	2.98	2.77
U	0.99	1.10	0.94	1.06	1.08	0.91	1.27	1.06	1.23	1.11	1.18
V	169.00	151.00	151.00	175.00	131.00	128.00	156.00	136.00	176.00	137.00	140.00
Y	17.40	17.20	16.60	19.90	15.60	14.40	20.90	15.60	19.30	9.20	14.60
Zn	100.00	103.00	108.00	107.00	85.00	88.00	105.00	91.00	112.00	83.00	77.00
Zr	113.00	112.00	110.00	122.00	111.00	103.00	129.00	118.00	130.00	127.00	131.00
Cs	3.06	4.86	3.03	4.24	3.46	2.59	3.79	2.79	4.74	6.41	4.10

La	13.40	18.00	16.80	16.20	17.10	11.80	21.40	17.40	21.10	18.20	16.00
Ce	29.10	38.20	35.60	36.10	35.40	25.50	45.00	36.30	44.40	37.60	35.40
Nd	14.00	19.40	17.70	18.50	17.70	12.70	22.80	18.30	22.20	18.40	17.20
Sm	2.94	3.98	3.50	4.04	3.58	2.57	4.50	3.54	4.34	3.41	3.40
Eu	0.90	1.02	0.82	0.93	0.94	0.68	1.15	0.85	1.25	0.88	0.80
Gd	2.68	3.39	3.33	3.48	3.03	2.41	3.78	3.05	3.65	2.55	2.84
Dy	2.74	3.10	2.83	3.52	2.79	2.41	3.69	2.80	3.51	1.55	2.58
Er	1.95	1.87	1.70	2.18	1.67	1.57	2.10	1.56	2.07	1.10	1.52
Yb	1.91	1.89	1.79	2.03	1.63	1.55	1.97	1.58	2.11	1.26	1.61
Lu	0.32	0.29	0.27	0.32	0.26	0.23	0.33	0.26	0.32	0.22	0.24
Total	69.94	91.14	84.34	87.30	84.10	61.42	106.72	85.64	104.95	85.17	81.59

Table 4.1 continued Sample	KRC D700	KRC D080	KRC D080	KRC D700	KRC D700	KRC D565	AVA CD42	AVAC D042	AVAC D043	AVAC D038	AVAC D038
major oxides in wt%											
SiO2	57.70	58.90	57.70	58.10	56.20	58.10	63.80	68.60	59.30	53.90	59.90
TiO2	0.72	0.73	0.73	0.72	0.69	0.70	0.59	0.55	0.68	0.81	0.77
Al2O3	18.15	18.30	18.45	18.25	18.35	17.75	15.65	14.50	17.75	20.50	17.90
Fe2O3	9.67	8.61	9.51	8.87	9.40	8.43	7.90	6.93	8.40	10.15	8.40
MnO	0.10	0.09	0.09	0.09	0.09	0.09	0.10	0.05	0.10	0.07	0.07
MgO	4.50	3.99	4.01	4.17	4.41	3.98	3.01	2.43	3.55	4.47	3.59
CaO	1.86	1.28	1.16	1.02	1.22	1.25	0.30	0.24	0.41	0.60	1.16
Na2O	2.63	2.16	1.91	1.64	1.44	1.73	3.09	0.94	3.31	1.18	2.17
K2O	2.02	2.84	3.02	3.18	3.18	3.01	1.49	2.34	1.66	3.10	2.01
P2O5	0.20	0.18	0.19	0.16	0.18	0.16	0.16	0.13	0.21	0.19	0.16
LOI	4.34	4.13	4.09	4.59	4.92	4.70	3.85	3.76	4.40	5.25	4.55
Total	102.00	101.32	100.97	100.92	100.21	100.03	100.04	100.59	99.88	100.35	100.81
CIA	65.96	66.52	67.26	67.81	67.95	66.77	68.87	73.19	69.48	73.67	69.76
PIA	70.74	74.43	76.37	78.30	78.47	76.01	73.76	86.84	74.47	86.39	76.19
CIW	74.54	79.37	81.30	83.23	83.35	81.19	76.77	89.83	77.36	89.27	79.53
ICV	1.56	1.43	1.47	1.43	1.47	1.43	1.39	1.24	1.34	1.31	1.34
AL2O3/SIO2	0.31	0.31	0.32	0.31	0.33	0.31	0.25	0.21	0.30	0.38	0.30
K2O/NA2O	0.77	1.31	1.58	1.94	2.21	1.74	0.48	2.49	0.50	2.63	0.93
AL2O3/TIO2	25.21	25.07	25.27	25.35	26.59	25.36	26.53	26.36	26.10	25.31	23.25
K2O/AL2O3	0.11	0.16	0.16	0.17	0.17	0.17	0.10	0.16	0.09	0.15	0.11
Trace Element (ppm)											
Ba	543.00	463.00	498.00	872.00	879.00	830.00	551.00	729.00	427.00	720.00	545.00
Co	28.00	30.00	30.00	27.00	27.00	29.00	22.00	21.00	27.00	35.00	29.00
Cr	180.00	200.00	210.00	180.00	160.00	180.00	160.00	160.00	260.00	220.00	210.00
Cu	63.00	71.00	59.00	69.00	64.00	68.00	44.00	33.00	56.00	80.00	65.00
Ga	27.10	23.70	22.60	25.50	25.70	24.40	17.10	20.30	20.10	27.30	22.20
Hf	3.50	3.40	3.70	3.90	3.60	3.60	3.40	2.80	4.00	4.10	3.60
Nb	5.80	5.80	5.70	5.90	5.60	7.10	6.30	4.80	5.30	6.20	6.10
Ni	101.00	99.00	100.00	94.00	98.00	94.00	80.00	81.00	87.00	120.00	102.00

Pb	7.00	9.00	5.00	4.00	6.00	5.00	7.00	5.00	8.00	4.00	4.00
Rb	73.00	99.50	108.00	107.50	102.50	102.00	54.00	83.20	60.60	110.00	74.50
Sc	21.00	21.00	21.00	20.00	21.00	21.00	16.00	18.00	19.00	24.00	20.00
Sr	289.00	207.00	154.00	124.50	110.00	139.00	195.00	144.00	144.50	164.50	308.00
Th	3.20	3.43	3.34	3.55	3.40	3.38	3.07	2.74	2.98	3.86	3.32
U	1.34	1.30	1.29	1.27	1.24	1.45	1.00	0.90	1.18	1.28	1.17
V	163.00	163.00	155.00	160.00	159.00	161.00	110.00	126.00	150.00	180.00	146.00
Y	20.10	19.80	20.10	17.70	19.90	17.80	17.30	15.00	18.50	22.20	17.10
Zn	126.00	98.00	102.00	116.00	113.00	107.00	110.00	88.00	96.00	128.00	114.00
Zr	135.00	137.00	137.00	139.00	129.00	134.00	132.00	107.00	163.00	156.00	134.00
Cs	3.23	3.67	4.46	3.76	3.57	3.66	4.35	7.91	2.89	12.10	10.15
La	21.60	21.30	21.90	18.10	22.70	17.30	22.00	15.10	18.40	23.00	20.70
Ce	47.30	46.70	48.40	39.40	48.40	38.60	46.30	32.50	40.60	49.90	45.20
Nd	24.20	23.00	24.80	20.60	24.10	20.60	22.80	16.10	21.00	26.00	23.00
Sm	4.79	5.00	5.19	4.47	5.42	4.24	4.71	3.61	4.33	5.28	4.68
Eu	0.95	1.18	1.17	0.89	1.01	0.98	1.15	0.87	1.09	0.99	0.96
Gd	3.86	4.44	4.15	3.68	4.34	3.71	3.65	2.80	3.54	4.52	3.60
Dy	3.35	3.50	3.56	3.14	3.68	3.20	3.06	2.61	3.25	3.87	2.92
Er	2.18	2.20	2.29	2.03	2.06	1.99	1.75	1.65	1.99	2.42	1.85
Yb	1.93	2.05	2.05	2.10	2.12	2.01	1.80	1.47	2.01	2.35	1.82
Lu	0.34	0.33	0.34	0.31	0.34	0.33	0.28	0.26	0.32	0.37	0.29
Total	110.50	109.70	113.85	94.72	114.17	92.96	107.50	76.97	96.53	118.70	105.02

CIA= $[Al_2O_3/ (Al_2O_3+CaO^*+Na_2O+K_2O)] \times 100$,

PIA=$100 \times [(Al_2O_3\ K_2O)/ (Al_2O_3+CaO^*+Na_2O - K_2O)]$,

CIW= $[Al_2O_3/ (Al_2O_3+CaO*+Na_2O)] \times 100$,

ICV = $[CaO+K_2O+Na_2O+Fe_2O_3\ (t) +MgO+MnO+TiO_2]/Al_2O_3$,

Eu/Eu* = $Eu_N/ (Sm_N*Gd_N)^{½}$, where N refers to normalized values. Normalizing values are from Boynton (1984).

4.4 GEOCHEMICAL CLASSIFICATION OF THE ROCKS

Several studies from various workers classify sedimentary rocks based on their chemical composition using various classification schemes (Crook, 1974; Petijohn et al., 1972; Blatt et al., 1980; Herron, 1988). Even though these classification schemes were initially proposed for sedimentary rocks, their application to metasedimentary rocks have gained attention in recent studies (Dampare, 2004; Roddaz et al., 2007; Manu et al., 2013).

The Herron diagram, of Fe_2O_3/K_2O and SiO_2/Al_2O_3 (Figure 4.6a; after Herron, 1988) of the studied shales display two main rock types: shales and Fe-shales. The Fe-shales have similar SiO_2 contents, slightly lower Al_2O_3 contents and higher Fe_2O_3 contents than the shales. The relatively moderate to high concentrations of Fe_2O_3*, MgO, TiO_2 and CaO and medium concentration of Si_2O suggest a derivative of an intermediate source.

The Na_2O-K_2O diagram after Crook, 1974, was also used to classify the geochemical characteristics of the studied shales. This diagram displays the data for the shales from parts of the Wa-Lawra belt which plot mostly in the quartz-intermediate field with a few sprawling within the quartz-rich field. Additionally, the studied shales show moderate concentrations of SiO_2 (58.68 wt %) this signifies some amount of quartz within the sediments (SiO_2 contents > 65 wt%; Crook, 1974).

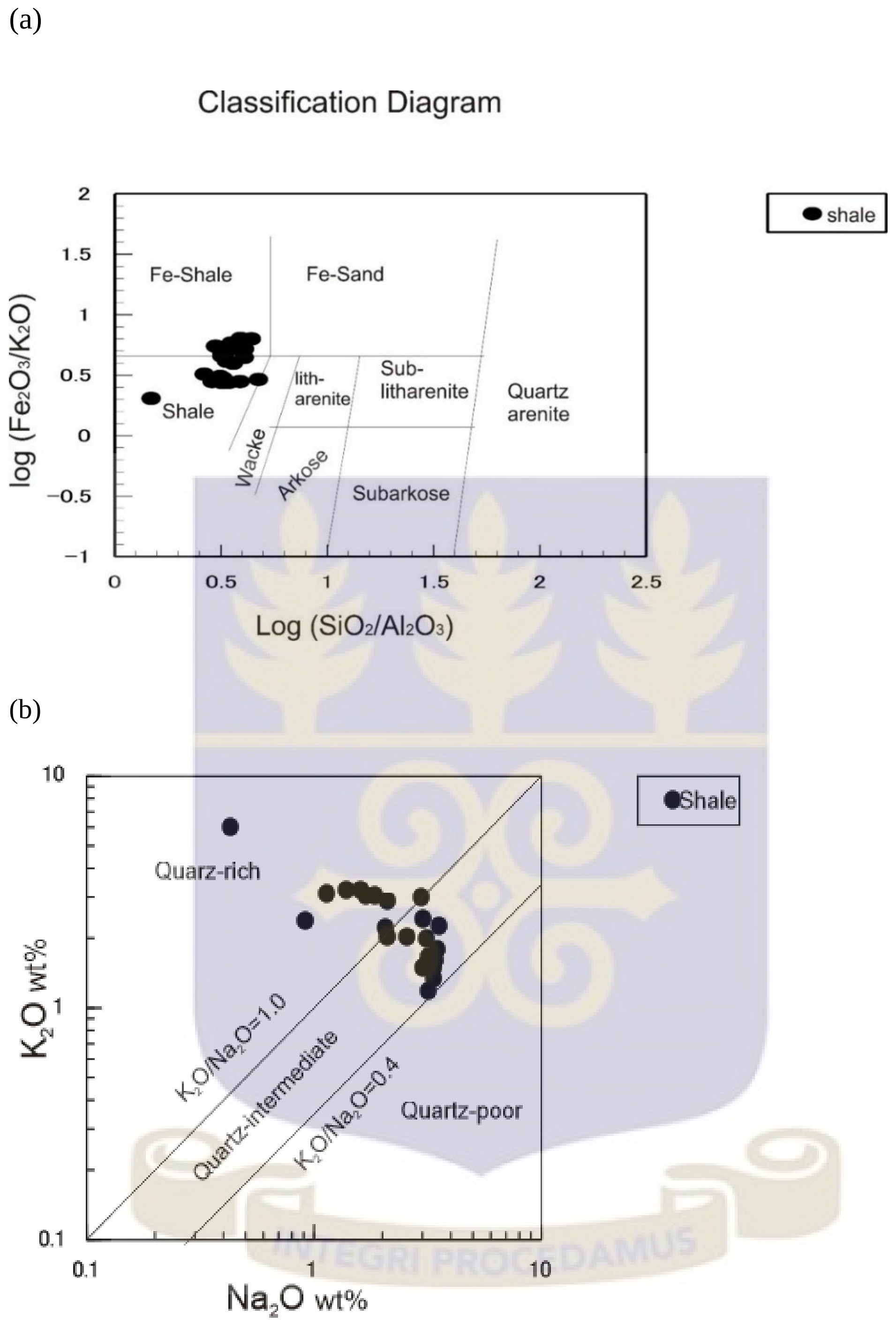

Figure 4.6 (a) Classification of the studied shales (Herron, 1988) (b) Major element chemical classification of the Wa-Lawra Paleoproterozoic Birimian metasediments (after Crook, 1974).

4.3 MINERAL CONTROLS ON MAJOR ELEMENT DISTRIBUTION

From Fig. 4.5, there is a negative correlation between SiO_2 and Al_2O_3 (correlation coefficient r=-0.88), SiO_2 and TiO_2 (r=-0.81), SiO_2 and MgO (r=-0.88), SiO_2 and Fe_2O_3 (r=-0.81), and this may suggest moderate to high concentrations of quartz content as well as moderate proportion of detrital grains (Rollinson 1993). P_2O_5, K_2O, MnO and CaO do not systematically vary with SiO_2, however, Na_2O (r=0.19) shows positive correlation with SiO_2 (Fig. 4.5 and Table 4.2). Also the negative correlation between SiO_2 and Al_2O_3 may reflect the SiO_2 present as quartz grains.

The concentration of Aluminum in sediments is a good indicator of measuring detrital flux (Nagarajan, 2007). Fe2O3 (r=0.70), MgO (r=0.68), CaO (r=0.13), K2O (r=0.46), P2O5 (r=0.52) have moderate to low correlation with Al_2O_3, this may suggest their association with Aluminous clay minerals such as illite or smectite and also indicate that weathering was an important factor in the source area, where K and Mg are preferentially fixed in clay minerals and Ca is preferentially leached (Nesbitt et al., 1980).

Camire et al. (1993) noted that if Cr, V, Sc are positively correlated to Al_2O_3 then it may suggest that they may be incorporated into clay minerals and concentrated during weathering (Table 4.3). Strong correlation between Al_2O_3 and Fe_2O_3 + MgO and total REE indicates Fe, Mg and REE are controlled by phyllosilicates (Camire et al., 1993). K_2O concentration of the shale samples show a strong positive correlation with Cs, Rb, Th, U, Ta, Nb and Ba (Table 4.3). According to McLennan et al. (1983), this may suggest the elements being influenced by clay minerals and/or micas hosting them. Deer et al. (1966) proposes that K_2O makes up about 5-10% by weight of most illite thereby element may also be controlled by illite present in the sediments.

Moreover, K_2O shows very strong correlation with total REE and this may show that REEs are mostly influenced by clay minerals and/or micas. McLennan et al. (1993) proposed that most trace elements are hosted in some heavy minerals such as zircon, and therefore as they are accumulated in high concentrations they may considerably influence in concentrations in sediments. A positive correlation existing between Zr and total REE reveals that clay minerals and mica as well as zircon are both essential in accommodating the REEs (Appendix, Fig. 4.8; Condie et al, 1992).

Table 4.2. Pearson correlation coefficient for studied shale samples from Wa-Lawra belt.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O
SiO_2	1.00								
TiO_2	-0.81	1.00							
Al_2O_3	-0.88	0.95	1.00						
Fe_2O_3	-0.88	0.82	0.82	1.00					
MnO	-0.38	0.17	0.23	0.49	1.00				
MgO	-0.90	0.79	0.84	0.91	0.50	1.00			
CaO	-0.49	0.38	0.39	0.21	0.19	0.40	1.00		
Na_2O	0.48	-0.49	-0.52	-0.51	0.01	-0.56	-0.08	1.00	
K_2O	-0.80	0.81	0.86	0.63	0.08	0.73	0.41	-0.78	1.00
P_2O_5	-0.73	0.71	0.73	0.71	0.36	0.71	0.23	-0.47	0.64

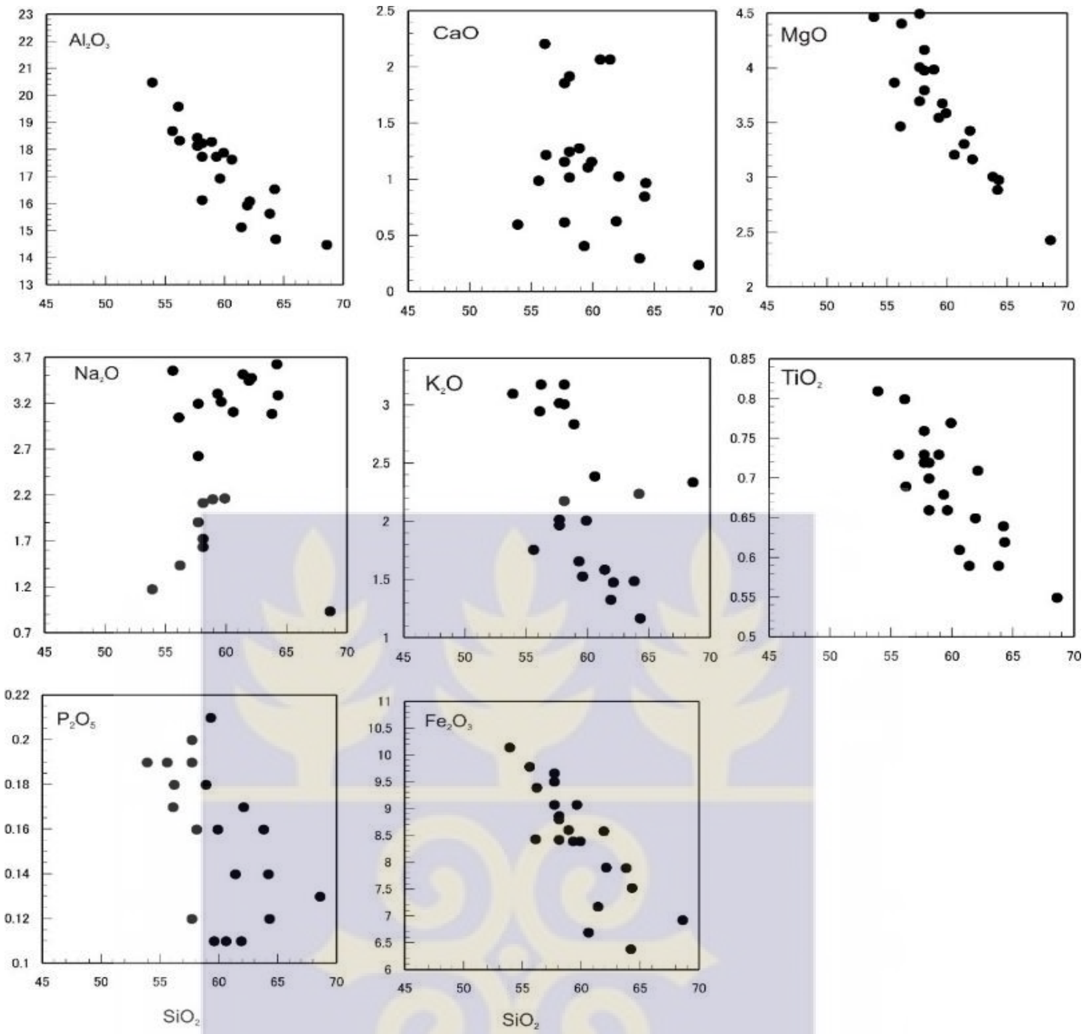

Fig. 4.7: Binary plots (Harker diagram) for the analyzed samples of the studied shales.

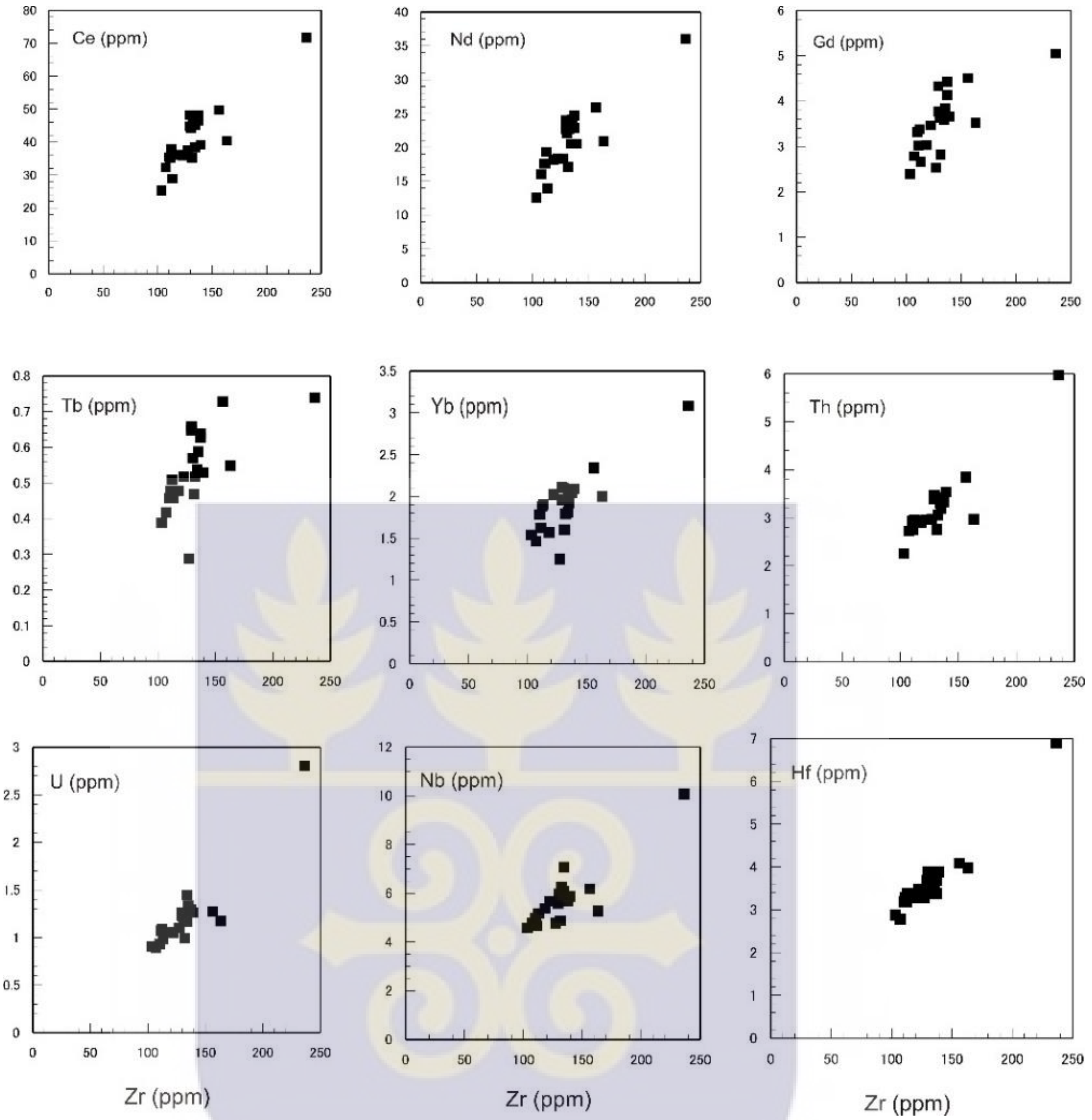

Fig. 4.8: Binary plots (Harker diagram) for the analyzed samples from the Wa-Lawra meta-sedimentary shales.

CHAPTER FIVE

DISCUSSION

5.1 SEDIMENTARY SORTING AND RECYCLING

According to McLennan et al. (1993), sorting is one of the most important sedimentary processes from which the energy and type of medium of transport, distance, and duration of transport as well as the tectonics of the source area can be deduced. Sorting is primarily determined by analyzing the textural maturity, grain sizes and shapes and mineralogical composition of sedimentary rocks. However, chemical composition of sedimentary rocks may also be used to evaluate sedimentary sorting. Sedimentary sorting may usually be inferred from the compositional or chemical maturity of concentrations of major and trace elements in sediments. This is focused on the mobility of the elements during various sedimentary processes. Sedimentary sorting usually leads to the distortion and removal of less stable elements in minerals (e.g., plagioclase) and subsequent enrichment of more stable elements in minerals (e.g., quartz) as proposed by McLennan et al. (1993); Kasanzu et al. (2008).

In terms of major elements, the studied shales have SiO_2 concentrations (average = 58.83 wt %), which are moderate. The moderate SiO_2 concentrations indicates medium maturity in the sediments. Also, the studied shales show low SiO_2/Al_2O_3 values (average = 3.40) which does not support sediment maturity and thus, poor sedimentary sorting according to (Pettijohn et al. (1972); Altrin et al. (2004).

Various minerals have different stabilities under surface conditions (Goldich, 1938). Potassium (K) feldspar is more stable under surface conditions and environments than sodium (Na) plagioclase (Goldich, 1938). As a result, the relative proportion of these minerals in sediments may also be used to deduce the maturity and degree of sorting of sedimentary and metasedimentary rocks. The relative proportion of K-feldspar and Na-plagioclase is given by the K_2O/Na_2O ratio (Bhatia, 1985). The studied shales exhibit variable K_2O/Na_2O values (0.31-2.63 average = 1.05) indicative of probable variable K-feldspar and Na-plagioclase content which may suggest that the sediments are immature and thus poorly sorted.

The bivariate plot of SiO_2 against total $Al_2O_3+K_2O+Na_2O$ proposed by Suttner and Dutta (1986) can be used to identify the maturity of the studied shales in relation to climatic conditions. On this plot (Fig. 5.1), the shales trend within the semi-arid and arid regions. This may support the interpretation of poor sedimentary sorting of the sediments. Generally, chemical weathering is more intense in the tropics relative to the temperate and arid regions as proposed by Basu, (1981) and Girty et al. (1988).

Sedimentary recycling also usually leads to high degree of sorting in clastic sediments (e.g., Veizer and Jansen, 1979; Johnsson, 1993) and this may result in the changes of their major element composition as recycled minerals, which are likely to be affected by weathering and alteration (Cox and Lowe, 1995b). As a result, more stable minerals such as illite tend to be enriched in recycled sediments more than compositionally complex clays such as smectites and chlorites (Potter et al., 1975; Potter et al., 1980; Cox and Lowe, 1995b). K_2O makes up about 5 - 10% by weight of most illite and thus, enriched in recycled sediments (Deer et al., 1966).

The shale samples exhibit low K_2O (average = 2.37) as compared to that of the average EPC (EPC, 3.22; Taylor and McLennan, 1985) which may suggest a relatively low illite content within the samples. Thus, indicating no sedimentary recycling.

Geochemical records proposed by various workers such as McLennan et al. (1993) as well as El - Gohary (2008) have shown that, the degree of sedimentary sorting may be inferred from the accumulation of heavy minerals especially zircon. Zircon is relatively stable and more resistant during sedimentary processes such as sorting, weathering and becomes relatively enriched in highly sorted sediments (McLennan, 1989). Zirconium (Zr) is a predominant constituent of zircon ($ZrSiO_2$), thus, the geochemical characteristics of zirconium can be used to evaluate the degree of sorting in clastic sediments. The shales show low concentrations of Zr (range = 103-163 ppm, average = 132 ppm) indicating moderate enrichment in zirconium which suggest poor sedimentary sorting (McLennan, 1989).

Th/U ratio observed in most upper crustal rocks is characteristically within the range of 3.5-4.0 (McLennan et al., 1993). Th/U values in sedimentary rocks are higher than 4.0 and may indicate intense weathering in the source area or sediment recycling (i.e., derivation from older sedimentary rocks). The studied shales from Table 4 however indicate average Th/U values of 2.13-3.1 with an average of 2.7. The Th/U value are relatively lower than 4.0 therefore this may suggest intermediate weathering in the source area thus, little sediment recycling.

The Th/U versus Th plot for the studied shales, shows a typical distribution comparable to the average values of fine-grained sedimentary rocks (Fig.5.2; Taylor and McLennan, 1985). From the diagram the studied shales follow the weathering trend from a depleted mantle crust (McLennan et al., 1993). This results supports the interpretation that the sediments for the studied shales have little recycled sediment and may have undergone intermediate degree of weathering.

The sedimentary sorting and weathering can also be examined by a plot of Th/Sc against Zr/Sc after McLennan et al. (1993). First order sediments exhibit simple positive correlation between Th/Sc and Zr/Sc, whereas recycled sediments exhibit significant increase in Zr/Sc with a far less increase in Th/Sc. In Fig. 5.3, the Th/Sc and Zr/Sc diagram of the studied follow a general trend with directions consistent to rocks derived from an igneous source. It can be, inferred from Fig.5.2 that the bulk of the studied shale rocks were directly derived from igneous rocks that had undergone some degree of weathering at source region (McLennan et al., 1993).

Also the Al-Ti-Zr ternary diagram monitors the effects of sorting processes (Garcia et al., 1994). On this diagram are mature sediments consisting of both sandstones and shales this shows a wide range of TIO_2/Zr variations whereas immature sediments of sandstone and shales show a more limited range of TiO_2/Zr variations. On the Al-Ti-Zr diagram (Fig, 5.4) the studied shales are confined in the center with a limited range of TiO_2/Zr variations, this suggests poor sorting and rapid deposition of the sediment. This may be possible since the study area has been proposed to be a subduction zone (E.g. Sakyi et al., 2014)

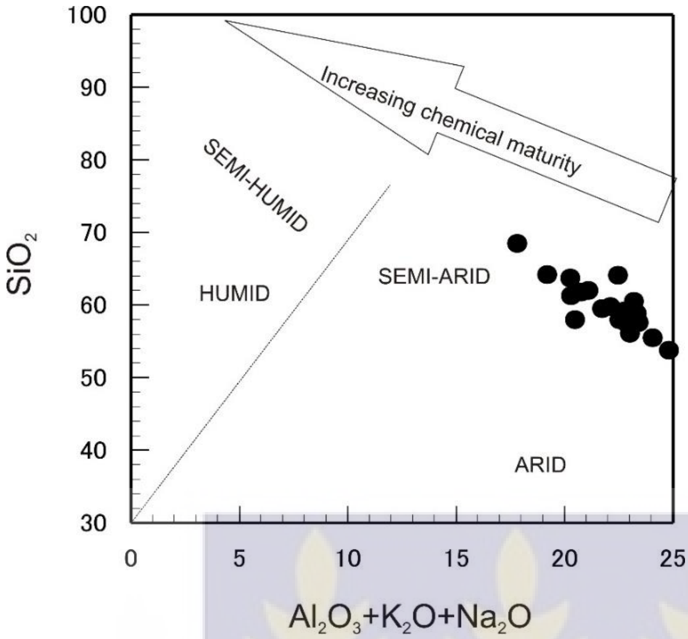

Figure 5.1: bivariate plot of SiO2 versus Al2O3+ K2O + Na2O of the studied shales in parts of the Wa-Lawra belt. (After Suttner and Dutta, 1986)

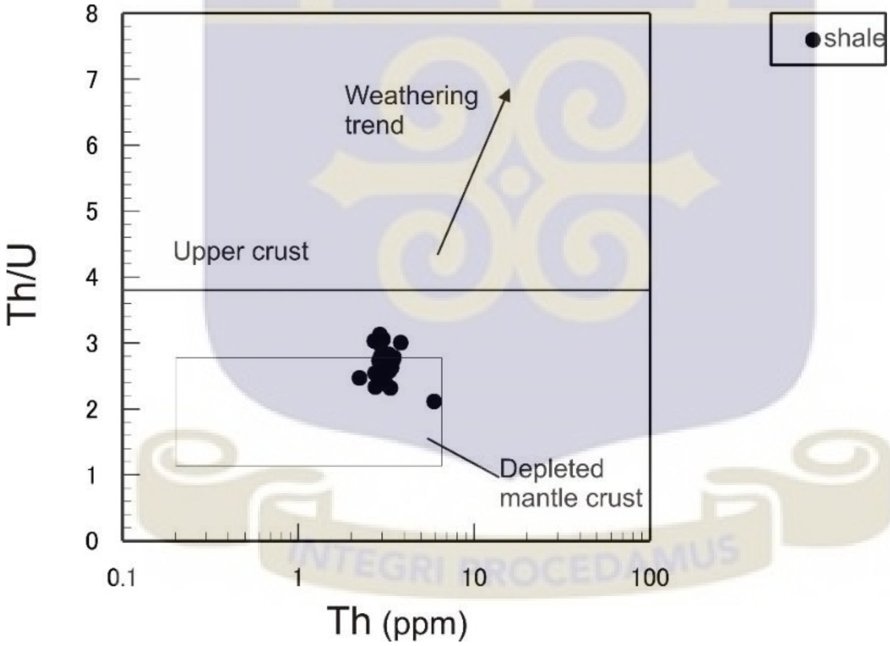

Figure 5.2: Th/U versus Th of the studied shales form parts of the the Wa-Lawra Birimian greenstone belt (after McLennan et al., 1993).

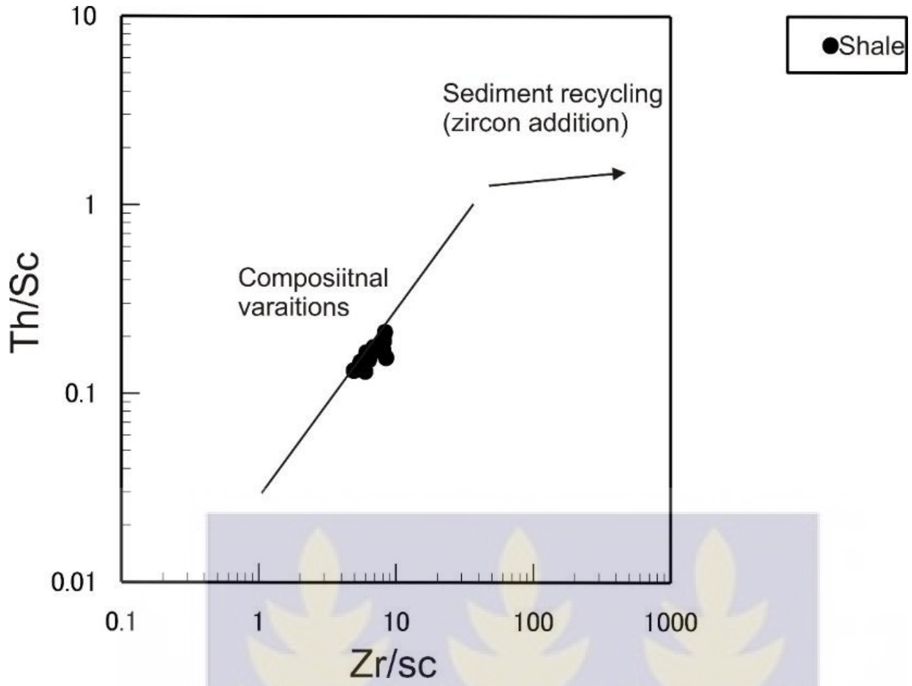

Figure 5.3 Th/Sc versus Zr/Sc for the Paleoproterozoic Birimian meta-sedimentary rocks of Wa-Lawra belt. (McLennan et al., 1993).

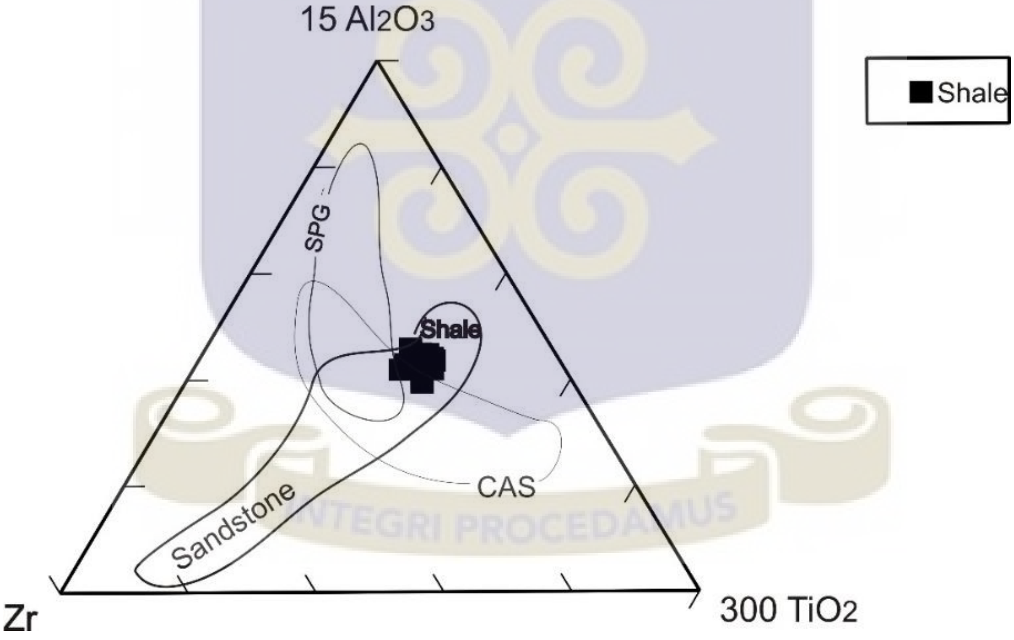

Figure.5.4: The Al-Ti-Zr ternary diagram shows the effects of sorting processes (Garcia et al., 1994).

5.2 PROVENANCE

5.2.1 Source Rock Composition

Geochemical studies have shown that the chemical composition of sedimentary and metasedimentary rocks generally reflect the provenance of their detrital source rocks (Roser and Korsch, 1986; McLennan et al., 1993). These studies are based on the direct correlation between the chemical composition of sedimentary and metasedimentary rocks expressed as abundances of certain major or trace elements or ratios of elemental abundances and their source rock composition (McLennan et al., 1993)

According McLennan et al. (1993) and Cullers, (1994a), the REE, HFSE as well as Th/Sc, Cr/Th and the Eu anomaly always prove to be beneficial tools for the determining the composition of the source area sediments. Considering the average compositions, SiO_2 concentrations (average 58.68 wt %) is moderate, this may suggest the rocks may be of an intermediate source, due to moderate concentration of quartz content or silica content.

According to (Hayashi et al., 1997; Nagarajan, 2007) the ratio of TiO_2 and Al_2O_3 can be used as an inference to source rock composition, TiO_2 is enriched in mafic rocks than in felsic rocks and Al_2O_3 incorporated in feldspars is relatively enriched in felsic or granitic sources than in mafic rocks. Al_2O_3/TiO_2 increases from a range of 3 to 8 for mafic rocks, 8 to 21 for intermediate rocks and a range of 21 to 70 for felsic igneous rocks (Hayashi et al., 1997). The studied shale samples record moderate values of Al_2O_3/TiO_2 (average=25.27), this may suggest a felsic rock composition at source.

The distribution of the K and Rb plot of the studied shales have fairly high K_2O and Rb concentrations and uniform K/Rb ratio of 232 which lies very close to a magmatic trend or to the main trend with a ratio of 230 according to Shaw (1986).

This feature emphasizes the chemically coherent nature of the sediment and derivation mainly from acidic to intermediate rocks (Figure 5.5).

According to Floyd and Leveridge, 1987, the coherence of K–Rb may be due to their redistribution by hydrothermal fluids during regional metamorphism at regional scale and metasomatism. However due to the high TiO_2 or moderate Al_2O_3/TiO_2 as mentioned earlier, the consistent trend in K/Rb ratio may be due to k-metasomatism during diagenesis. Hence we may suggest an intermediate with mafic contributions from source. Another tool used for the discrimination of different arc compositions and its source is the La/Th versus Hf plot in figure 5.6. According to Floyd and Leveridge, 1987, Arcs with dominant felsic compositions are characterized by low and uniform ratios of La/Th which is less than 5 and about (3-5ppm) contents of Hf. The studied shales sampled from specified areas of the Wa Lawra belt have La/Th ratios with an average of 5.93, which is above 5 and Hf content of 3.64ppm strictly within the range of (3-5ppm). This result may suggest contribution from mafic igneous rocks with an intermediate source rock input.

The previous mentioned discrimination diagrams are also supported by another tool used to constrain the source rock composition of the studied shales, this is the Silica-Alkali-Mafic (SAM) diagram proposed by (Roser and Korsch, 1988; Figure 5.7). The studied shales plot within the andesites and basalts, this may suggest that the rocks may have been derived from an intermediate source rock with some mafic contributions.

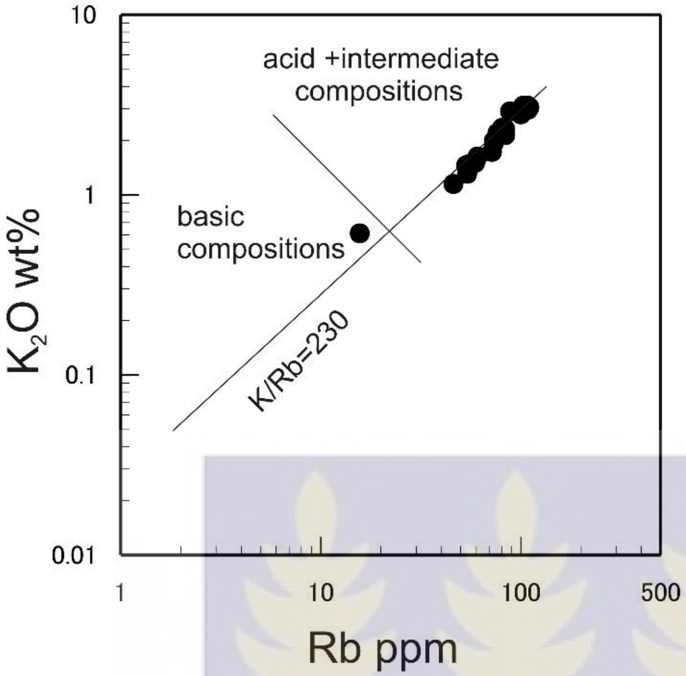

Figure 5.5: distribution of K and Rb plot of the studied shale samples relative to a K2O-Rb ratio of 230 (main trend of Shaw, 1968).

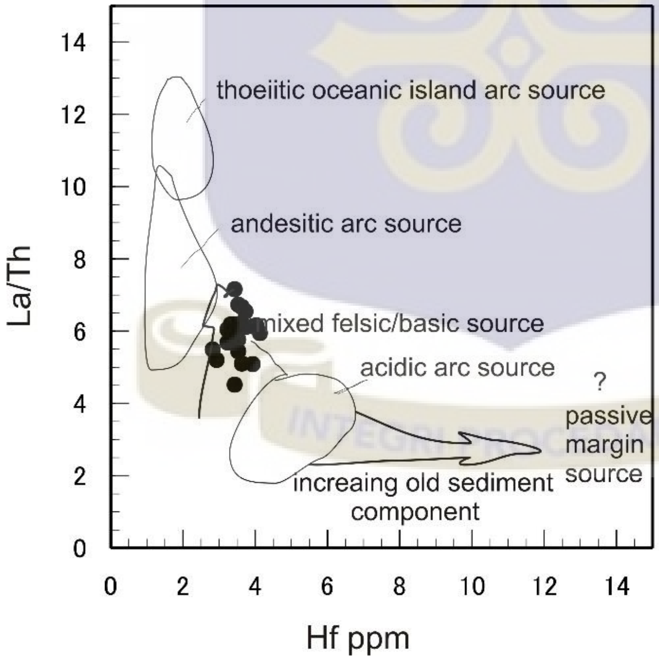

Figure.5.6: Plot of La/Th against Hf for the studied shale samples (composition fields after Floyd and Leveridge, 1987).

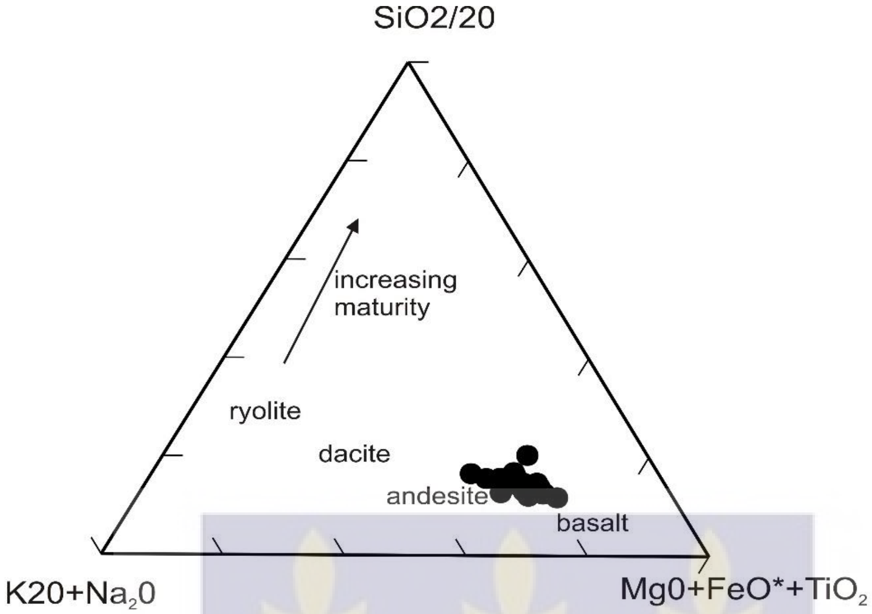

Figure 5.7: Plot of the studied sedimentary rock samples showing the primary igneous compositional trend between basalt and rhyolite (Roser and Korsch, 1988).

Another discrimination diagram after Roser and Korsch (1988) was used to further constrain the source rock composition of the studied shales, (Fig.5.8). This diagram discriminates between four sedimentary provenances. On the diagram the studied shales plot majorly within the intermediate igneous provenance with a few sprawling towards a felsic igneous provenance and few samples falling within the mafic igneous provenance (Fig. 5.8); this shows resemblance to an Island Arc-derived sediments (Roser and Korsch, 1988).

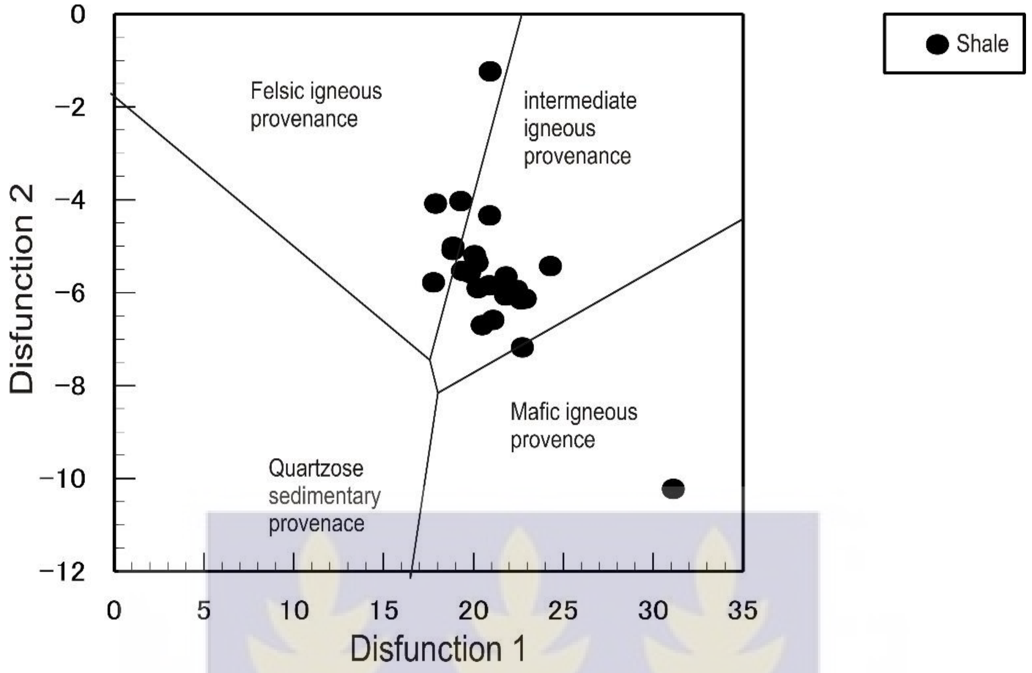

Figure 5.8: Discriminant function diagram for Paleoproterozoic Birimian shales from Wa-Lawra Belt North Wester Ghana (after Roser and Korsch, 1988).

The transition metals (e.g., Cr, Co, Ni, V and Sc) behave similarly during magmatic processes (Feng and Kerrich, 1990), and are usually enriched in mafic and ultramafic igneous rocks (Bock et al., 1998). The transition elements are more concentrated in mafic rocks due to the much smaller size of their ions allowing them to enter early crystallizing minerals (Taylor and McLennan, 1985). As a result, the relative abundance of transition metals in sediments may provide important clues about their source rock compositions. In general, the studied shales show fairly high concentrations of Cr, Ni, V and Sc with slight enrichment of Co compared to the post - Archean Australian average shale (PAAS) (Figure 4.1). This suggests some contributions of mafic rocks were exposed in the source area. In addition, the studied shales have Cr/Ni (average = 2.04), values compared to that of PAAS (2; Taylor and McLennan, 1985) suggesting probable intermediate or felsic source rocks for the sediments with minor mafic contributions (Wrafter and Graham, 1989).

McCann (1991) suggested that V is highly concentrated in mafic rocks. From data of studied shales Vanadium concentrations of 110 – 402ppm (average=161.96ppm) are higher relative to the common levels of V usually recorded in sediments (20ppm). Thus, the studied shales may be suggested to have mafic contribution into its depositional system.

Also, on a ternary plot of V-Ni-Th*10 in (figure 5.9; after Bracciali et al., 2007), the studied shales mainly plot within the mafic rocks with a few clustered close to it, this thereby supports the interpretation that the sediments were derived mainly from a mafic source. Figure 5.10 below shows a ternary diagram of Th-Hf-Co. Numerous worker such as Taylor and McLennan, (1985); Bhatia and Crook, (1986); Jahn and Condie, (1995), have shown that this diagram may be crucial in constraining the source rock composition of clastic sediments. The studied shales are mainly clustered in the region of the oceanic crust; this may suggest an intermediate to mafic source composition as this is known to be a characteristic of an oceanic crust setting.

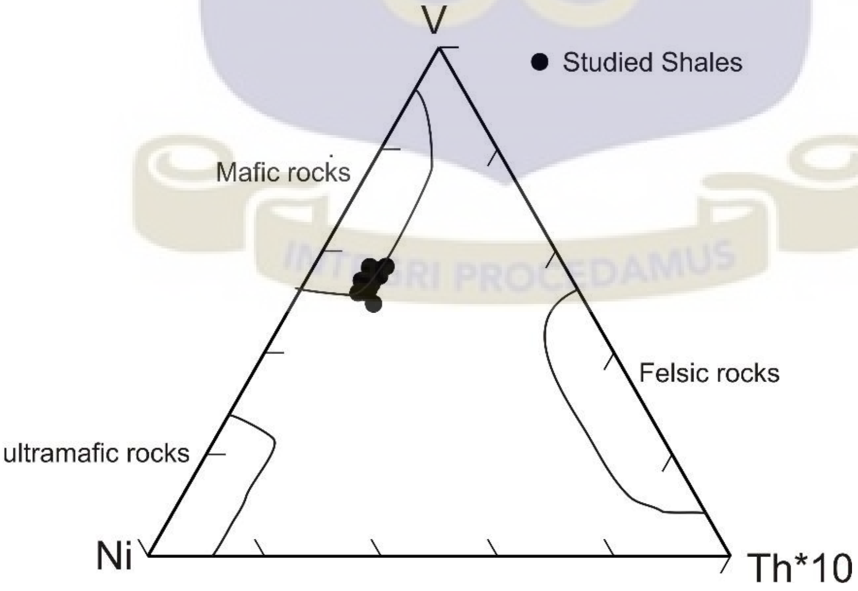

Figure 5.9: A ternary plot of V - Ni - Th*10 for studied shales in parts of the Wa-Lawra belt, Northwestern Ghana (fields are after Bracciali et al., 2007)

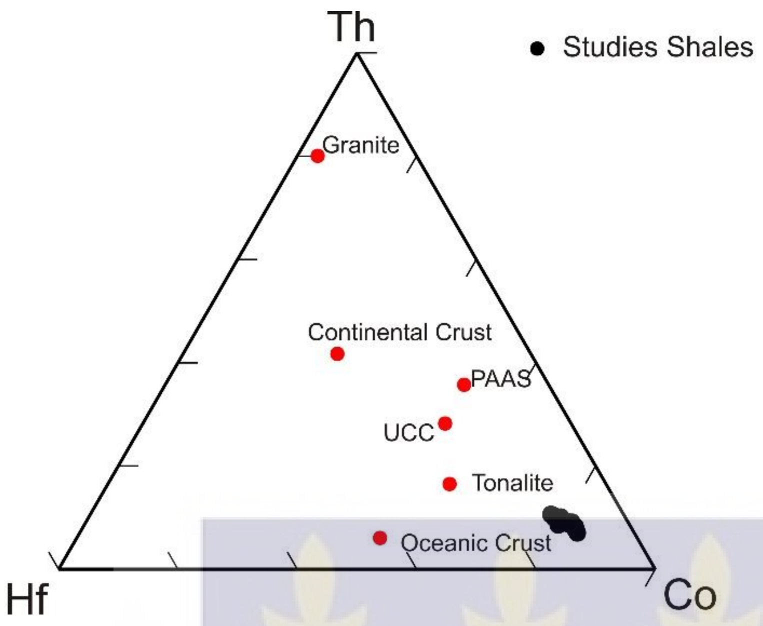

Figure 5.10 (a) Th - Hf - Co ternary diagram, for the studied Shales in parts of the Wa Lawra belt, Northwestern Ghana (compositional fields are after Roddaz et al., 2007). Post- Archean Australian average shale (PAAS) and Upper Continental Crust (UCC) are plotted for comparison (values are from Condie, 1993).

According to Taylor and McLennan, (1985), high field strength elements (HFSE) such as Zr, Hf, Th, and U are included in melts during crystallization and anataxis. HFSE along with REEs may reflect provenance compositions as a result of their immobility. They are mostly enriched in felsic rocks than in mafic rocks as proposed by Feng and Kerrich (1990). The studied shales show relatively low HFSE as compared to PAAS (Table 4.1 and Figure 4.4), suggesting some contribution from mafic source (Taylor and McLennan, 1985).

According to Taylor and McLennan, (1985); McLennan et al. (1993); Cullers, (2000), Cr/Th and Th/Sc ratios are very useful in constraining the compositions of sediments at source. From Fig. 5.11, the studied shales cluster within the region of the Basalts. This indicates the studied shales may be from a mafic rock source which is supported by interpretations from earlier diagrams.

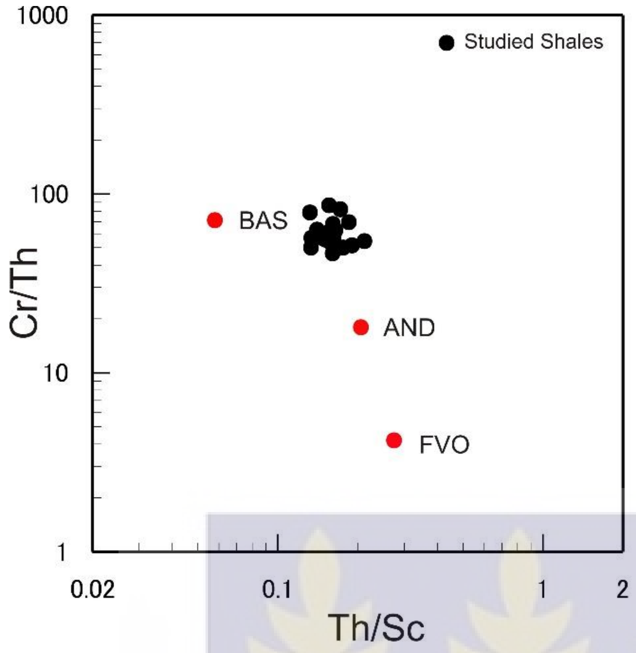

Figure 5.11: A plot of Cr/Th versus Th/Sc for the distribution of studied Shales from parts of Wa-Lawra belt, Northwester Ghana. (FVO: felsic volcanics; AND: andesites; BAS: basalts are inferred from Condie, 1993).

According to Wronkiewicz and Condie (1990), the distribution of immobile elements such as La and Th in metasedimentary rocks can be used to infer their relative contributions from mafic and felsic source rocks at different source regions. The ratios of Eu/Eu*, La/Sc, Th/Sc, and Th/Cr also display significant characteristics in acidic and basic rocks and may allow constraints on the average provenance composition (Cullers, 2000). The studied shales have range of Th/Sc and Th/Cr ratios that suggest their derivation from basic sources as well as the La/Sc ratios of the studied shales. However, whereas the range of Eu/Eu* values do not point to any particular source lithology (Table 5.1).

Table 5.1. Comparison of range of provenance elemental ratios of the studied shales

Elemental ratios	Birimian sediments (studied shales)	Range of fine-grained sediments from silicic sources	Range of fine-grained sediments from basic sources
Eu/Eu*	0.62 – 0.98	0.32 – 0.83	0.7 – 1.02
La/Sc	0.60 – 1.19	0.7 – 27.7	0.4 – 1.1
Th/Sc	0.13 – 0.21	0.64 – 18.1	0.05 – 0.4
Th/Cr	0. 011 – 0.021	0.067 – 4.000	0.002 – 0.045

The range of values for fine-grained sediments from felsic and mafic rock sources are from Cullers (2000).

The enrichment of incompatible elements relative to compatible elements as well as Eu anomaly of elemental compositions provide crucial information about the source rock composition of the sediments (Taylor and McLennan, 1985). The light rare-earth elements (LREE) known to be incompatible elements preferentially go into melts phases during partial melting and thus are relatively enriched in upper continental Crust and/or felsic rocks.

The anomalous behavior of Eu is generally inherited from sediment sources which makes it an important factor to distinguish mantle sources from intracrustal sources (McLennan et al., 1993; McLennan and Taylor 1991). Sedimentary and metasedimentary rocks with negative Eu anomaly are typical of sediments derived from felsic rocks (Cullers, 1994; Gao and Wedepohl, 1995). However, the studied shales have Eu anomaly (0.8) which is slightly higher than that of PAAS (0.66; Taylor and McLennan, 1985). This indicates that shale samples may be derived from a mantle source with substantial mafic contributions.

McLennan et al. (1993, 1995) proposed five diverse kinds provenance depending on their geochemical characteristics. An Old Upper Continental Crust (OUC), the Recycled Sedimentary Rocks (RSR), Young Undifferentiated Arc (YDA) and Exotic components as summarized in Table 5.2. The studied shales have fairly uniform composition, of Th/U (average=2.70), a negative Eu Anomaly (Eu/Eu*, 0.62-0.98) and Th/Sc ratios (mostly less than 1.0, 0.16). Also the SiO_2/Al_2O_3, Th/Sc and La/Sc (less than 4.0) Also the studied shales have lower SiO_2/Al_2O_3, Th/Sc and La/Sc values as compared to EPC. (4.49, 0.72, 2.16 respectively after Taylor and McLennan, 1985). These ratios may suggest to contribute to the Young Arc Derived materials. The young differentiated arc provenance components constitute the young (mantle derived) volcanic or plutonic igneous rocks from Island and continental arcs that have undergone significant intracrustal differentiation.

Table5.2 Summary of the various provenance types (McLennan et al. 1993, 1995).

Provenance Type	Eu/Eu*	Th/Sc	Th/U	Other geochemical features
Old Upper Continental Crust	0.6-1.1	~1.0	>3.8	Evolved major element compositions (e.g., high Si/Al, CIA); high LILE abundances; uniform compositions.
Recycled Sedimentary Rocks	0.6-1.1	>1.0	>3.8	Evidence of heavy mineral concentration from trace elements (e.g., Zr, Hf for zircon)
Young Differentiated Arc	0.5-0.9	~1.0 to<0.01	<3.0	Evolved major element compositions (e.g., high Si/Al, CIA); high LILE abundances; variable compositions.
Young Undifferentiated Arc	~1.0	~1.0 to<0.01	<3.0	Evolved major element compositions (e.g., low Si/Al, CIA); low LILE abundances; variable compositions.

To identify several likely source components of the studied shales, an attempt was made to quantitatively model the relative contributions from Upper Continental Crust (UCC), average granites, and tonalite - trondhjenite - granodiorite (TTG) as well as basalts. The average chemical compositions of Proterozoic Upper Continental Crust, Tonalite-Trondhjenite-Granodiorite (TTG) and arc related basalts from Condie (1993) were used as potential sources for the studied shales. The trace element data of studied shales were modeled after Fedo et al., (1996). The general idea behind modelling is to attempt to preserve mass balance amongst the relatively immobile REEs and Th/Sc ratios which is sensitive index of bulk compositions (Taylor and McLennan, 1985).

The model REE values were derived by the following mass balance equation proposed by Albarède (2000):

WRmix = $\alpha C1 + \beta C2 + \gamma C3$, where WRmix represents the calculated whole rock compositions, α, β and γ represent the proportion of basalt, TTG and UCC, obtained from modeling the source rocks, C1, C2 and C3 represent the rare earth elements in basalt, TTG and UCC. With reference to the source compositions listed in Table 5.3, the average Birimian shales in parts of the Wa- Lawra Belt are composed of a mixture of 60% basalt, 20% TTG and 20% UCC. The modeled chondrite-normalized REE for the studied shale samples are similar in pattern for that of the average shales (Figure 5.12). This supports the results obtained for the mixing calculations for the source rocks of the studied Birimian shales. From this model the possible mafic source of the study may be derived from the mafic volcanic rocks and their associated granitoids in the Birimian greenstone belts (E.g. Amponsah et al., 2015) and also Leube et al. (1990).

Table 5.3 Results from mixing calculation modeled for the studied shales from Wa-Lawra belt.

Elements	Average Birimian Shales		mixing end members						mixing results
			Basalt		TTG		upper crust		Model shale 60:20:20
	ppm	N	ppm	N	ppm	N	ppm	N	
La	19.25	62.10	11.00	35.48	26.00	83.87	30.90	99.68	58.00
Ce	41.47	51.32	27.00	33.42	45.00	55.69	65.30	80.82	47.35
Nd	20.92	34.87	15.00	25.00	20.00	33.33	29.80	49.67	31.60
Sm	4.20	21.54	3.80	19.49	4.50	23.08	5.59	28.67	22.04
Eu	1.00	13.61	1.30	17.69	1.30	17.69	1.19	16.19	17.39
Gd	3.55	13.71	4.22	16.29	4.09	15.79	5.24	20.23	16.98
Tb	0.54	11.39	0.72	15.19	0.63	13.29	0.82	17.30	15.23
Yb	1.92	9.19	2.70	12.92	1.50	7.18	2.32	11.10	11.41
Lu	0.31	9.63	0.45	13.98	0.23	7.14	0.38	11.80	12.17
La/Sm		2.88		1.82		3.63		3.48	2.63
Eu/Eu*		0.79		0.99		0.93		0.67	0.90
Gd/Yb		1.49		1.26		2.20		1.82	1.49
Th/Sc		0.16		0.06		0.83		0.72	0.19

N denotes chondrite - normalized value. Values for Upper Continental Crust, Granite and tonalite - trondhjenite - granodiorite (TTG) are from Condie (1993).

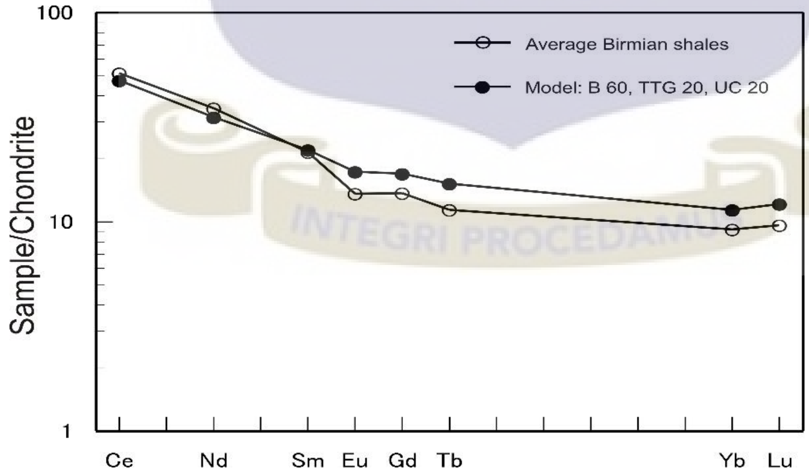

Figure5.12: Results from mixing calculations for the REEs of the Paleoproterozoic Birimian shales from Wa-Lawra belt, Northwestern Ghana (Parameters are in Table 5.3).

5.2.2 Source - Area Weathering and Diagenesis

In provenance studies, major element composition of sedimentary and metasedimentary rocks shows mineralogy prone to chemical weathering (Harris and Adams, 1966; Middleburg et al., 1988). When sediments weather chemically various signatures are imparted into these sediments and this may be transferred into their chemical data (Wronkiewicz and Condie, 1987) thus, useful for determining the source- area weathering conditions thereby verifying some geological processes involved. At source region various important effects may occur on the composition of siliciclastic rocks. Large cations such as (e.g. Rb, Ba), remain stationary within the weathered residue, as preferred to smaller cations such as (Na, Ca, Sr), which are mostly leached (Nesbitt et al., 1980).

Also whiles there's generally depletion of alkalis (e.g., Na) and alkaline earth elements (e.g., Ca), there's preferential enrichment of SiO_2 and Al_2O_3 (Cox et al., 1995). However, the studied shales show moderate to low concentration of Na_2O and CaO and moderate to high SiO_2 and Al_2O_3. This is indicative of depletion of alkalis and alkaline earth elements which may suggest high chemical weathering in the studied shales which might have occurred at source.

Intensity of chemical weathering of sedimentary and metasedimentary rocks can be quantified using indices proposed by various workers (Fedo et al., 1995; Nesbitt and young, 1982; Harnois, 1998 and Cox et al., 1995). The chemical index of alteration (CIA) has been established as a guide to assess the extent of conversion of feldspars (which dominate the upper crust) to clays.

CIA = [Al2O3/ (Al2O3 + CaO* + Na2O + K2O)] × 100; in molecular proportions. Where: CaO* refers to CaO in silicates only.

Ca in carbonates could not be corrected to obtain CaO* due to the lack of CO_2 data. But the LOI of the average sample is less than 10% suggesting that carbonates were uncommon in the analyzed sediments (Table 4.1). Therefore, CaO concentrations were used as CaO* for the calculation (Bock et al., 1998).

CIA values of less than 70% indicate weak weathering and values of 70-80% indicate moderate weathering whereas values 80-100 indicate intense weathering in the source area. Also, CIA values for unweathered terrestrial basalts are in the range of 40 to 50 whereas for granites the range is 50 to 55 (Fedo et al., 1996).

The studied shales have CIA values (average = 66.77 %), this is slightly lower than that of PAAS (70; Taylor and McLennan, 1985). This suggests that the studied shales may have experienced weak weathering.

During diagenesis, K - metasomatism (i.e., illitisation of smectite and/or plagioclase albitization) leads to the addition of post - depositional potassium (K) to older clastic rocks (Fedo et al., 1995). This limits the use of the chemical index of alteration parameter which does not correct for this effect. The effect of K-metasomatism can be evaluated using the Al_2O_3- CaO* + Na_2O – K_2O (A-CN-K) compositional space.

The data for the shales are plotted in an Al_2O_3- CaO* + Na_2O – K_2O (A-CN-K) compositional space (molecular proportions) in Fig. 5.13. Also shown on this diagram are the positions of idealized minerals, average Archean upper crust, and a line showing the limit of weathering, to the right of which indicates K enrichment. The solid and dashed lines with arrows emanating from the Plagioclase-K-feldspar join show the weathering trends for tonalite and granite, respectively (Nesbitt and Young, 1984, 1989). The vertical dimension (percent Al_2O_3) in A-CN-K compositional space corresponds with values of CIA.

The shales plot at an angle parallel to the A-CN join (Fig. 5.13) consistent with K-addition to the original composition. The corrected CIA values ranges from 70 to 85 (Fig. 5.13), suggesting intermediate intensity of weathering at the source area. The corrected weathering trend follows the average tonalite trend (Fig. 5.13) suggesting that the source rocks of the shales were dominantly tonalitic in composition.

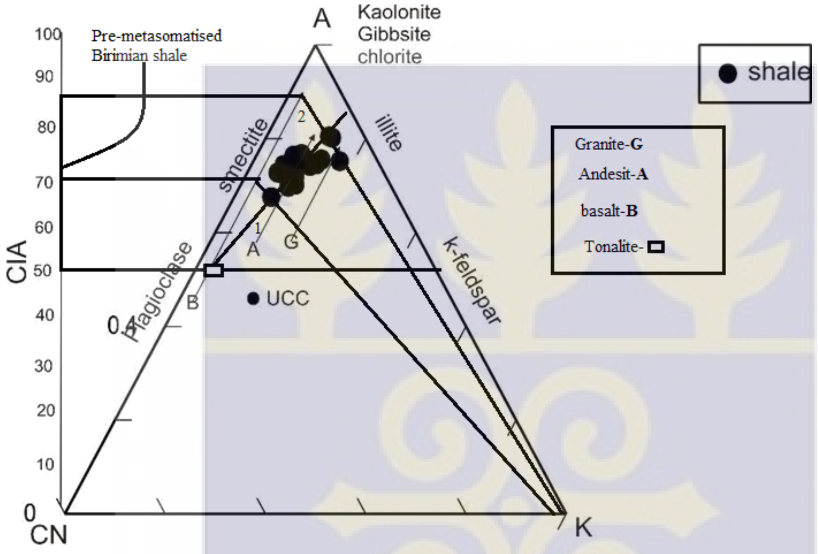

Fig.5.13 Ternary A - CN - K (Al_2O_3 - $CaO+Na_2O$ - K_2O) studied shales in parts of Wa-Lawra Belt (after Nesbitt and Young, 1984; 1989). Average values of G: granite; a: andesite; B: basalt; values taken from Condie (1993). Upper Continental Crust (UCC) plotted for comparison (values taken from Taylor and McLennan, 1985).

5.2.3 Tectonic Environment of Source Area

Geochemistry of clastic rocks have shown to provide vital information about the tectonic setting of source rocks (Bhatia and Crook, 1986; McLennan et al., 1993). It is based on the assumption that different tectonic settings impart characteristic geochemical signatures on rocks which are generally retained in the sediments during various sedimentary processes (Bhatia, 1983; Dickinson et al., 1983; McLennan et al., 1993;).

Major element composition of clastic sediments is very useful in the determination of tectonic setting of their source areas. According to Crook (1974) sedimentary or metasedimentary rocks which are quartz - rich (> 65% quartz) are associated with passive continental margins, quartz - poor greywackes (< 15% quartz) are associated with magmatic island arcs and greywackes with intermediate quartz (15 - 65% quartz) are indicative of an active continental margin. The SiO_2 concentration with average 58.68 wt% of the shales is in the range the intermediate quartz sediments which is between 15-65% indicates that the sediments were established from an active continental margin.

Studies by Bhatia (1985) showed that ratios of SiO_2/Al_2O_3 and K_2O/Na_2O increase with sandstone and mudstone maturity, which is somewhat due to the change in the dominant source rock. This assertion is supported by studies of Roser and Korsch (1986) which showed that the SiO_2 content and K_2O/Na_2O ratios of sandstone and mudstone suites can be used to infer their provenance and tectonic setting. Roser and Korsch (1986) proposed three tectonic settings based on ancient sandstone - mudstone pairs. The three tectonic settings are passive continental margin (PM), active continental margin (ACM) and oceanic island - arc (ARC).

from the K_2O/Na_2O versus SiO2 plot (Figure 5.14), the shales under study plot mostly within the oceanic Island Arc and spread towards the Active Continental Margin. This supports the interpretation of moderate maturity of the sediments which suggest that the sediments were probably derived from an Arc environment confirmed from literature. Maynard et al. (1982) also used a similar tectonic settings discriminant plot of SiO_2/Al_2O_3 versus K_2O/ Na_2O to differentiate the provenance of modern sediments. As seen in (Figure 5.15), the shales mainly plot in the A2, evolved arc setting; felsic - plutonic detritus.

Immobile trace elements in clastic sediments give very important evidences on the tectonic setting of sedimentary and metasedimentary rocks as these elements are transferred quantitatively into clastic sediments during weathering and transportation, therefore reflecting the signature of their parent material (Armstrong - Altrin et al., 2004).

According to McLennan and Taylor (1991), Th/Sc values ≥1.0 can be found in most tectonic settings where stable crust or recycled sediments are exposed (where the samples are above line = 1). From the table of analyzed data for trace elements, Th/Sc ratio ranging from 0.13-0.21 with an average of 0.16 indicates that the samples are not within the range of recycled sediments (McLennan and Taylor, 1991). This thereby confirms samples being derived from an Oceanic Island Arc setting. To further verify the tectonic setting of the shale sample Th - Co - Zr/10 and La - Th - Sc ternary diagrams were employed (Bhatia and Crook, 1986) to differentiate between Oceanic Island Arc (OIA), Continental Island Arc (CIA), Active Continental Margin (ACM) and Passive Margin (PM) setting.

On the Th - Co - Zr/10 plot (Fig.5.16b), the studied shales plot within the Oceanic Island Arc setting. This plot verifies all deduced variables discussed earlier. In general, the mineralogical and geochemical characteristics of the shales indicate that the Paleoproterozoic Birimian metasediments in parts of the Wa-Lawra Belt, are derived from an Island Arc setting. The La - Th – Sc plot also places the shale sediments mostly within the Oceanic Island Arc setting and a few sprawling within the continental arc margin. (Figure 5.16a and b)

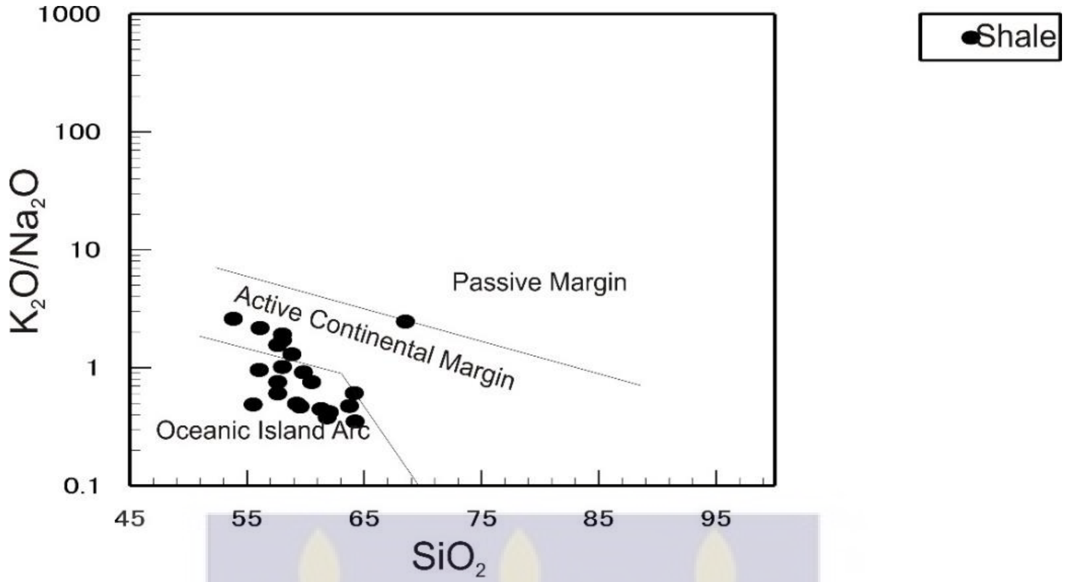

Fig.5.14: K_2O/Na_2O versus SiO_2 diagram for the Paleoproterozoic Birimian metasediments, Wa-Lawra Belt (fields are after Roser and Korsch, 1986).

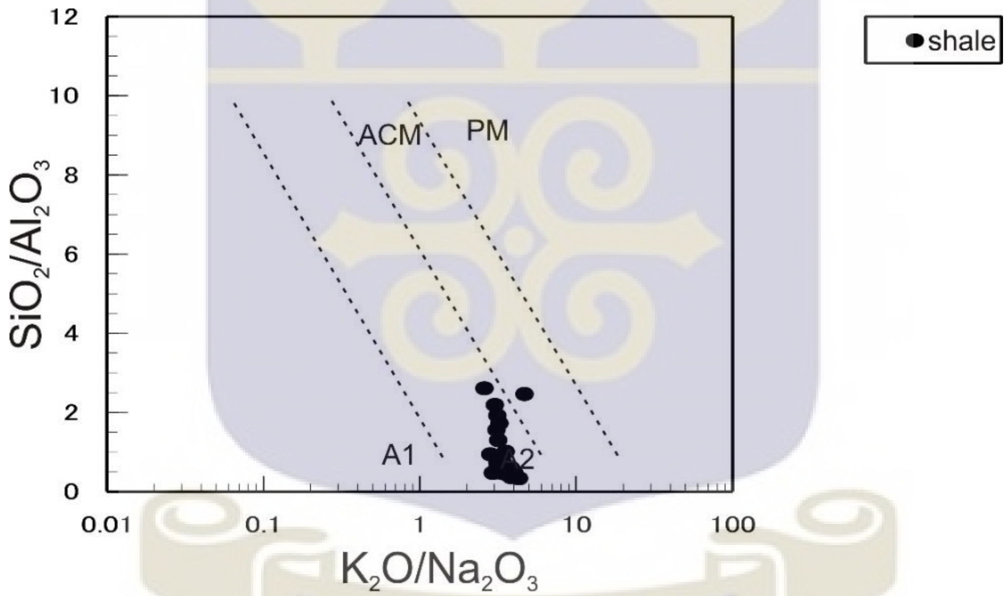

Fig.5.15: Plot of SiO_2/Al_2O_3 versus K_2O/Na_2O for the studied shales Wa-Lawra Belt. Boundary lines for different tectonic settings from Roser and Korsch (1986). ACM, active continental margin; PM, passive margin; A1, arc setting, basaltic and andesitic detritus; A2, evolved arc setting, felsitic - plutonic detritus.

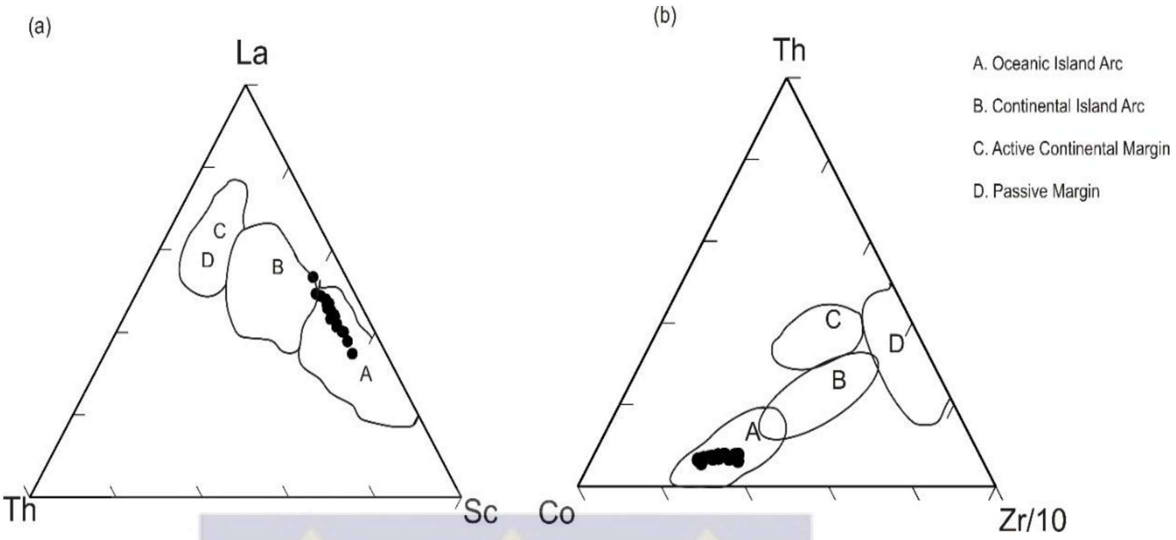

Figure 5.16: (a). La-Th-Sc discriminant diagram for shales. (b). Th-Sc-Zr/10 discriminant diagram for shales. (After Bhatia and Crook, 1986). The fields include: A, oceanic Island arc; B, continental Island arc; C, active Continental margin; D, Passive Margin.

5.3 CRUSTAL EVOLUTION

Recent studies have shown that variations in the chemical composition, specifically trace element abundance occur between the Archean and post - Archean Upper Continental Crust (Condie, 1993; Plank and Langmuir, 1996; Asiedu et al., 2004). From research established by Taylor and McLennan (1985), these variations were as a result of sedimentary processes. Plank and Langmuir (1996) suggested that the dilution of marine terrigenous sediments with low trace elements bearing siliceous and carbonate sediments probably lead to the variation in chemical composition of the upper crust. Research work by Asiedu et al. (2004) on the Birimian metasediments from the Cape Coast basin showed typical Archean signatures; low Th/Sc ratios (<0.5, with exception of one sample), high Sm/Nd ratios (>2.1, with exception of 3 samples), high Th/Sc ratios (>20, with exception of 3 samples), and high Cr/Sc ratios (>6, with exception of 2 samples).

These features suggest that the continental crust of the region in Ghana (and possibly for West Africa), during the Early Proterozoic had chemical compositions comparable to those of the Archean crust (Abouchami et al., 1990; Leube et al., 1990; Sylvester and Attoh, 1992; Taylor et al., 1992).

However, the studied shales from parts of Wa-Lawra Belt show trace element variations Eu anomalies (average Eu/Eu* = 0.8), decrease in Gd_N/Yb_N values (average = 1.5), a minimum ratio of Sm/Nd (average = 0.21) a decrease in Cr/Sc (average = 9.76) and increase in Th/Sc values (average = 0.16), suggesting a significant compositional variation through time when compared to that of Asiedu et al. 2004.

The plot of Eu/Eu* against Gd_N/Yb_N (after McLennan and Taylor, 1991) is very useful in the evaluation of trace element variation of the Upper Continental Crust composition through time. In this diagram, the studied shales from the Paleoproterozoic Birimian metasediments in parts of Wa-Lawra Belt plot mainly in Archean field. Therefore, not very much different from the interpretation of Asiedu et al (2004) that the Birimian metasedimentary rocks show Archean geochemical signatures (Figure 5.17).

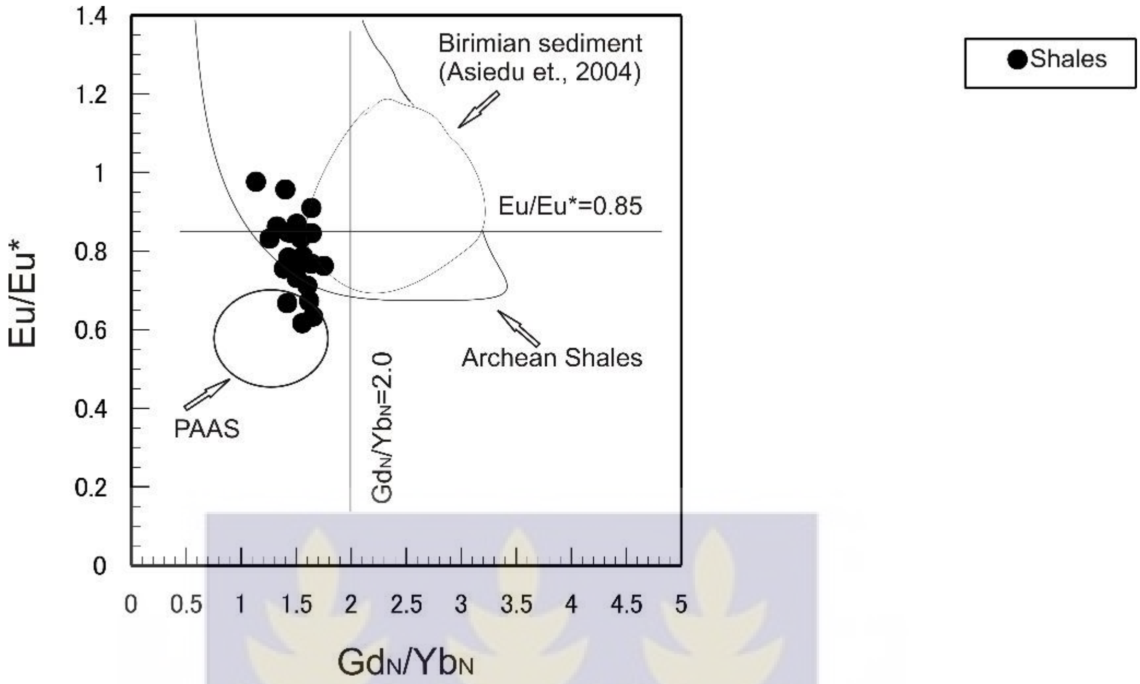

Figure 5.17: Plot of Eu/Eu* versus GdN/YbN for Paleoproterozoic Birimian metasediments, Wa Lawra Belt. (After McLennan and Taylor, 1991). Birimian metasediments and post - Archean Australian average shale (PAAS) are plotted for comparison (values are from Asiedu et al., 2004; Taylor and McLennan, 1985, respectively).

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATION

6.1 CONCLUSIONS

A geochemical study of shales from the Paleoproterozoic Birimian metasedimentary rocks from parts of the Wa-Lawra Belt was undertaken in order to determine the provenance and tectonic settings of the sedimentary rocks. The following conclusions were made:

1) The geochemical characteristics of the studied shales shows that they are immature in nature and first cycle in origin, with little or no recycled component.

2) Chemical Index of Alteration and Plagioclase Index of Alteration calculations indicate moderate degree of chemical weathering took place at the sediment source area.

3) The trace element compositions suggest that the shales were predominantly derived from juvenile arc rocks of mixed felsic and mafic compositions. Model calculations based on the REEs suggest that the source materials are composed of about 60% basalt, 20%TTG and 20% granite.

4) The shales were most likely derived from the mafic volcanic rocks and their associated granitoids in the Birimian greenstone belts.

5) The geochemical characteristics of the shales further suggest that deposition took place in an Oceanic Island Arc settings.

6.2 RECOMMENDATION

I recommend that Nd-isotopic analysis be carried out on the studied shales. Nd-isotopic study on the shales can either support or disprove the juvenile nature of the source rocks inferred from the whole-rock geochemistry. Nd-isotopic data can also be used to quantitatively model the contribution of Archean sources, if any, to the provenance of the shale.

In addition, further provenance studies are recommended on other areas of the Wa-Lawra belt to give a better and broad understanding of the provenance of this unit. Such a study may not only be limited to shales but can include sandstones and also other provenance techniques such as detrital zircon dating to directly locate sediment sources.

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APPENDIX

Table 4.3 Linear correlation coefficients for specific elements of the studied shales

Elements	Linear correlation
K_2O-Ba	0.81
K_2O-Cs	0.49
K_2O-Rb	0.99
K_2O-Th	0.89
K_2O-U	0.88
K_2O-Ta	0.87
K_2O-Nb	0.82
K_2O-total REE	0.80
Al_2O_3-Fe_2O_3+MgO	0.84
Al_2O_3-TiO_2	0.95
P_2O_5-Cs	0.26
P_2O_5-Ni	0.67
P_2O_5-Co	0.62
Th-Sc	0.50
Th-total REE	0.91
Al_2O_3-total REE	0.87
Zr-total REE	0.86
La-Al_2O_3	0.85
Yb – Zr	0.82
Yb - Al_2O_3	0.88
La – Zr	0.84
Zr - Eu/Eu*	-0.07
Fe_2O_3 - Al_2O_3	0.82
Sc - Al_2O_3	0.82
V - Al_2O_3	0.90
Cr - Al_2O_3	0.75
Ni - Al_2O_3	0.87
Co - Al_2O_3	0.89
Cu - Al_2O_3	0.66
Rb - Al_2O_3	0.87
Sr - Al_2O_3	0.13
Cs - Al_2O_3	0.47
Ba - Al_2O_3	0.56
Y - Al_2O_3	0.73
Nb - Al_2O_3	0.86
Ta - Al_2O_3	0.83
Th - Al_2O_3	0.95
U - Al_2O_3	0.90
Cr – Ni	0.59
Cr – Co	0.64
Ni – Co	0.94

Zr – Hf	0.96
Th – U	0.95

LIST OF SAMPLE LOCATIONS

SAMPLE 1D	EASTING	NORTHING
ABACD010 (163.0-163.5m)	526992	1148725
ABACD017 (186.5.0-187.0m)	524420	1166079
ABACD028 (191.0-191.5m)	526985	1148473
ABACD031 (251.0-251.5m)	523036	1164099
ABACD032 (163.0-163.5m)	526925	1149247
AVACD038 (211.0-211.5m)	524468	1166276
AVACD038 (217.5-218.0m)	524468	1166276
AVACD042 (194.0-194.5m)	524420	1166079
AVACD042 (201.1-201.6m)	524420	1166079
AVACD043 (202.0-202.5m)	524765	1166074
AVACD043 (228.0-228.5m)	524765	1166074
BRCD203 (251.5-252.0m)	527047	1152225
BRCD223 (84.4-85.0m)	527186	1151474
BRCD258 (117.5-118.0m)	527046	1152173
BRCD263 (144.5-145.0m)	527076	1152123
BRCD265 (147.7-218.2m)	527050	1152095
BRCD302 (185.5-186.0m)	527022	1152224
BRCD450 (228.0-228.5m)	527052	1152351
BRCD450 (234.0-234.5m)	527052	1152351
KRCD080 (150.0-151.0m)	527028	1149108
KRCD080 (156.0-156.5m)	527028	1149108
KRCD560 (228.0-228.5m)	526992	1148575
KRCD565 (163.0-163.5m)	526845	1149499
KRCD565 (209.0-209.5m)	526994	1148621
KRCD567 (217.0-217.5m)	526940	1149222
KRCD573 (177.0-177.5m)	526990	1148778
KRCD579 (179.0-179.5m)	526998	1148372
KRCD694 (276.8-277.3m)	526995	1148902
KRCD695 (229.5-230.0m)	526990	1148778
KRCD699 (276.0-276.5m)	526992	1148575
KRCD700 (229.0-229.5m)	524765	1166074
KRCD700 (261.0-261.5m)	526925	1149247
KRCD700 (264.0-264.5m)	526925	1149247
KRCD700 (297.5-280.0m)	526990	1148778
KRCD700 (299.0-299.5m)	526925	1149247