UNIVERSITY OF GHANA

COLLEGE OF BASIC AND APPLIED SCIENCES

GEOCHEMISTRY OF NEOPROTEROZOIC PHYLLITES FROM THE AKUAPIM RANGE, SOUTHEASTERN GHANA

By

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DECLARATION

This is to certify that this thesis is the result of research undertaken by Samuel Bonsu towards the award of Master of Philosophy in Geology in the Department of Earth Science, University of Ghana.

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ABSTRACT

Neoproterozoic phyllites from the Akuapim range, a prominent part of the Togo Structural Unit forms part of the Pan-African Dahoeyide orogen exposed at the southeastern part of Ghana. The area of study exhibit three varieties of phyllites which are carbonaceous, iron-stained and micaceous phyllites. These phyllites have been analyzed for their mineralogical and geochemical characteristics to infer their source -area weathering, source rock composition and tectonic setting. The mineralogical content of ten (10) samples were determined using X-ray diffraction method. Twenty-eight (28) samples were analyzed for their major, trace and rare earth element compositions using ICP-AES and ICP-MS. From the mineralogy, the phyllites are composed of quartz, feldspar, muscovite, chlorite, illite with some siderite, graphite and calcium carbonate. Compared to post-Archean Australian average Shale (PAAS), the phyllites are depleted in major elements with the exception of SiO_2 and MnO which are enriched relative to PAAS. The phyllites show relative depletions in transition metals such as Sc, V and Cr whereas high field strength elements such as Zr, Hf, Y and Th are at an average to above-average concentrations as compared to PAAS. The phyllites show a single trend of LREE enrichment (average La_N/Sm_N = 3.78), nearly flat HREE and negative Eu anomaly (average Eu/Eu* = 0.61) similar to the trend of post-Archean Australian average shale. From geochemistry, the phyllites can be classified mostly as quartz-rich with few quartz-intermediate. Al_2O_3 shows positive correlations with Sc, V, Cr, Rb, Sr, Cs, Ba and Y suggesting that these elements are primarily controlled by the dominant clay minerals. High values of K_2O/Na_2O (average = 54.31) and SiO_2/Al_2O_3 (average = 8.17) of the phyllites indicates compositional maturity of the sediments. The phyllites reveal high concentrations of Zr (average = 408.08 ppm) which suggests sedimentary sorting. This is supported by the plot of Th/Sc against Zr/Sc. High Chemical Index of Alteration (average = 74.73%), Plagioclase Index of Alteration (average = 87.68%), Chemical Index of Weathering (average = 98.36%), Rb/Sr (average = 4.22), Th/U (average = 4.09) values and low Index of Compositional Variability (average = 0.64) values of the analyzed samples indicate intense chemical weathering in the source areas. On the A-CN-K ternary diagram, data for the Neoproterozoic phyllites from the Akuapim range plot in a trend (along A-K line) indicating intense chemical weathering. The phyllites show geochemical characteristics typical of sediments derived from old Upper Continental Crust. Modeling of the average phyllites using the relatively immobile REEs and Th/Sc shows that the sediments are composed of a mixture of 80% Upper Continental Crust and 20% granite. The phyllites show mineralogical and geochemical characteristics indicative of sediments deposited within a passive continental margin and/or intra-cratonic terrane. The phyllites exhibit provenance characteristics similar to that of the Kwahu/Bombouaka Group of the Voltaian Basin and the Buem Structural Unit which are believed to be lateral equivalents and are probably derived from the same source in the Amazonian Craton.

DEDICATION

This research work is dedicated to the Almighty God and to my parents Mr. and Mrs. Bonsu.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Geochemical methods furnish important information about the provenance, geological processes and formation history of sedimentary and metasedimentary rocks (Getaneh, 2002; Drost et al., 2003). This is based on the assumption that the final chemical composition of clastic sediments is controlled by interaction of factors such as source rock composition, tectonic setting, chemical weathering, and hydrodynamic sorting during transport and in the depositional environment and diagenetic processes (Johnsson, 1993; McLennan et al., 1993; Rollinson, 1993; Fedo et al., 1996). The mineralogy of detrital particles provides the principal evidence for the composition of source rocks (Johnsson, 1993). These detrital materials are generally produced by weathering of rocks which is directly controlled by climate. The intensity of weathering is influenced by the slope and relief of the source area (Johnsson, 1993). The slope and relief of the source area are mainly dependent on the tectonic setting which is considered as the overall primary control on the composition of sedimentary rocks (Dickinson, 1985). Sedimentary rocks formed in different tectonic environments have distinctive provenance characteristics and are characterized by distinctive sedimentary processes as plate tectonic processes impart unique petrological and geochemical signatures to sedimentary rocks (Bhatia, 1983; Dickinson et al., 1983; McLennan et al., 1993).

Chemical composition of fine-grained sedimentary rocks are particularly valuable for provenance studies as they provide a representative view of the average crust in the area due to their grain size homogeneity and post-depositional impermeability (Taylor and McLennan, 1985; Cox and Lowe, 1995). Chemical composition can be extracted by whole-rock mineralogical and geochemical analyses of the sediments (Taylor and McLennan, 1985). These analyses determine the mineralogical content as well as the major and trace element (including REEs) abundances which give significant evidence used in constraining the source rocks, source area weathering and tectonic setting of sedimentary and metasedimentary rocks.

The Togo Structural Unit which forms part of the Pan-African Dahomeyide belt in southeastern Ghana (Figure 1.1) occurs as a north northeast to south southwest trending mountains and hills from the Volta River towards the Ghana-Togo border and beyond (Junner and Service, 1936; Junner and Hirst, 1946; Kesse, 1985). Prominent among these hills and mountains is the Akuapim range which is comprised of cataclastic quartzites interbedded with phyllites (Junner and Service, 1936; Junner and Hirst, 1946).

The rocks of the Togo Structural Unit have been investigated by numerous workers such as Kitson (1928), Junner and Hirst (1946), Affaton et al. (1980), Kesse (1985), Blay (1991) and Amoah (2009). However, little work has addressed the Togo phyllites and its geochemical characteristics which can give a wealth of information about provenance and crustal evolution of the unit. The aims of this research are to define the geochemical characteristics of the Neoproterozoic phyllites from the Akuapim range of the Togo Structural Unit based on their major and trace elements compositions, to discuss the source-area weathering conditions and to constrain their provenance and tectonic setting as well as contribute to the geochemical database of the Neoproterozoic rocks of Ghana which can be used for any future computation of the Neoproterozoic crustal compositions.

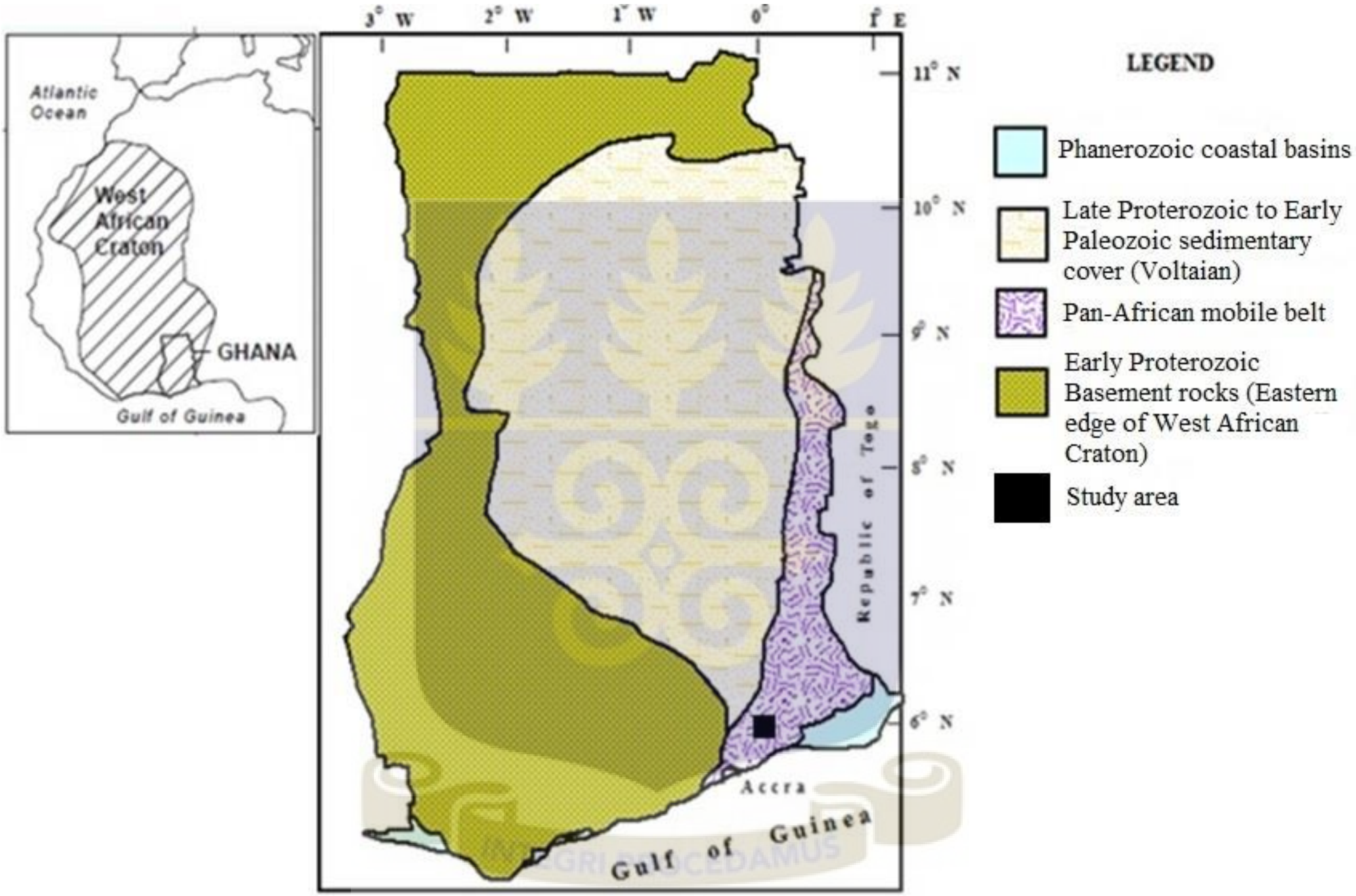

Figure 1.1 Generalised tectono-stratigraphic map of Ghana showing the study area (modified from Osae et al., 2006).

1.2 OBJECTIVE

The objectives of this study were to:

1. Generate a geochemical database for the Togo phyllites;
2. Characterize the geochemical composition of these phyllites;
3. Identify the source rock composition and tectonic setting of the Togo phyllites; and
4. Infer the source-area weathering conditions.

1.3 STUDY AREA

1.3.1 Location

The study area is located in the southeastern part of Ghana and lies between latitudes 05˚ 45' 30" N and 05˚ 51' 00" N and longitudes 00˚09' 40" W and 00˚14' 00" W (Figure 1.2). Notable towns in the study area include Aburi (which lies in the northeastern part of the study area), Kitase, Peduase, Agyemanti, Ayim, Ayimensa and Kponko,

1.3.2 Accessibility

The study area is easily accessed by the Oyarifa-Ayimensa-Aburi road, a first class road which leads from the southwestern to northwestern part of the study. Other parts of the study area can be accessed by a third class road from Kitase to Agyemanti. Most of the study area are linked by footpaths. However, accessibility to some parts is difficult due to the relief and vegetation.

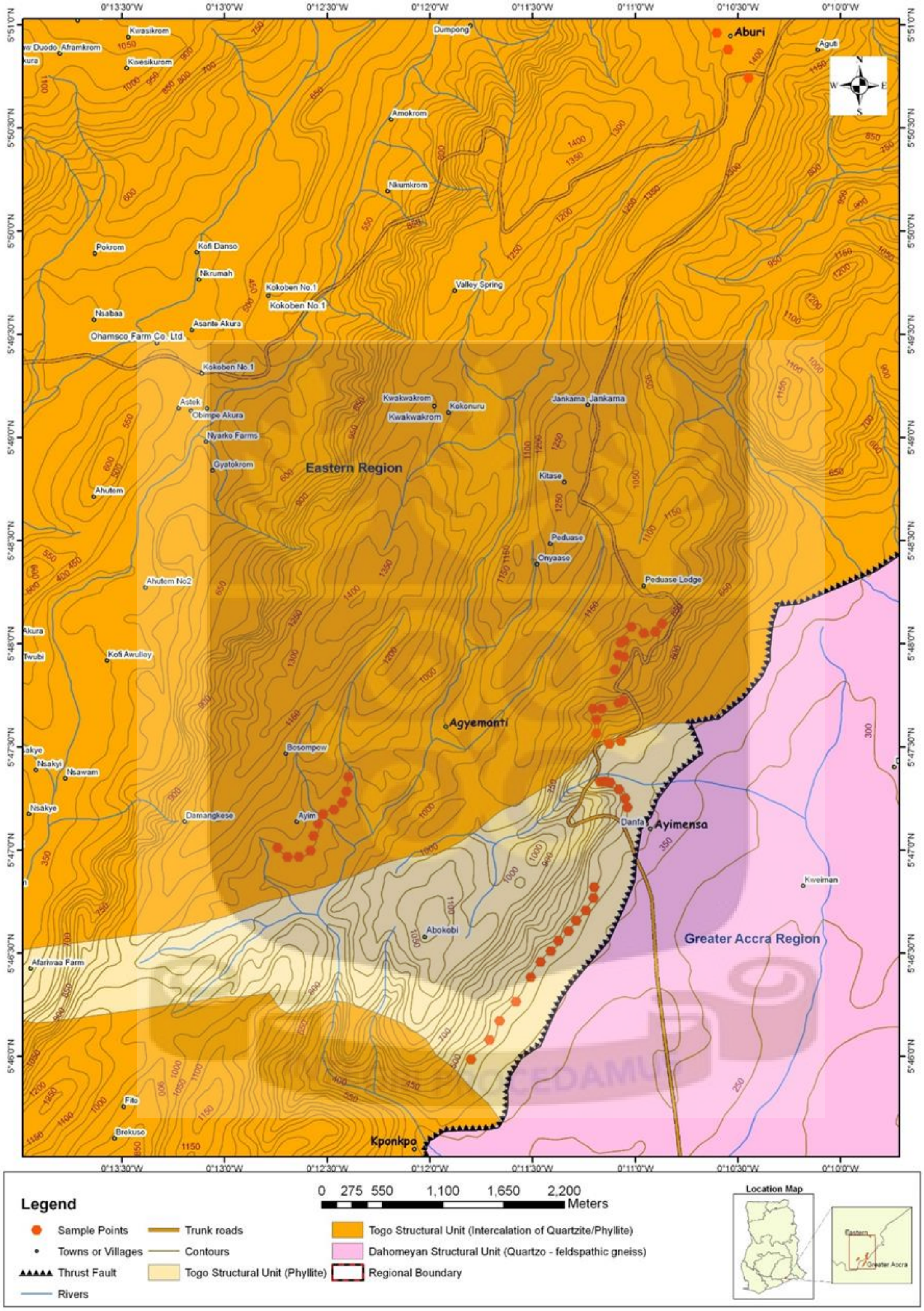

Figure 1.2 Geological map of the study area showing the sample locations (modified from Ghana National Geological Map Project, 2009).

1.3.3 Topography and Drainage

The study area consists of gentle slopes interspersed with plains in the west with the Akuapim range rising steeply above the western end. The Akuapim range generally lies at 375-420 m north of Aburi and falls to 300 m southward (Dickson and Benneh, 1988). The highest highlands stretch from Kitase to northwestern part of Peduase and the lowlands occur around Teiman.

River Ntare and Dakobi are the major rivers which flow through the study area. River Ntare flows from the northwestern to the southwestern part of the area from Onyaase to Agyemanti and has its diversion to Gyankama and Obuom. The Dakobi River flows from the southwest to Teiman. The area has few seasonal streams most of which are threatened by farming activities. Groundwater serves as the main source of water for residents in the area.

1.3.4 Climate

The study area falls within the savannah agro-ecological zone (Dickson and Benneh, 1988). The area experiences a bi-modal rainfall pattern with the major rainy season occurring from March to July and minor rainy season from September to November. The average annual temperature ranges between 25.1^{O}C in August and 28.4^{O}C in February and March (Dickson and Benneh, 1988).

1.3.5 Vegetation and Soil

The vegetation of the area is generally depicted by shrub lands and grassland (Dickson and Benneh, 1988). The shrub lands occur mostly in the western peripheries and in the north towards the Aburi hills and consist of dense cluster of small trees and shrubs that grow to an average height of about 5 m (Dickson and Benneh, 1988). The grassland which has now been encroached upon by human activities such as settlements occur to the southern parts of the area.

The soil types found in the area are deep, orange brown to bright red, sandy clay loam containing abundant ironstone concretions and gravels which are suitable for maize, yam, cassava, groundnut, sweet potato, vegetables (Dickson and Benneh, 1988).

1.4 GEOLOGICAL SETTING

The geology of Ghana (Figure 1.1) can generally be divided into four tectono-stratigraphic units on the basis of age, tectonics and lithological characteristics of the supracrustal rocks (Kitson, 1928; Bates, 1955; Asihene and Barning, 1975; Hasting, 1977, 1983; Kesse, 1985; Blay, 1991; Davis et al., 1994). These divisions are:

1) Early Proterozoic basement rocks, the Birimian and Tarkwaian which form the western units, found at the eastern margin of the West African Craton;
2) Late Proterozoic to Early Paleozoic sedimentary cover, the Voltaian Supergroup;
3) The Precambrian mobile belt, Dahomeyide Belt which was developed during the Pan-African (around 600 Ma) orogeny and located in the south eastern part of the country; and
4) Late Paleozoic to Early Mesozoic sedimentary basins.

The Dahomeyide belt which is part of the Pan-African belt is believed to have resulted from the breakup of Rodinia supercontinent which led to the assemblage of cratonic material on the northwestern part of the Gondwana supercontinent (Hoffman, 1991; Cordani et al., 2003). The Togo Structural Unit (Figure 1.2) forms part of the Dahomeyide belt exposed in the southeastern part of Ghana. It is bordered to the west by the Cape Coast granitoid complex rocks, Voltaian and Buem Structural Unit. To the east of the Togo Structural Unit is a generally low-lying area (Accra plains) underlain by high-grade, Dahomeyan metamorphic terrain. The Togo Structural Unit consists of quartz sericite-schists, quartzites, phyllites and chlorite (Robertson, 1925; Junner and Hirst, 1946; Grant, 1969). Hornstones, jaspers and hematite quartz-schists occur as post-depositional rocks within the unit (Junner and Service, 1936). The quartzites are metamorphosed and deformed. The degree of metamorphism and deformation increases towards the southeast (Wright et al., 1985).

The study area is part of the Akuapim range which occurs as north northeast to south southwest trending mountains and hills from the Volta River towards the Ghana-Togo border and beyond (Kesse, 1985). It comprises of cataclastic quartzites interbedded with phyllites (Ahmed et al., 1977). The cataclastic quartzites are the predominant members of the unit. They are generally grey, medium to fine-grained, thickly foliated with joints and micro-fractures. The phyllites underlie the quartzites and are mostly composed of mica and chlorite which are formed from metamorphism of clays (Ahmed et al., 1977). They are mostly grey on fresh surface, fine-grained, thinly foliated with joints and microfractures. Folds which occur within the quartzites and phyllites are predominantly isoclinal with axial planes inclined to southeast at 30^0 to 60^0 and minor recumbent folds with general dip of less than 30^0 (Kesse, 1985).

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, provenance studies in fine-grained sedimentary rocks, factors that control the final composition of clastic sediments and their geochemical significance related to this study are presented. In addition, the geology of the study area which falls within the Togo Structural Unit, a part of the Dahomeyide Belt, is presented.

2.1.1 Provenance studies in fine-grained sedimentary rocks

Provenance studies of sedimentary rocks usually involve the determination of the source rock composition, the tectonic setting or the source area, source area weathering, and the climate and relief of the source area (Johnsson, 1993). Numerous workers have proposed various techniques and approaches for the provenance studies of fine-grained siliciclastic sedimentary rocks. One of the techniques is the detrital heavy mineral assemblages. This involves the extraction of information from heavy minerals such as garnet (Morton, 1987), chrome spinel (Pober and Faupl, 1988; von Eynatten, 2003), tourmaline (von Eynatten and Gaupp, 1999), amphibole (Faupl et al., 2002), white mica (von Eynatten et al., 1996; von Eynatten and Wijbrans, 2003) and epidote (Spiegel et al., 2002) for quantitative provenance studies. Another technique which has been used by numerous workers is the whole-rock geochemistry (e.g., Nesbitt and Young, 1984; Bhatia, 1985; Asiedu et al., 2004). This method involves the determination of major, trace as well as rare earth element abundance in sediments. These elements provide important information about the source rock composition, source area weathering and tectonic setting of sediments (e.g., Nesbitt and Young, 1984; Bhatia, 1985; McLennan, 1989; McCann, 1991; McDaniel and McLennan, 1991; McLennan and Taylor, 1991; McLennan et al., 1993; Johnsson, 1993). Other techniques such as zircon dating and isotope geochemistry have also been used in recent studies to determine the provenance of sediments (e.g., Heller and Frost, 1988; Kalsbeek et al., 2008; Chen et al., 2014; De et al., 2015).

2.1.2 Source rock composition of clastic sediments

Studies have shown that the source rock composition of clastic sediments may be determined from their chemical composition (McLennan et al., 1993). This is based on the direct link between the mineralogy, chemical composition of clastic sediments and their source rock composition (Johnsson, 1993). However, the tectonic setting is believed to chiefly control the composition of clastic sediments (Pettijohn et al., 1972; Dickinson and Suczek, 1979; Bhatia, 1983; Chamley, 1990). Plate tectonic processes impart distinctive petrological and geochemical signatures to sedimentary rocks (Bhatia, 1983; Dickinson et al., 1983; McLennan et al., 1993). Therefore, sedimentary rocks formed in different tectonic environments have distinctive provenance characteristics as they are characterized by distinctive sedimentary processes (Bhatia, 1983; Dickinson et al., 1983; McLennan et al., 1993). Studies on sedimentary and metasedimentary rocks by numerous workers such as Enkeboll (1982), Bhatia and Crook (1986), Johnsson (1993), Asiedu et al. (2004), Armstrong-Altrin et al. (2004) and Osae et al. (2006) support the interaction between the composition of clastic sediments, source rock composition and tectonic setting of source area.

Provenance studies of clastic sediments by geochemical methods basically involves the application of major and trace element (including rare-earth element) geochemistry to discriminate source rock composition and tectonic setting (e.g., Bhatia, 1983; Bhatia and Crook, 1986). The application of elemental geochemistry in identifying source rocks for sedimentary rocks is based on the relative immobility of certain elements such as rare-earth element (REEs), high field strength elements (HFSE), Cr, Co, Sc and Th during weathering, diagenesis, hydrothermal overprint and low-grade metamorphism (Taylor and McLennan, 1985; Bhatia and Crook, 1986). These elements are transported, in effect quantitatively, in the terrigenous component of sediment and therefore, their concentration and elemental ratios are not the same for different types of rocks and tectonic environments and therefore, reflect their source composition (Roaldset, 1973; Ronov et al., 1967, 1974; Cullers et al., 1979, 1975; Bavinton and Taylor, 1980; McLennan et al., 1983; Bhatia, 1985; Bhatia and Crook, 1986; Getaneh, 2002).

The correlation between sediments composition and tectonic setting is mostly ascertained by plotting the rock suites on discrimination diagrams using mineralogical and chemical composition of the sediments. The cluster of the rock suites that emerges is correlated with tectonic environment of the inferred source terrains. Different 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). 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 (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 intensity and duration of weathering are dependent on climate (i.e., rainfall, temperature) and relief (i.e., elevation differences, slope angle) (Johnsson, 1993). In general, chemical weathering is more intense in the tropics relative to the temperate and arid regions (Woolnough, 1930; Krynine, 1936; Mann and Cavaroc, 1973; Basu, 1976; Suttner and Basu, 1981; Girty et al., 1988). Low relief and gentle slopes support chemical weathering because the duration of weathering is longer on gentle slopes (Johnsson, 1993). On the other hand, high relief and steep slopes support erosion and rapid removal of minerals from the weathering environment before they are rigorously altered by weathering processes (Johnsson, 1993). Under chemical weathering conditions, less stable minerals (e.g., olivine, pyroxenes, amphiboles, calcium plagioclase) are destroyed whiles the more stable minerals (e.g. sodium plagioclase, potassium feldspars, muscovite, quartz) are enriched. This is because common rock forming minerals have different stabilities with respect to chemical weathering processes (Goldich, 1938). Therefore, the principal effect of weathering on silicilastic sedimentary rocks is very important in the evaluation of provenance of sedimentary and metasedimentary rocks.

Chemical weathering can be measured by the compositional changes resulting from mineralogical alteration and chemical changes (Okada, 1971; Folk, 1974; Nesbitt and Young, 1984). The effect of weathering on the composition of sediments has been by numerous workers (Woolnough, 1930; Krynine, 1936; Goldich, 1938; Basu, 1976; Potter, 1978a; Nesbitt, 1979; Nesbitt et al., 1980; Suttner and Basu, 1981; Knoll and James, 1987; Hansley, 1987; Bennet and Siegel, 1987; Mast and Drever, 1987; Johnsson et al., 1988). Nesbitt and Young (1982, 1984) evaluated 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). Chemical index of alteration (CIA) is defined as:

CIA = 100 x [Al_2O_3/(Al_2O_3+CaO*+Na_2O+K_2O)]; In molecular proportions. Where CaO* represents the CaO in silicate only.

However, the occurrence of post-depositional potassium (K) in older clastic rocks limits the use of the CIA parameter (Potter, 2005). Hence, a potassium free index such as chemical index of weathering (CIW) and plagioclase index of alteration (PIA) have been proposed by Harnois (1988) and Fedo et al., (1995), respectively.

Plagioclase Index of Alteration is defined as:

PIA = 100 x [(Al_2O_3-K_2O)/(Al_2O_3+CaO*+Na_2O-K_2O)]; and

The Chemical Index of Weathering (CIW), defined as:

[Al_2O_3/(Al_2O_3+CaO*+Na_2O)] x 100; In molecular proportions. Where CaO* represents the CaO associated with the silicate fraction.

Also, the index of compositional variability (ICV), proposed by Cox et al. (1995) and reflects the intensity of chemical weathering and source rock composition can be used to quantify the intensity of chemical weathring. Index of compositional variability (ICV) is defined as:

[CaO+K_2O+Na_2O+Fe_2O_3(t)+MgO+MnO+TiO_2]/Al_2O_3; In weight percents (wt%). Where Fe_2O_3(t) = total iron and CaO includes all sources of Ca.

2.1.4 Transportation of sediments

Transport of sediments serves as an important link between source and depositional areas. However, various sedimentary processes occur prior to the deposition of sediments which affect the composition of the 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).

2.1.4.1 Abrasion and mechanical breakdown

Abrasion and mechanical breakdown are the most important processes during transportation of sediments 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). Abrasion usually leads to the rounding of coarser grain size sediments to finer grain size materials (Kuenen, 1962, 1964). According to Hubert (1962), Hayes (1967) and Pittman (1970), the process of rounding and reducing sediment sizes results in hydrodynamic sorting of the sedimentary materials and increases quartz/feldspar ratios.

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. Therefore, 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.

2.1.4.2 Sorting and mixing

Sorting and mixing of clastic sediments during transport affects the composition of clastic sediments. 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 (Garvanti, 1986; Koehnken, 1990; Johnsson et al., 1991). An example is the separation of most clay minerals and other fine materials from coarser-grained quartz, feldspars, and rock fragments during current transport. Additionally, compositional sorting owing to shape and density differences of grains results in changes in the energy and velocity of the transporting medium results in the enrichment of heavy minerals (Johnsson, 1993). 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 ($ZrSiO_2$) can be used to evaluate the degree of sorting in clastic sediments.

Long transport distances characteristic of fine-grained sediments favour mixing of sedimentary components from different provenance and history which result in the variation of the composition of clastic sediments (Johnsson, 1993; Potter, 2005). The effect of mixing of sedimentary composition with variable history and provenance may introduce complexities in the interpretation of provenance (Whetten et al., 1969; Kelley and Whetten, 1969) and as such techniques including rare-earth elements (REEs) patterns, comparison of trace elemental ratios to values of known provenance and other discrimination diagrams are useful in ascertaining the provenance of sediments.

2.1.5 Diagenesis

Burial of sediments during deposition leads to changes in the geochemical conditions within the burial environment which can produce intense post-depositional modifications in composition (Scholle and Schluger, 1979; McDonald and Surdam, 1984). Diagenesis generally involves the destruction or replacement of metastable grains by another mineral or alteration of metastable minerals to another mineral (Johnsson, 1993). One of the most important diagenetic processes in sedimentary rocks is cementation and the importance of this process can also be observed in the evaluation of petroleum reservoir rocks. According to Johnsson (1993), progressive diagenetic alteration produces complex sets of compositional modifications relative to chemical weathering, mechanical breakdown and abrasion, sorting and mixing effect.

Even though the chemistry of diagenetic processes are not established, most of the reactions involved in this process may be very important in the studies of sedimentary and metasedimentary rocks (Land and Milliken, 1981; Boles, 1984; Surdam et al., 1984; Morton, 1984; Moncure et al., 1984; Market and Al-Sharieb, 1984; Helmhod and van de Kamp, 1984; Franks and Forester, 1984; Morad et al., 1990). Diagenesis may result in alterations of sedimentary materials producing different geochemical signatures relative to the protolith and therefore significant loss in provenance information. Diagenetic effect in metasedimentary rocks may be obscured by the effect of metamorphism. However, rare-earth elements (REEs) and trace elements such as Th, Sc, Cr, Zr are relatively immobile during diagenesis and metamorphism are considered more reliable.

2.2 DAHOMEYIDE BELT

The Dahomeyide belt is part of the 2000 km long Pan-African Trans-Saharan orogen located on the eastern margin of the West African Craton (Caby, 1987; Trompette, 1997). The Trans-Saharan belt is postulated to have resulted from the breakup of Rodinia supercontinent which led to the assemblage of cratonic material on the northwestern part of the Gondwana supercontinent (Hoffman, 1991; Cordani et al., 2003). Boullier et al. (1986) maintains that the Pan-African Trans-Saharan belt resulted from oceanic closure and oblique collision between the West-African Craton and the Tuareg-Nigerian shields around 600 Ma ago.

The Dahomeyide orogen belt is the southeastern segment of the Trans-Saharan belt and it occurs between the passive continental margin of West Africa Craton (WAC) and the Saharan Meta-Craton (SMC) (Black et al., 1979; Caby et al., 1981). It is exposed in southeastern Ghana and adjoining parts of Togo and Benin, its northern extension being the Iforas of Mali and the western Hoggar in Algeria (Affaton et al., 1991; Castaing et al. 1993; Attoh et al. 1997). The Dahomeyide belt has been interpreted as the product of the easterly subduction of oceanic lithosphere (Attoh, 1998; Agbossoumonde et al., 2004).

In Ghana, the Dahomeyide belt can be subdivided into three domains which:

- The Dahomeyan basement rocks;
- The Togo structural units at the eastern and western side of the Dahomeyan basement rocks; and
- The Buem Structural Unit to the western side of the Togo Structural Unit.

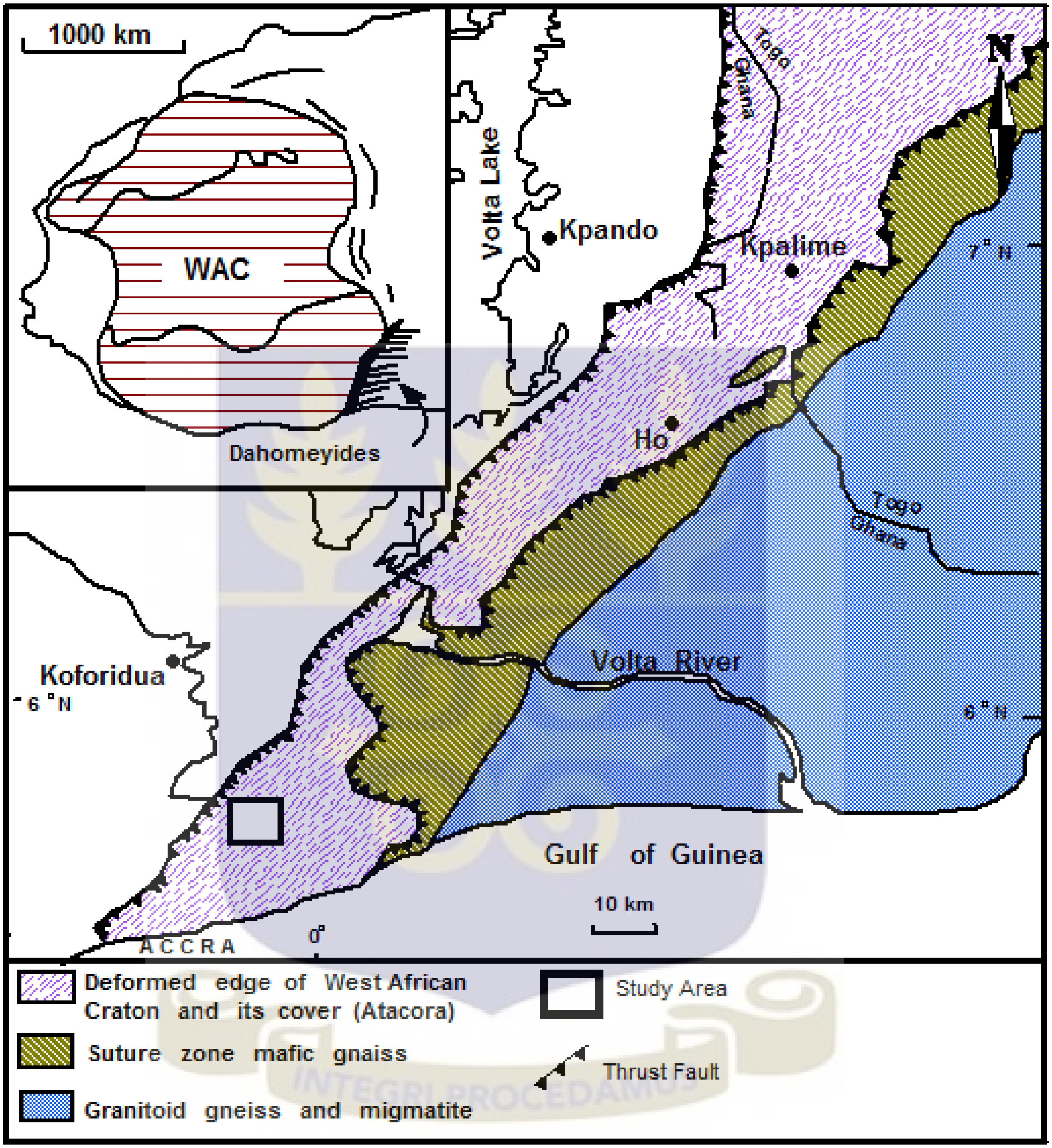

Figure 2.1 Geological map showing the Dahomeyide Orogeny in Ghana with the location of study area (after Attoh, 1998).

2.2.1 Dahomeyan Structural Unit

The Dahomeyan, a type locality name which was first given by Roques (1948), belongs to the Pan-African terrain and underlies the Accra plains as well as the southern part of the Volta Region (Kesse 1985). The Dahomeyan occupies a total area of approximately 7000 square km (Mani, 1978). Kennedy (1964), Grant (1969) and Holm (1973) described the Dahomeyan as a reworked Achaean basement of the late Precambrian Pan-African orogen with records of polycyclic deformation. Clifford (1972) maintained that the Dahomeyan represents cratonic chains of reactivated continental basement and supracrustal rocks formed during the Neoproterozoic Pan-African orogeny. However, studies by Villeneuve and Cornée (1994) and Trompette (1997) suggested that the Dahomeyan represents a pre-orogenic rift phase that evolved to an active margin, with subduction and calc-alkialine magmatism occurring between 700 Ma and 600 Ma and final collision against the eastern margin of the WAC at 610 – 600 Ma and producing granulite facies metamorphism. Burke and Dewey (1972) postulated that the Dahomeyan belt was formed by subduction of oceanic crust and collision of two continental plates.

In general, the Dahomeyan is considered to consist of two belts of felsic gneisses that alternate with two belts of mafic gneisses (Grant, 1967; Adjei, 1968; Holm, 1973; Kesse, 1985). The belts are up to 30km wide and trend in a south-southwest to north-northeast from the coastal plains extending into Togo (Kennedy, 1964). The acid gneisses are believed to be metamorphosed volcaniclastic and sedimentary rocks (Kesse, 1985). Holm (1974) described the mafic gneisses as relatively uniform oligoclase, andesine, hornblende and garnet gneisses of igneous origin and generally of tholeiitic composition. The Dahomeyan has suffered, at least, two phases of metamorphism with the latter having resulted in retromorphism and mylonitization (Kesse, 1985).

In recent literature, the Dahomeyan is classified into three structural units based on age and tectonics (Attoh et al., 1997; Attoh, 1998; Agbossoumonde et al., 2004; Attoh and Nude, 2008). These are: (a) the deformed edge of the WAC locally referred to as the Ho-gneiss, (b) the suture zone representing the eastern boundary of the autochthonous WAC and (c) exotic rocks that form the granitoid gneiss complexes east of the suture zone. The Ho-gneiss consists of quartzo-feldspathic and augen-gneiss with basic intrusions of norite, pyroxenite and dolerite (Kesse, 1985). In general, the suture zone consists of high pressure mafic granulites locally referred to as Shai-Adaklu Hills and alkaline gneiss complex locally referred to as the Kpong complex (Attoh et al., 1997; Attoh and Nude, 2008). The exotic rocks mainly consist of felsic gneisses and migmatites (Kesse, 1985).

2.2.2 Togo Structural Unit

The Togo Structural Unit has been investigated by numerous workers and different names developed for the rocks of this unit. Such names include Akwapimian (Kitson, 1928), Togo (Junner and Hirst, 1946), Togo Structural Unit (Affaton et al., 1980), Togo Series (Kesse, 1985), and Togo Tectonic Unit (Blay, 1991). However, Togo Structural Unit has been generally accepted and used by recent workers (Asiedu et al., 2006; Osae et al., 2006). The Togo Structural Unit is an irregular, fault-bounded belt of metamorphosed sediments that comprise the series of hills and ridges (Akuapim range) which trend in a north north-east to south south-west from the Volta River towards the Ghana-Togo border and into northern Benin where it is called the Atacora Range (Kesse, 1985). The Togo Structural Unit marks the western limit of a very large area affected by the Pan-African thermo-tectonic event that peaked at about 600-550 Ma and whose effects extend right across Nigeria (Griffis et al., 2002). Studies by Hoffman (1999) indicated that the Togo Structural Unit is a collisional belt and suture zone between the West African Birimian craton and an eastern cratonic block that became welded together at a time the supercontinent of Gondwana was being created. The Togo Structural Unit is bordered to the east by a generally low-lying area (Accra plains) underlain by high-grade, Dahomeyan metamorphic terrain. To the west of the Togo Structural Unit are the Cape Coast granitoid complex rocks, the Voltaian and Buem Structural Unit.

The Togo Structural Unit mainly consists of metamorphosed sediments which are quartzite, schist, phyllite and marble with some minor amounts of metavolcanics. Junner and Hirst (1946) suggest that the Togo Structural Unit was originally alternating arenaceous and argillaceous sediments which have been metamorphosed into phyllites, schists and quartzite, except in few places where unaltered shales and sandstones occur. Robertson (1925), Junner and Hirst (1946) and Grant (1969) explained that the Togo Structural Unit is predominantly composed of quartz-sericite-schists, quartzites, quartz-schists, sericite schist and chlorite. Others rocks that occur in this unit are hornstones, hematite quartz-schists, jaspers, pebbly grits and argillaceous schists with quartz pebbles (Junner and Service, 1936; Kesse, 1985). However, Junner and Service (1936) considered the hornstones, jaspers and hematite quartz-schist as post-depositional rocks.

The rocks of the Togo Structural Unit are metamorphosed and strongly deformed with the degree of metamorphism and deformation increasing toward the southeast (Wright et al., 1985). The strong deformation is manifested by intense folds, fractures, joints and faults in the Togo Structural Unit which indicate a series of deformation of which the latest is related to the

600 Ma – 500 Ma Pan-African Orogeny event (Robertson, 1925; Crook, 1963; Kennedy, 1964; Grant, 1969). The Togo structural unit dates 579.4 +/- 0.8 Ma (^{40}AR/^{39}Ar dates from muscovite in the quartzites (Attoh et al., 1997). Kaslbeek et al. (2008) showed that the rocks (quartzite) of the Togo Structural Unit have ages (1000-1300 Ma) typical of sediments derived from sources outside the West African Craton and possibly from the Amazonian Craton. Studies by Koert (1910) suggested that the Togo Structural Unit to be younger than the Dahomeyan. This assertion was supported by Crook (1970), who indicated that the occurrence of Dahomeyan gneisses within the Togo sediments. Studies by Mani (1978) and Blay (1991) suggested that the Dahomeyan is older than the Togo Structural Unit because the Togo occurs as outliers in the Dahomeyan. Detailed studies by Affaton et al. (1980) indicated that the Togo Structural Unit is probably a lateral equivalent of the Kwahu Group of the Voltaian Basin. This assertion is supported by the Pb–Pb dating of detrital zircons from the quartzites of the Togo Structural Unit (Kalsbeek et al., 2008). According to Kalbeek et al. (2008), the quartzites of the Togo Structural Unit show zircon age distributions similar to those from the Kwahu/Bombouaka Group of the Voltaian Basin and therefore they may be lateral equivalents.

Provenance studies of the Togo quartzites and phyllites have shown that the rocks of the unit were probably derived from an intensely weathered source area and mainly from Recycled Upper Continental Crust (Amoah, 2009). According to Amoah (2009), the rocks of the Togo Structural Unit show geochemical characteristics typical of sediments derived from stable continental areas and deposited on a passive continental margin.

2.2.3 Buem Structural Unit

The Buem Structural Unit consists of a thick sequence of shale, sandstone, and volcanic rocks with subordinate limestone, tillite, grit and conglomerate. The shale and conglomerate forms the basal beds which are overlain by sandstones with the tillite on top of the sandstone (Dapaah-Siakwan and Gyau-Boakye, 2000). Volcanic rocks (lava, tuff, and agglomerate) interbedded with shale, limestone, and sandstone form the upper part of the Buem Structural Unit (Dapaah-Siakwan and Gyau-Boakye, 2000). According to Kesse (1985) the Unit can be divided into two sequences; a lower sequence of clastic sediments with some carbonate and tillite units succeeded by clastics and volcanics that include mafic flow units and pyroclastics.

However, Junner (1940) and Blay (1991) classified the Buem structural unit into four (4) main units. These are (a) clastic units, (b) limestone and jasperoids, (c) serpentinites and (d) volcanic rocks. The clastic units form the uppermost and lowermost parts of the succession and they comprise of sandstones, fine-grained quartzites, siltstones and red shales (Junner, 1940). The sandstones overlie the basal beds of shale and the conglomerate and tillite overlie the sandstone (Dapaah-Siakwan and Gyau-Boakye, 2000). The jasperoids occur as series of bedded, normally red cherts of massive appearance and sometimes brecciated (Osae et al., 2006). According to Junner (1940) and Jones (1990), some of the jasperoids may have been formed by metasomatic alteration of clastic units, limestone and volcanic rocks. The serpentinites which are rich in chromite are schistose and massive. The serpentinites and volcanic rocks are unrelated since the serpentinites mark a continental collision at about 500 Ma whereas the volcanic rocks erupted probably during a period of tension related to continental break-up at about 650 Ma (Jones, 1990).

Buem Structural Unit are generally not metamorphosed, although a weak metamorphic and metasomatic imprints, which are marked by alterations in the volcanics, formation of quartz veins in the volcanics and the sandstones have been identified (Affaton et al., 1996). Deformation in the Buem Structural Unit are largely as the result of thrust tectonics. Studies by Wright et al. (1985), indicated that the thrust sheets are closely associated with serpentinized ultramafic bodies. The mafic and ultramafic units probably represent tectonically emplaced slices of paleo-oceanic crust caught up in the suturing of adjacent continental blocks during the Pan-African orogeny (Griffis et al., 2002). Consequently, the development of imbricated thrust systems and duplexes in the rocks with a large-scale thrusting towards the west of the unit.

In general, folds in the rocks are not well developed but chevron folds occur in the fine-grained material (Kesse, 1985). The Buem generally strikes north northeast to south southwest and dips in the southeastern direction (Kesse, 1985). Kesse (1985) considered the Buem to be older than the Voltaian basin sediments. However, detailed studies by Affaton et al. (1980) indicate that the Buem is probably a lateral equivalent of the Kwahu Group of the Voltaian Basin. This assertion is supported by Kalsbeek et al. (2008), who showed that the Buem Structural Unit is a lateral equivalent of the Kwahu Group.

2.3 A GEOCHEMICAL APPROACH

From studies, various techniques and approaches have been proposed for the provenance studies of fine-grained sedimentary and metasedimentary rocks. However, geochemical method was used for this study because of the fine-grained and metamorphosed nature of the rock samples. This method usually involves analysis of the major and trace element (including REEs) concentration in sediments and is mostly employed in the provenance studies of fine-grained sedimentary rocks for the following reasons:

a) The rare-earth elements (REEs) have low solubilities and short residence times in the ocean (McLennan and Taylor, 1991). This allows them to be faithfully preserved in terrigeneous sediments and validate their use as accurate indicators of provenance;

b) The rare-earth elements (REEs) and high field strength elements are relatively immobile during diagenesis, weathering, hydrothermal overprint and low-grade metamorphism and therefore may provide important clues on the provenance of clastic sediments (McLennan et al., 1993; Johnsson, 1993; McCann, 1991; McLennan and Taylor, 1991; McLennan, 1989; Bhatia and Crook, 1986; Bhatia, 1985; Taylor and McLennan, 1985)

c) The major and trace elements (including REES) allow for the identification of the occurrence and extent of some secondary processes such as weathering (Nesbitt and Young, 1982, 1984; McDaniel and McLennan, 1991; Cox et al., 1995; Fedo et al., 1995, 1996).

d) It can be used to study mineralogically altered rocks such as phyllites which would have been difficult to study by optical methods (Potter, 2005, Barbera et al., 2006).

CHAPTER THREE

MATERIALS AND METHODS

This research was carried out in two main phases.

3.1 DESK STUDY AND FIELD WORK

3.1.1 Desk Study

A desk study and literature review were carried out prior to reconnaissance survey and main field work. These activities were performed to obtain a good knowledge of pre-existing work in the study area. At this stage, literature pertinent to the research were gathered and reviewed via electronic search and consultation of scientific journals, articles, publications and existing books about the study area and research interest. Literature gathered and reviewed were on geology of the study area, geochemistry and provenance studies of sedimentary and metasedimentary rocks.

In addition, topographical and geological maps of the area were so as to decide the suitable time to embark on the field work, how the area could be accessed and the number of days needed for the field work. Field logistics required to undertake the field work were then acquired. The field logistics included Global Position System (GPS), topographic maps of the area, field notebook, dilute hydrochloric acid for carbonate test, geological hammer, tape measure, sample bags, marker pen and other equipment required for the fieldwork.

3.1.2 Field Work

The field work basically involved rock sampling and was carried out for a period of four (4) weeks. The field work was preceded by a reconnaissance survey to ascertain the exposure and distribution of outcrops throughout the area and to learn more about the geology of the study area. The reconnaissance survey lasted five days and was helped by information gathered from pre-existing geological maps of the area. The reconnaissance survey was followed by a more detailed rock sampling. Rock locations and sampling were aided by extracting the coordinates of possible locations of phyllites in the study area, which is the rock of interest from the recent geological map of Ghana. These coordinates were then input into the global positioning system (GPS). The GPS showed positions in terms of WGS 84 geo-reference coordinates at any time. From the reconnaissance survey, the phyllites mostly outcropped along road cuts, pits and quarries in the study area. This knowledge together with the coordinates extracted from the recent geology of Ghana, aided in the location and sampling of rocks in the study area. During sampling, outcrops were described based on colour, texture and structure and accordingly given field names. Structural attitudes were measured where appropriate.

About 50 representative samples of phyllites were collected from outcrops on the Akuapim range of the Togo Structural Unit, southeastern Ghana. These samples were taken at irregular intervals from locations in the study area to give a representative view of the study area. Fresh rock exposures were scarce due to intense tropical weathering. Great care was taken in collecting the least altered samples for geochemical analysis. This is because sample collection for geochemical studies is often hampered by deep lateritic weathering and thick soil cover (Asiedu et al., 2004). The samples were given identities (I.D), placed in sample bags and marked with names corresponding to the sample ID and sent to the laboratory for mineralogical and geochemical analyses.

3.2 LABORATORY WORK

3.2.1 Sample preparation

Sample preparation began with the removal of weathered surfaces by chipping until a fresh surface was achieved. Great care was taken in selecting the least altered samples for the analysis. Samples containing visible quartz veins, which may represent remobilization of elements, were avoided for the analysis. Any stained chips were also discarded. Rock samples selected for whole-rock geochemical analyses were cut into rectangular blocks with dimensions of about 7 centimetres in length, 3 centimetres in breadth and about 2 centimetres in thickness using a rock saw with a diamond blade. The samples for geochemical analysis were selected based on their locations to give a representative view of the study area. They were labelled, packed in a box and sent to the ALS laboratory in Vancouver, Canada for geochemical analyses.

Some of the rock samples were then selected for mineralogical analysis by the X-Ray diffraction (XRD) method which was carried out at the Department of Physics of the University of Ghana. The X-ray diffraction (XRD) method was used because of the fine-grained and metamorphosed nature of the sediments (from hand samples) which made it difficult to determine the mineralogical content of the rocks using optical methods such as petrographic microscope. Rock samples selected for mineralogical analyses were dried and pulverized using an agate hand mortar. Agate hand mortar was used as it does not contribute metals to sample powders as do steel or tungsten carbide components. Additionally, grinding using agate hand mortar provides highly controlled conditions which aid in virtual removal of contamination from the mortar and pestle set itself. During grinding, the samples were frequently scraped from the mortar surfaces using a spatula to ensure the grinding of all particles. The pulverized samples were sieved (< 200 mesh) and the sieved sample reground. Care was taken to sweep the pestle over the powder to produce very fine powder. In order to avoid cross-contamination, ethanol was used to clean the mortar and pestle several times between samples, followed by some amount of the next sample to be ground. About 100-200 mg of each of the powdered samples were sealed into labelled sample bags and sent to the laboratory for X-ray diffraction analysis.

3.2.2 Mineralogical analysis

Ten (10) rock (phyllites) samples were selected for mineralogical analysis using the X-ray diffraction (XRD) method at the Department of Physics of the University of Ghana. Mineralogical analyses were carried out on the selected samples for phase (mineral) identification and quantification. The samples were selected based on the colour and compositional differences of the various phyllites observed in the field. The XRD whole-rock analyses were conducted using a PANalytical Empyrean series 2 diffractometer with the setting conditions of Cu-Kα, 45 kV, 40 mA, slits (divergence slit size = 0.4354 mm, receiving slit size = 0.38 mm).

X-ray diffraction (XRD) analysis involved the use of an X-ray tube, a sample holder and an X-ray detector. About 0.5 g of very fine pulverized sample was tightly packed in the sample holder as loose powders will give poor intensities. The sample was then rotated in the path of the collimated X-ray beam. As the sample and detector are rotated, the intensity of the reflected

X-rays is recorded. When the geometry of the incident X-rays striking the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity is detected. The detector records and processes this X-ray signal converting it to a count rate which is then output to a computer monitor. The semi-quantitative percentages of mineral phases were obtained by the Rietveld method on the basis of the published crystal structure data. Depending on the structure and matrix, the detection limit is specified between 0.5 and 5 wt%. The total of all mineral phases detected was recalculated to 100 %.

3.2.3 Geochemical analysis

Twenty-eight (28) selected samples were sent to the ALS laboratory mentioned above for their whole rock major and trace elements (including REEs) analyses. Major and trace elements analyses were carried out by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and multi elements fusion Inductively Coupled Plasma-Mass spectrometry (ICP-MS), respectively. Loss of ignition was determined at 1000^0C. For the major elements analyses, a mixture of about 0.200g of prepared sample and lithium metaborate was fused in a furnace at 1025^0C. The resulted melt was then cooled and dissolved in an acid mixture. The acid mixture contained nitric, hydrochloric and hydrofluoric acids. The solution was then analysed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for the major element composition.

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 analysed using the ICP-AES. A 0.25 g prepared sample was digested with perchloric, nitric, hydrochloric and hydrofluoric acids. Dilute hydrochloric acid was then added to the residue and the solution was analysed by the ICP-AES. Results obtained were corrected for spectral inter-element interferences (ALS laboratory). Precision is better than 2%.

3.2.4 Data analyses

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 graph software version 5.6.5 was used to plot variation diagrams, ternary diagrams and discrimination diagrams. Coreldraw 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 maps.

CHAPTER FOUR

RESULTS

4.1 PETROGRAPHY

4.1.1 Field Observations

Phyllites in the study area form prominent exposures and outcrop in many localities including Kponkpo, Agyemanti, Ayimensa, Aburi and Peduase. In hand specimen, the phyllites are mostly grey to reddish brown, fine-grained and thinly foliated. In general, the phyllites are composed of quartz, and muscovite with some amount of feldspars. Most of the phyllites observed along road-cuts are highly weathered and brittle which made sampling difficult in the study area. Three varieties of phyllites occur within the study area based on colour and composition. The three varieties of phyllites observed are carbonaceous (dark-grey) phyllites, iron-stained (reddish) phyllites and micaceous (brownish-grey) phyllites.

4.1.1.1 Carbonaceous (dark-grey) Phyllites

The carbonaceous (dark grey) phyllites were observed along Peduase road-cut and Kponkpo. In hand specimen (Figure 4.1), the carbonaceous phyllites are dark-grey, fine-grained and thinly foliated. These phyllites fizz when drops of dilute (5% to 10%) hydrochloric acid were placed on them indicating the presence of carbonate minerals. From hand samples, phillites showed quartz, pyrite and some amount of feldspar. The pyrite minerals were observed along the foliation planes of the phyllites suggesting a post-depositional process. The presence of pyrite in the phyllites indicates sulphate and organic content in the sediments. The carbonaceous phyllites are thinly foliated and crenulated. The dark grey coloration of the phyllites is probably due to the presence of organic carbon (graphite) (Potter et al., 1980).

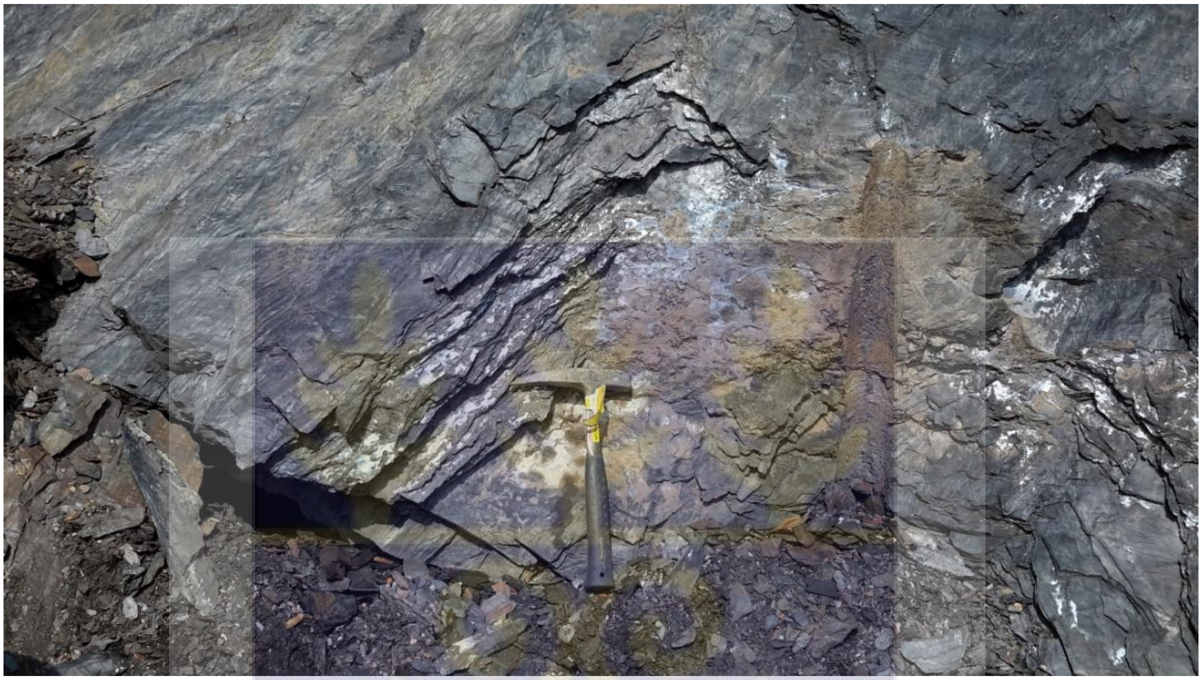

Figure 4.1 Field photograph of thinly foliated carbonaceous phyllites observed along Peduase road-cut. Picture taken facing northwest.

4.1.1.3 Iron-stained (reddish) Phyllites

The iron-stained (reddish) phyllites were observed at Agyemanti, along the Peduase road-cut and Kponkpo. Mesoscopically (Figure 4.2), the rock is reddish, fine-grained with thin foliations. From hand samples, phyllites contain quartz, siderite and some feldspar content. The presence of siderite is indicative of the presence of sulphate and organics, probably associated with freshwater (Kholodov and Butuzowa, 2008). The reddish phyllites did not fizz when drops of dilute (5% to 10%) hydrochloric acid were placed on them. The reddish coloration of the phyllites is probably due to the oxidization of iron oxide in the rocks. The iron-stained phyllites are weathered and contain some clay minerals.

Figure 4.2 Field photograph of iron-stained phyllites observed along Peduase road-cut. Picture taken facing northwest.

4.1.1.3 Micaceous (brownish-grey) Phyllites

The micaceous (brownish-grey) phyllites observed occur in Agyemanti, along Peduase road-cut and Kponpko. These phyllites are brownish-grey, fine-grained and thinly foliated (Figure 4.3). From hand samples, phyllites are composed of quartz, chlorite and some feldspar content (Table 4.1). The brownish-grey phyllites did not fizz when drops of dilute (5% to 10%) hydrochloric acid were placed on them. The micaceous phyllites are highly weathered and contain some clay minerals such as illite.

From field relations, the micaceous phyllites underlie the carbonaceous (dark-grey) phyllites which is overlain by the iron-stained (reddish) phyllites (Figure 4.4).

Figure 4.3 Field photograph of micaceous phyllites observed along Peduase road-cut. Picture taken facing northwest.

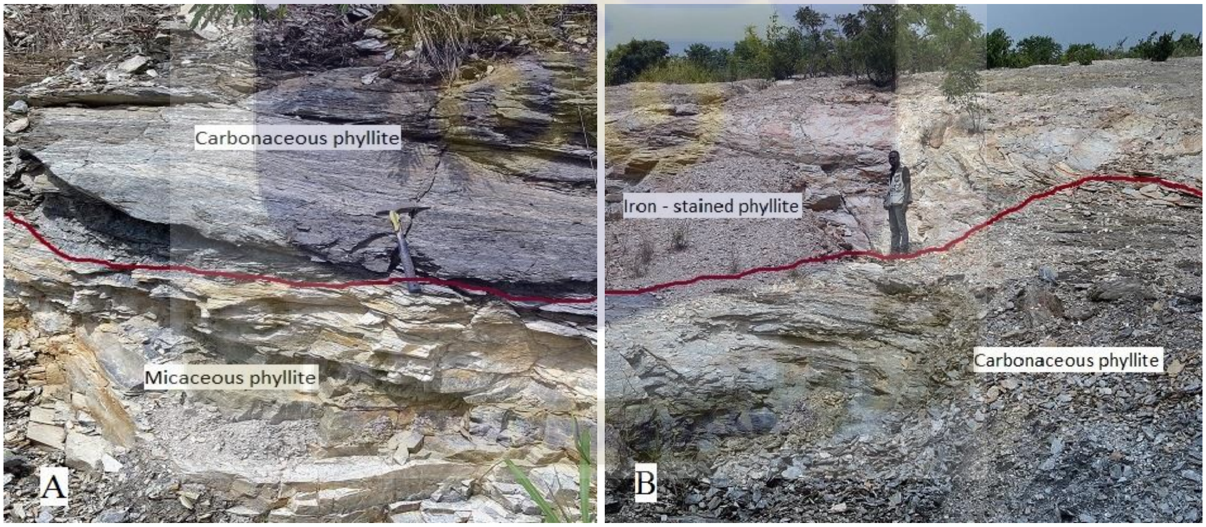

Figure 4.4 (a) Carbonaceous phyllite underlain by micaceous phyllites, (b) Carbonaceous phyllite overlain by iron-stained phyllites. Pictures taken facing northwest.

4.1.1.4 Structures

The rocks within the study area have undergone deformation which is characterized by the presence of foliations, crenulations, lithons observed in the phyllites.

4.1.1.4.1 Foliations

The phyllites of the study area are thinly foliated with an average thickness of about 0.2 cm (Figure 4.5). In general, the foliation surface strikes northeast-southwest and dip in the southeastern direction (Kesse, 1985).

Figure 4.5 Field photograph of thinly foliated phyllites observed along Peduase road-cut. Picture taken facing northwest

4.1.1.4.2 Crenulations

The phyllites of the study area have several crenulations which depict deformation probably due to tensile stress exerted on the rock.

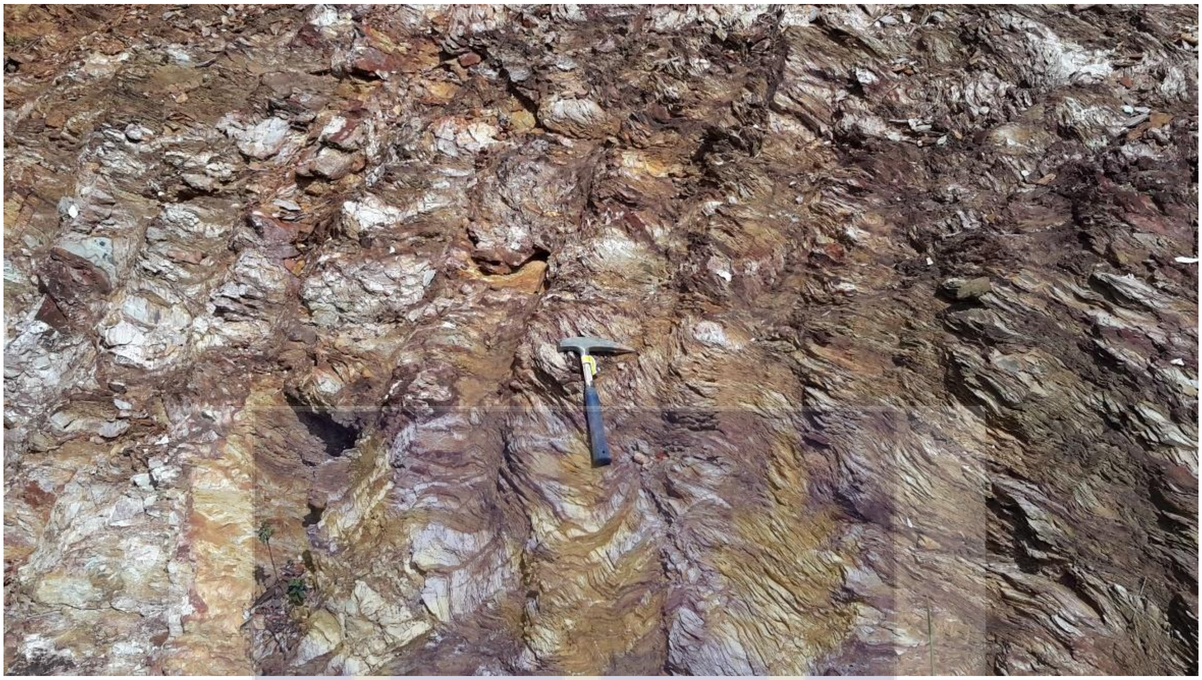

Figure 4.6 Crenulations in phyllites observed along Peduase road-cut. Picture taken facing northwest.

4.1.1.4.3 Lithons

In general, the rocks found within the study area are phyllites and quartzites with the quartzites overlying the phyllites. However, at some places in the study area, the quartzites occur as lithons within the phyllites. These structures were observed along the Peduase road-cut. This structure formed probably due to the tensile stress which occurred in the rock which causes the more competent rock to stretch and break into oval shape. The lithons are sheared and the direction of shearing in the southeastern direction.

Figure 4.7 Lithon in phyllites observed along Peduase road-cut. Picture taken facing northwest.

4.1.2 Mineralogical Content of the rocks

The mineralogical compositions of the analysed phyllites are given in Table 4.1. These include three (3) samples of carbonaceous (dark-grey), four (4) samples of iron-stained (reddish) phyllites and three (3) samples of micaceous (brownish -grey) phyllites. Quartz is the abundant mineral with concentrations between 30-49 wt% (average 35.5 wt%). The results show relatively high contents of muscovite and chlorite of 8-27 wt% (average 17.8 wt%) and 15-25 wt% (average 17.2 wt%), respectively. The phyllites also have relatively low feldspar content of 10-20 wt% (average of 14.6 wt%). Samples KP8A, KP16B and KP18A which are the carbonaceous (dark-grey) phyllites sampled exhibit calcium carbonate ($CaCO_3$) and graphite contents of 6-21 wt% and 13-21 wt%, respectively. The iron-stained (reddish) phyllites (samples KP2A, KP10A, KP15A and KP19A) show siderite content of 10-18 wt%. Sample KP18A show illite content of 9 wt%.

Table 4.1 Mineralogical composition of whole rock samples of Neoproterozoic phyllites from the Akuapim range detected

Sample	KP8A	KP16B	KP18A	KP2A	KP10A	KP15A	KP19A	KP1A	KP3A	KP5A
Minerals (wt%)										
Quartz	30	32	31	35	49	32	31	47	30	37
Feldspar	11	12	12	14	10	13	16	20	24	13
Muscovite	13	8	9	19	13	15	27	18	23	25
Chlorite	10	12	18	15	16	22	16	15	23	25
Siderite				17	12	18	10			
$CaCO_3$	21	15	6							
Graphite	15	21	15							
Illite			9							

4.2 GEOCHEMISTRY

The results of major and trace element (including REEs) analyses of twenty eight (28) rock samples of Neoproterozoic phyllites from the Akuapim range of the Togo Structural Unit are listed in Table 4.2.

4.2.1 Major Elements

The phyllites have relatively high SiO_2 concentrations of 52.6-94.1 wt% (average 75.14 wt%). They show somewhat variable and high concentrations of Al_2O_3 ranging from 4.7-20.41 wt% (average 13.25 wt%) and relatively high concentrations of K_2O between 0.77 to 6.38 wt% (average 3.90 wt%). The results also show low TiO_2, MgO, MnO, CaO and Na_2O concentrations of 0.12 – 1.06 wt%, 0.07-1.75 wt%, 0.01-0.77 wt%, 0.01-0.02 wt% and 0.01-0.46 wt%, respectively. In addition, the phyllites exhibit relatively low Fe_2O_3 concentrations averaging 3.09 wt%. The phyllites exhibit variable and relatively high SiO_2/Al_2O_3 values of 2.98-30.55 (average 8.17). They also show high K_2O/Na_2O and Al_2O_3/TiO_2 values of 8.93-139.00 with an average of 54.31 and 18.31-33.57 (average 21.87), respectively.

From the calculation of the chemical index of alteration (CIA), the phyllites have high CIA values of 70.88-79.92 % (average 74.73 %). The phyllites also show relatively high plagioclase index of alteration (PIA) and chemical index of weathering (CIW) values of 94.97-98.94 % (average 97.68 %) and 96.20-99.28 % (average 98.36 %), respectively. Additionally, the phyllites have low index of compositional variability (ICV) values of 0.34-1.40 (average 0.64). Comparing with the Post-Archean Australian (average) Shale (PAAS; Taylor and McLennan, 1985), the phyllites show general depletion in major oxides with the exception of SiO_2 and MnO which are enriched relative to PAAS (Figure 4.8).

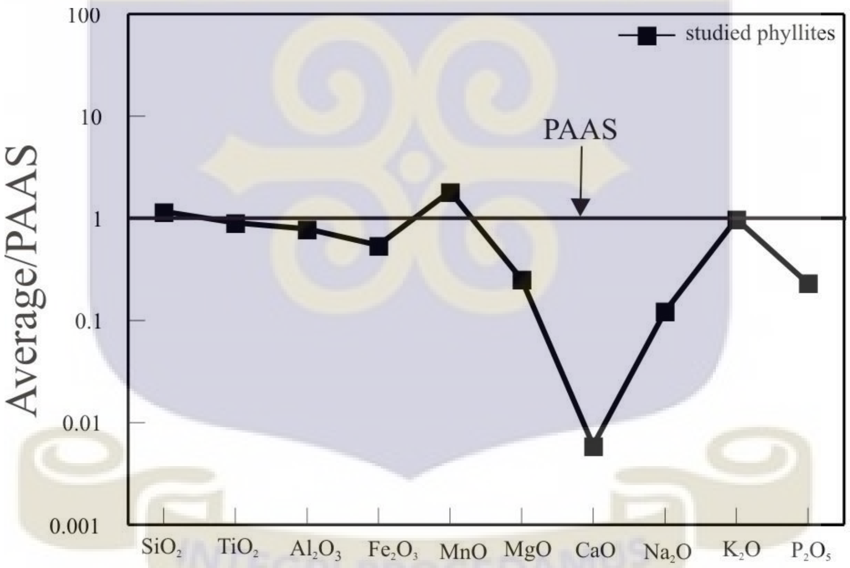

Figure 4.8 PAAS-normalized average major element compositions for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana. Post-Archean Australian (average) Shale (PAAS) data are from Taylor and McLennan (1985).

Table 4.2 Chemical compositions of the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana

Sample	KP1A	KP2A	KP3A	KP4A	KP5A	KP6A	KP7A	KP8A	KP9A	KP10A	KP11A	KP11B	KP12A	KP13A
Major oxides (wt%)														
SiO_2	68.8	62.3	71.5	93.4	90.5	86.7	82.3	52.6	90.4	94.1	70.7	73.4	79	76.8
TiO_2	1.06	0.99	0.9	0.2	0.17	0.35	0.45	0.77	0.2	0.12	0.7	0.71	0.54	0.56
Al_2O_3	20.1	19.65	17.95	4.92	4.75	7.46	8.3	15.25	4.57	3.08	16.1	13.55	12	12.2
Fe_2O_3	0.81	4.04	1.4	0.41	0.42	2.19	4.06	13.95	1.85	1.28	2.57	2.65	1.37	1.4
MnO	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.77	0.01	0.01	<0.01	<0.01	<0.01	<0.01
MgO	0.21	1.28	0.62	0.16	0.16	0.11	0.12	1.66	0.29	0.07	1.08	0.85	0.71	0.73
CaO	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.17	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na_2O	0.46	0.1	0.12	0.02	<0.01	0.06	0.07	0.14	0.02	0.01	0.08	0.06	0.05	0.05
K_2O	4.74	6.38	5.04	1.39	1.39	2.05	2.34	4	1.11	0.77	5.61	4.67	4.29	4.51
P_2O_5	0.03	0.02	0.01	0.01	<0.01	0.01	0.02	0.1	0.01	0.01	0.01	0.01	<0.01	0.01
LOI	3.43	3.93	3.36	1.08	1.1	1.6	1.98	8.88	1.17	1.1	3.09	2.69	2.21	2.24
Total	99.67	98.72	100.92	101.61	98.53	100.55	106.56	90.58	99.57	102.55	99.56	98.13	100.23	98.79
CIA	77.24	73.44	75.99	75.98	75.53	76.16	75.8	78.49	78.01	72.13	72.38	71.67	71	72.77
PIA	94.97	98.45	98.3	98.53	98.94	97.82	95.29	98.51	98.48	98.53	98.64	98.65	98.65	98.24
CIW	96.2	98.99	98.81	98.97	99.28	98.46	96.58	98.89	98.89	99.08	99.14	99.17	99.18	98.87
ICV	0.34	0.65	0.44	0.44	0.45	0.63	1.4	0.76	0.73	0.62	0.66	0.58	0.59	0.58
SiO_2/Al_2O_3	3.42	3.17	3.98	18.98	19.05	11.62	3.45	19.78	30.55	4.39	5.42	6.58	6.3	5.89
K_2O/Na_2O	10.3	63.8	42	69.5	139	34.17	28.57	55.5	77	70.13	77.83	85.8	90.2	54.88
K_2O/Al_2O_3	0.24	0.32	0.28	0.28	0.29	0.27	0.26	0.24	0.25	0.35	0.34	0.36	0.37	0.34
Al_2O_3/TiO_2	18.96	19.85	19.94	24.6	27.94	21.31	19.81	22.85	25.67	23	19.08	22.22	21.79	20.79
Trace elements (ppm)														
Sc	14	16	14	3	3	5	7	14	3	3	12	10	10	11
V	115	118	90	17	17	28	36	106	19	15	80	61	65	69
Cr	90	70	60	20	20	30	40	60	20	10	40	40	40	40
Co	<1	3	1	<1	1	2	5	25	5	2	4	3	4	4
Ni	5	10	11	5	7	5	9	24	14	14	7	8	11	10
Cu	3	10	2	4	4	10	23	5	6	12	17	11	5	5
Rb	154	210	165	41.4	41.6	63.8	68.1	126.5	35.4	24	158.5	137	117.5	120
Sr	205	33.5	46.9	11.6	10.6	37	44.3	82.7	13.5	9.5	24.7	20.6	13.8	14.2
Cs	3.8	5.41	3.62	0.81	0.77	1.44	1.69	3.2	0.7	0.5	4.71	4.09	2.85	2.98
Ba	1575	1165	945	228	223	411	437	777	281	155.5	978	843	755	775
Y	33.2	47.8	34.4	14.4	13.4	19.1	27.8	39.4	11.6	10	26.7	24.9	16.3	17.2
Zr	479	559	460	407	331	542	594	285	271	274	406	468	378	387
Hf	12.3	14.7	11.8	10	8.4	13.2	15.3	7.7	7.1	6.6	10.5	12	9.8	9.9
Nb	20	18.2	18.3	4.6	4.2	7	8.8	15.4	4	2.7	13.6	14.2	9.7	10
Ta	1.4	1.3	1.3	0.3	0.3	0.5	0.6	1.1	0.3	0.2	0.9	1	0.7	0.7
Th	18.55	17	17.35	4.73	4.21	6.85	9.83	16.75	4.39	2.84	13	13.55	9.43	9.84
U	3.92	5.06	4.69	1.67	1.52	2.95	2.8	4.21	1.28	1.14	3.36	3.45	3.05	3.13
La	50.8	30.9	41.7	18.2	16.9	22.7	31.5	44.9	19.4	10.7	36.9	34.9	23.6	24.3
Ce	99.8	69.7	81.4	41	39	52.5	73.1	94.8	37.4	24.3	75.1	71.5	50.1	51.2
Pr	10.35	7.71	9.11	4.94	4.59	5.97	8.27	10.5	4.12	2.94	8.34	7.84	5.43	5.46
Nd	35.8	30.2	34	18.6	18.4	23.8	33.1	42	15.9	12.2	30.7	29	19.7	20.8
Sm	6.11	6.66	6.62	3.9	3.43	4.77	6.04	8.69	2.85	2.54	5.41	5.21	3.45	3.39
Eu	1.16	1.31	1.21	0.57	0.58	0.78	1.2	1.6	0.54	0.43	0.97	0.87	0.58	0.61
Gd	4.86	6.78	5.61	3.15	2.75	3.39	5.06	7.91	2.28	1.87	4.34	3.69	2.57	2.68
Tb	0.86	1.28	0.92	0.41	0.43	0.52	0.79	1.16	0.32	0.3	0.74	0.64	0.41	0.43
Dy	6.02	8.46	6.12	2.63	2.48	3.35	5.17	7.35	2.15	1.78	4.97	4.41	2.92	3.01
Ho	1.22	1.82	1.27	0.53	0.54	0.68	1.05	1.42	0.44	0.38	1.06	0.95	0.62	0.67
Er	3.64	5.56	3.85	1.66	1.41	2.02	2.78	4.27	1.32	1.05	2.96	2.83	2.18	2.32
Tm	0.54	0.77	0.57	0.25	0.18	0.32	0.43	0.55	0.19	0.16	0.47	0.44	0.31	0.33
Yb	3.75	5.12	3.86	1.44	1.41	2.23	2.94	3.96	1.48	1.06	3.3	3.11	2.28	2.51
Lu	0.6	0.73	0.6	0.27	0.23	0.34	0.45	0.58	0.22	0.16	0.48	0.49	0.37	0.39
Rb/Sr	0.75	6.27	3.52	3.57	3.92	1.72	1.54	1.53	2.62	2.53	6.42	6.65	8.51	8.45
Th/U	4.73	3.36	3.7	2.83	2.77	2.32	3.51	3.98	3.43	2.49	3.87	3.93	3.09	3.14
Th/Sc	1.33	1.06	1.24	1.58	1.4	1.37	1.4	1.2	1.46	0.95	1.08	1.36	0.94	0.89
Cr/Th	4.85	4.12	3.46	4.23	4.75	4.38	4.07	3.58	4.56	3.52	3.08	2.95	4.24	4.07
∑REE	225.51	177	196.84	97.55	92.33	123.37	171.88	229.69	88.61	59.87	175.74	165.88	114.52	118.1
La_N/Yb_N	9.13	4.07	7.28	8.52	8.08	6.86	7.22	7.64	8.84	6.81	7.54	7.57	6.98	6.53
La_N/Sm_N	5.23	2.92	3.96	2.94	3.1	2.99	3.28	3.25	4.28	2.65	4.29	4.21	4.3	4.51
Gd_N/Yb_N	1.05	1.07	1.17	1.77	1.57	1.23	1.39	1.61	1.24	1.42	1.06	0.96	0.91	0.86
Eu/Eu*	0.65	0.6	0.61	0.5	0.58	0.59	0.66	0.59	0.65	0.6	0.61	0.61	0.6	0.62

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 = $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O)]\times100$, ICV = $[CaO+K_2O+Na_2O+Fe_2O_3(t)+MgO+MnO+TiO_2]/Al_2O_3$,

Eu/Eu* = $Eu_N/(Sm_N{*}Gd_N)^{1/2}$, where $_N$ refers to normalized values.

Normalizing values are from Boynton (1984).

Table 4.2 continued. Chemical compositions of Neoproterozoic phyllites from the Akuapim range, southeastern Ghana

Sample	KP14 A	KP14 B	KP15 A	KP15 B	KP16 A	KP17 A	KP17 B	KP18 A	KP18 B	KP19 A	KP19 B	NP11	NP12	NP13 B
Major oxides (wt%)														
SiO_2	77.2	83.1	70	74	79.2	77.1	90.1	64.8	76	69.3	68	60.75	61.54	60.36
TiO_2	0.63	0.39	0.8	0.8	0.55	0.68	0.14	0.9	0.69	0.88	0.84	0.934	0.848	0.882
Al_2O_3	13.1	9.15	16.6	14.65	11.85	12.95	4.7	17.4	12.75	19.85	18.6	20.41	19.67	19.31
Fe_2O_3	1.7	1.3	2.26	2.25	1.5	1.39	0.59	6.79	2.21	1.91	4.04	7.05	6.61	8.46
MnO	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.005	0.022	0.221
MgO	0.88	0.62	1.18	1.07	0.78	0.82	0.28	1.13	0.81	0.22	0.23	0.71	1.75	1.51
CaO	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	<0.01	<0.01
Na_2O	0.08	0.03	0.08	0.06	0.06	0.09	0.03	0.13	0.1	0.38	0.33	0.45	0.34	0.4
K_2O	4.39	3.41	5.97	5.15	4.21	4.25	1.5	5.65	4.53	5.19	4.55	4.02	4.1	3.91
P_2O_5	0.01	0.01	0.02	0.01	0.02	0.02	0.05	0.02	0.02	0.03	0.04	0.1	0.05	0.08
LOI	2.51	1.7	2.91	2.76	2.2	2.57	1.1	3.81	2.48	3.72	3.69	5.3	4.17	4.8
Total	99.71	100.94	99.69	99.99	100.39	99.89	98.51	100.65	99.61	101.5	100.34	99.749	99.11	99.943
CIA	70.88	71.52	72.02	75.69	71.72	73.1	73.54	73.27	71.49	76.02	77.22	79.92	79.68	79.73
PIA	98.78	98.54	98.73	97.74	98.42	98.05	97.85	97.99	97.72	95.68	96.06	95.39	96.35	95.71
CIW	99.27	99.11	99.21	98.42	99.02	98.73	98.58	98.68	98.59	96.86	97.07	96.33	97.15	96.62
ICV	0.63	0.62	0.63	0.84	0.6	0.55	0.54	0.83	0.65	0.41	0.52	0.62	0.68	0.78
SiO_2/Al_2O_3	9.08	4.22	5.05	9.92	6.68	5.95	19.17	3.72	5.96	3.49	3.66	2.98	3.13	3.13
K_2O/Na_2O	113.67	74.63	85.83	33.43	70.17	47.22	50	43.46	45.3	13.66	13.79	8.93	12.06	9.78
K_2O/Al_2O_3	0.37	0.36	0.35	0.28	0.36	0.33	0.32	0.32	0.36	0.26	0.24	0.2	0.21	0.2
Al_2O_3/TiO_2	23.46	20.75	18.31	18.44	21.55	19.04	33.57	19.33	18.48	22.56	22.14	21.85	23.2	21.89
Trace elements (ppm)														
Sc	10	7	14	12	9	12	3	17	12	15	17	19	19	19
V	58	37	88	79	51	69	27	114	74	88	97	87	90	84
Cr	40	30	50	60	40	50	20	70	50	60	70	63	65	62
Co	3	2	4	2	1	1	<1	3	2	1	<1	3	14	22
Ni	8	3	9	8	5	10	4	10	4	8	3	<20	21	22
Cu	7	2	4	3	3	1	1	38	10	12	19	18	21	32
Rb	124.5	95.4	170	147.5	120	128	44.7	161.5	126.5	172	165	200	209	190
Sr	18.4	17.5	25.2	21.2	22.9	29.9	18.7	32.2	30.2	75.9	78.7	70	60	74
Cs	3.64	3.02	4.72	4.26	3.93	4.35	1.49	5.46	4.46	4.81	4.75	7.9	7.8	9.5
Ba	759	680	1050	892	651	772	260	789	622	875	840	579	647	591
Y	24.7	25.3	41.5	31.7	21.9	33.7	9.3	34.1	25.9	34.7	42.6	30	32	36
Zr	571	719	486	568	374	558	132	320	349	517	429	196	182	184
Hf	14.8	16.9	12.5	14.5	10.1	13.7	3.4	8.4	9.1	13.5	11.3	5.6	5.7	5.8
Nb	12.4	8.4	16.4	16.2	11.6	13.2	2.7	17.4	12.9	18.7	17.5	17	17	18
Ta	0.8	0.6	1.2	1.2	0.8	1	0.2	1.2	1	1.4	1.3	1.5	1.5	1.4
Th	12.5	8.93	17.05	16.8	11.45	13.45	4.06	17.65	12.65	19	19.85	22.7	20.9	21.1
U	3.13	2.55	3.66	3.89	2.95	2.96	0.94	4.78	2.84	4.54	4.51	2.9	2.9	3.3
La	31.5	28.8	60.7	37.2	33.4	44.4	122	35.3	32.4	42.6	46	50.5	50.5	56.6
Ce	66.2	65.3	139.5	76	73.3	100.5	261	87.1	68.1	77.8	92.1	106	112	131
Pr	7.31	7.21	16.65	8.51	8.08	11.2	26.4	9.87	7.74	8.28	10.55	10.9	11.4	13.6
Nd	28.5	27.7	67.3	31.9	30	44.3	95.5	39.1	28.4	29.6	41.7	39.6	42.3	51.7
Sm	5.24	4.92	12.95	5.79	5.32	8.79	13.85	7.9	5.07	5.52	8.03	7.7	8.3	10.2
Eu	0.95	0.93	2.2	1.11	0.99	1.59	2.39	1.3	1.01	1.1	1.21	1.34	1.41	1.81
Gd	4.11	4.32	9.6	4.73	4.09	7.51	6.51	6.34	4.01	5.32	7.89	6.1	6.4	8.2
Tb	0.66	0.66	1.37	0.79	0.63	1.11	0.56	0.99	0.69	0.9	1.26	1	1.1	1.3
Dy	4.55	4.34	7.72	5.87	3.91	6.45	2.45	6.37	4.84	6.09	7.93	6	6.5	7.3
Ho	0.96	0.93	1.59	1.22	0.88	1.29	0.37	1.32	0.98	1.3	1.6	1.2	1.3	1.4
Er	2.87	2.64	4.62	3.5	2.63	3.75	1.08	3.86	3.16	3.93	4.77	3.6	3.9	4.2
Tm	0.44	0.42	0.66	0.57	0.43	0.52	0.14	0.61	0.43	0.6	0.65	0.58	0.63	0.66
Yb	3.14	2.89	4.51	3.92	2.72	3.64	0.82	3.86	3.07	4.08	4.63	3.6	3.7	3.9
Lu	0.49	0.47	0.7	0.61	0.42	0.51	0.14	0.58	0.45	0.59	0.72	0.5	0.54	0.58
Rb/Sr	6.77	5.45	6.75	6.96	5.24	4.28	2.39	5.02	4.19	2.27	2.1	2.9	3.5	2.6
Th/U	3.99	3.5	4.66	4.32	3.88	4.54	4.32	3.69	4.45	4.19	4.4	7.8	7.1	6.5
Th/Sc	1.25	1.28	1.22	1.4	1.27	1.12	1.35	1.04	1.05	1.27	1.17	1.19	1.1	1.11
Cr/Th	3.2	3.36	2.93	3.57	3.49	3.72	4.93	3.97	3.95	3.16	3.53	2.79	3.12	2.93
∑REE	156.92	151.53	330.07	181.72	166.8	235.56	533.21	204.5	160.35	187.71	229.04	238.62	249.98	292.45
La_N/Yb_N	6.76	6.72	9.07	6.4	8.28	8.22	100.31	6.17	7.12	7.04	6.7	9.46	9.2	9.78
La_N/Sm_N	3.78	3.68	2.95	4.04	3.95	3.18	5.54	2.81	4.02	4.85	3.6	4.13	3.83	3.49
Gd_N/Yb_N	1.06	1.21	1.72	0.97	1.21	1.66	6.41	1.33	1.05	1.05	1.38	1.37	1.4	1.7
Eu/Eu*	0.63	0.62	0.6	0.65	0.65	0.6	0.77	0.56	0.68	0.62	0.46	0.6	0.59	0.61

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

CIW = $[Al_2O_3/(Al_2O_3+CaO^*+Na_2O)]\times100$, 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).

4.2.2 Trace Elements (including REEs)

Concentrations and elemental ratios of trace elements such as large ion lithophile elements (LILE) (e.g., K, Sr, Rb, Cs, Ba, Pb), transition metals (e.g., Ni, Cr, Co, V, Sc), high field strength elements (HFSE) (e.g., Zr, Hf, Nb, Ta, Ti, Y), and rare-earth elements (REE) (La-Lu) are listed in Table 4.2 above.

4.2.2.1 Large Ion Lithophile Elements (LILE)

The phyllites show high concentrations of Rb and Ba of 24 to 210 ppm (average 125.6 ppm) and 155.5-1275 ppm (average 698.41 ppm), respectively. They also show Sr and Cs concentrations of 9.5-205 ppm (average 40.8 ppm) and 0.5-9.5 ppm (average 3.8) ppm, respectively (Table 4.2) and Rb/Sr values of 0.75-8.51 (average 4.2).

In comparison with the Post-Archean Australian (average) Shale(PAAS; Taylor and McLennan, 1985), the phyllites exhibit relative depletion of Sr and Cs whereas Rb and Ba have average to above-average concentrations, with the exception of samples KP4A, KP5A and KP6A which show depletion in Rb and Ba relative to PAAS (Figure 4.9).

4.2.2.2 Transition Metals

In general, the phyllites show low concentrations of Sc, V and Cr of 3-19 ppm (average 11.09 pm), 15-118 ppm (average of 67.11 ppm) and 20-90 ppm (average of 46.8 ppm), respectively (Table 4.2). They also show low concentrations of Co and Ni of 1-25 ppm (average 4.34 ppm) and 3-24 ppm (average 9.82 ppm), respectively. The phyllites have relatively high Cr/Ni values of 0.71-23.33 (average 6.29) (Table 4.2).

In comparison with the Post-Archean Australian (average) Shale(PAAS; Taylor and McLennan, 1985), the phyllites show general depletion of V, Cr, Co and Ni with the exception of samples KP8A and NP13B which are slightly enriched in Co relative to the PAAS (Figure 4.9).

4.2.2.3 High Field Strength Elements (HFSE)

The phyllites have high concentrations of Zr ranging from 184-719 ppm (average 408.1 ppm). The phyllites also show Y, Hf and Nb concentrations of 9.3-42.6 ppm (average 27.1 ppm), 3.4-16.9 ppm (average 10.52 ppm) and 2.7-18.7 ppm (average 12.5 ppm), respectively. They exhibit Ta, Th and U concentrations of 0.2-1.5 ppm (average 0.92 ppm), 2.8-22.7 ppm (average 13.1 ppm) and 0.9-5.1 ppm (average 3.2 ppm), respectively. The phyllites show relatively high Th/U values of 2.3 – 7.8 (average 4.1).

Comparing to the Post-Archean Australian (average) Shale(PAAS; Taylor and McLenan, 1985), the phyllites show general enrichment of Zr, Hf, Y, Th and U and depletion of Nb with the exception of samples KP7A, KP9A, KP10A, KP11B, KP16A and KP17B which show depletion of Y, Th and U relative to the PAAS (Figure 4.9).

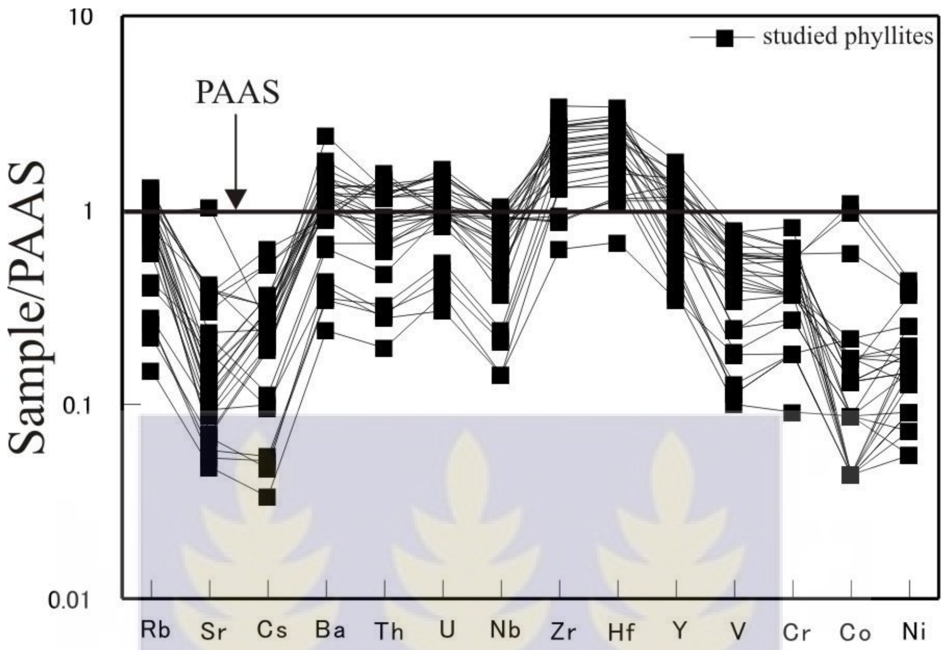

Figure 4.9 PAAS-normalised patterns for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana. Data for Post-Archean Australian (average) Shale(PAAS) are from Taylor and McLennan (1985).

4.2.2.4 Rare-earth element (REEs)

The REE data for the phyllites are somewhat variable with total REE (∑REE) values of 88.61-533.21 ppm averaging of 191.26 ppm which is relatively higher than that of the Post-Archean Australian (average) Shale (PAAS; ∑REE, average = 184.8 ppm; Taylor and McLennan, 1985). The REE data for the phyllites display a single trend based on curve which is similar to the trend of the Post-Archean Australian (average) Shale (Figure 4.10). The phyllites show light rare-earth element (LREE) enrichment relative to the heavy rare-earth elements (HREE) and La_N/Yb_N values of 4.07-9.78 with an average of 7.56 (except for sample KP17B which shows extremely high La_N/Yb_N value of 100.31). The phyllites also exhibit LREE enrichment (La_N/Sm_N) of 0.86-6.41 (average 3.78), low Gd_N/Yb_N values of 0.91-1.77 (average 1.46), except for sample KP17B which has Gd_N/Yb_N value of 6.41. They also show Eu anomalies [($Eu/Eu^* = Eu_N/(Sm_N{*}Gd_N)^{½}$; where $_N$ refers to normalised values] of 0.46-0.77 (average 0.61).

In comparison with the Post-Archean Australian (average) Shale(PAAS; Taylor and McLennan, 1985), the phyllites show a general enrichment of REEs except for samples KP4A, KP5A, KP6A, KP9A, KP10A, KP12A and KP13A which have average to below average REE concentrations compared to the PAAS (Figure 4.11).

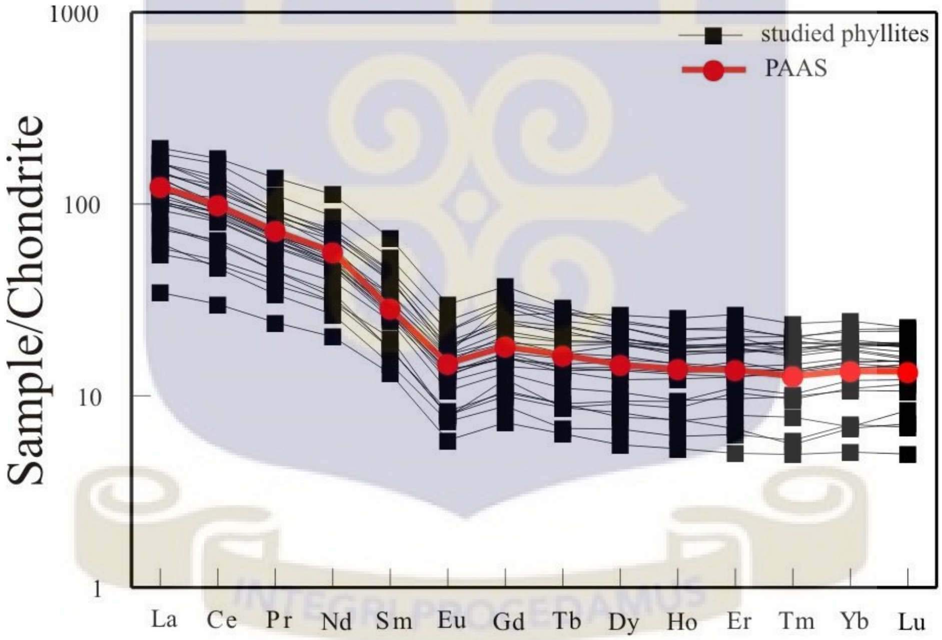

Figure 4.10 Chondrite-normalized REE patterns in Neoproterozoic phyllites from the Akuapim range, southeastern Ghana. Normalizing values are from Boynton (1984). Post-Archean Australian (average) Shale(PAAS) is plotted for comparison (values are from Taylor and McLennan, 1985).

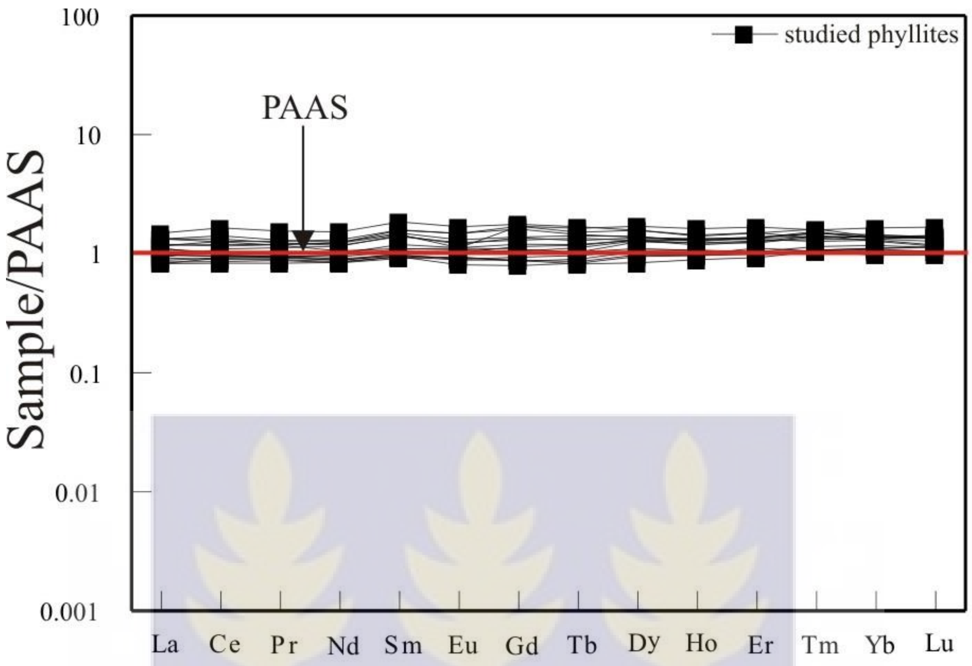

Figure 4.11 PAAS-normalized REE patterns in Neoproterozoic phyllites from the Akuapim range, southeastern Ghana. Post-Archean Australian (average) Shale (PAAS) values are from Taylor and McLennan (1985).

4.2.3 Role of Metamorphism

In general, rocks of the Togo Structural unit have undergone low-grade metamorphism (Kesse, 1985). The phyllites show greenschist minerals such as chlorite which is indicative of low-grade metamorphism (Table 4.1). Siderite in the sediments may suggest that the rocks have undergone a low-grade metamorphism as siderite is extremely unstable and undergoes secondary alterations during high-grade metamorphism (Table 4.1; Kholodov and Butuzowa, 2008). Additionally, the major, trace, and rare-earth element concentrations of the sphyllites show little variation suggesting that metamorphism did not greatly affect their chemical composition.

4.3 GEOCHEMICAL CLASSIFICATION OF THE ROCKS

Various workers have classified 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 the 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 phyllites were also classified using the geochemical classification of Herron (1988), the plot of Fe_2O_3-K_2O and SiO_2-Al_2O_3 ratio. On the Fe_2O_3/K_2O versus SiO_2/Al_2O_3 diagram (Figure 4.12; after Herron, 1988), the Neoproterozoic phyllites from the Akuapim range are classified as mostly arkose and shale with minor wacke, subarkose, sublitharenite and litharenite. However, the regions within which these phyllites plot are probably due to the bulk-geochemical analyses of the samples which do not depict the various detrital components of the rocks.

Geochemical classification proposed by Crook (1974), which employs the Na_2O and K_2O contents was also used to classify the geochemical characteristics of the phyllites. On this diagram (Figure 4.13; after Crook, 1974), the data for the Neoproterozoic phyllites plot predominantly in the quartz-rich field with few straddling the quartz-intermediate field. Additionally, the phyllites have high SiO_2 contents (average = 75.14 wt%) typical of quartz-rich sediments (SiO_2 contents > 65 wt%; Crook, 1974). This sugests that the sediments are rich in quartz indicating that the sediments are derived from old/recycled sedimentary sources.

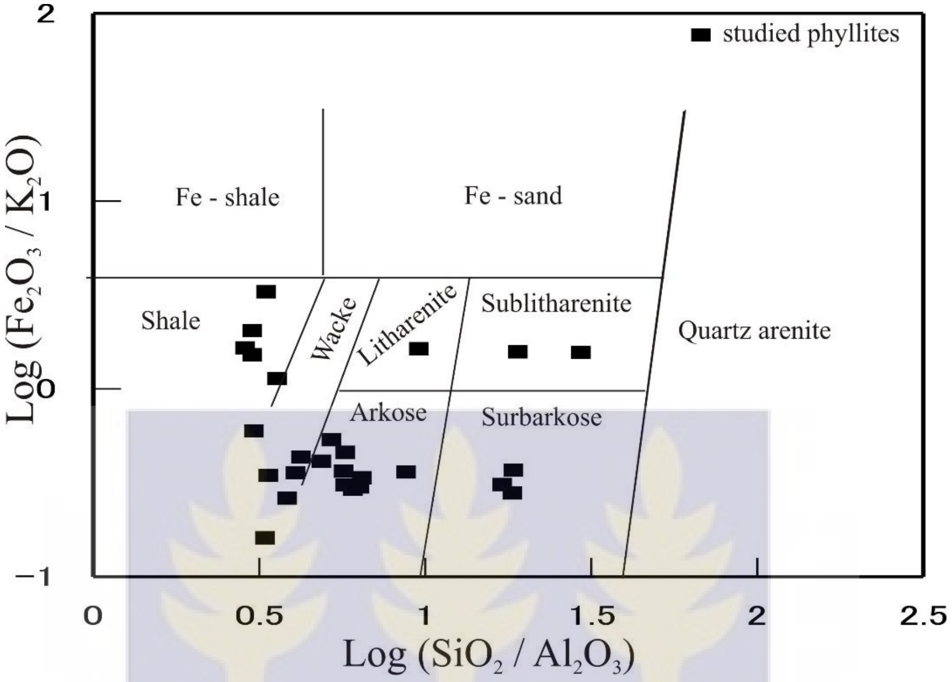

Figure 4.12 Chemical classification of Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (fields after Herron, 1988).

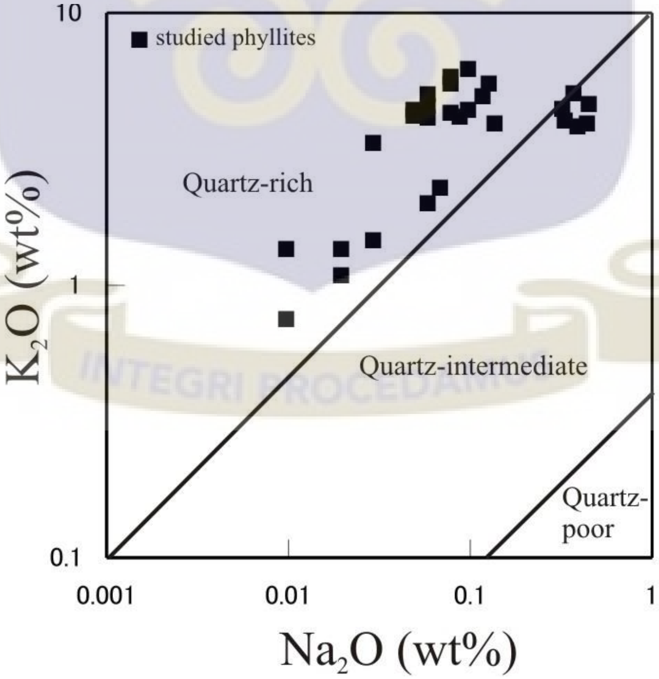

Figure 4.13 Major element chemical classification of the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Crook, 1974).

4.4 MINERAL CONTROLS ON MAJOR AND TRACE ELEMENT DISTRIBUTION

SiO_2 shows a strong negative linear trend with the other major elements (Figure 4.14) which may suggest greater quartz content and a smaller proportion of detrital grains (Rollinson, 1993). SiO_2 content also exhibits a strong negative correlation with Al_2O_3 (linear correlation coefficient, r = -0.92) showing that much of SiO_2 is present as quartz grains. Aluminium concentration is a reasonably good measure of detrital flux (Nagarajan, 2007), and therefore the positive correlations between Al_2O_3 and TiO_2, MgO, Na_2O, and K_2O suggest that these elements are associated entirely with detrital phases such as clay minerals and micas (Dabard, 1990; Condie et al., 1992). Al_2O_3 also shows positive correlations with Sc, V, Cr, Rb, Sr, Rb, Cs, Ba, Y, Nb, Ta, Th and U (Table 4.3) suggesting that these elements are associated with clay minerals and/or micas. Moderate correlation between Al_2O_3 and Fe_2O_3 + MgO and total REE infers that Fe, Mg and REE (Table 4.3) are partly controlled by phyllosilicates.

The K_2O contents of the phyllites show a strong positive correlation with Al_2O_3, Ba, Cs, Rb, Th, U, Ta, Nb and Ba (Table 4.3). This suggests that these elements are controlled by clay minerals and/or mica (McLennan et al., 1983). K_2O makes up about 5-10% by weight of most illite (Deer et al., 1966) and therefore, these elements are probably controlled by illite identified in the sediments. K_2O shows moderate correlation with total REE indicating that the REEs are partly controlled by clay minerals and mica. A negative correlation exists between Zr and total REE which reveals that the REE are hosted in mica (Condie et al., 1992). Th shows positive but low correlation with total REE which may indicate that REE is partly controlled by allanite-monazite (Condie et al., 1992).

According to Roddaz et al., (2007), P_2O_5 contents in sediments are usually associated with accessory phases such as apatite and monazite. Therefore, the moderate correlation between P_2O_5 and Cs, Ni and Co suggests that these elements are partly controlled by accessory minerals such as apatite and monazite. In general, the large ion lithophile elements (e.g, Rb, Cs, Th, U), high field strength elements (e.g., Zr, Nb, Hf), ferromagnesian elements (e.g., Sc, V, Cr) as well as REE show strong interrelationships. This indicates the chemical coherence and uniformity of the phyllites. Strong correlation between Zr and Hf and Nb and Ta suggest that these elements are mainly concentrated in stable heavy minerals (Roddaz et al., 2007). Ni and Co show moderate correlation with Al_2O_3 but strong correlation with Cr, Ni and V which shows that Co and Sc are concentrated in oxides and other accessory non-aluminous silicate minerals (Asiedu et al., 2000).

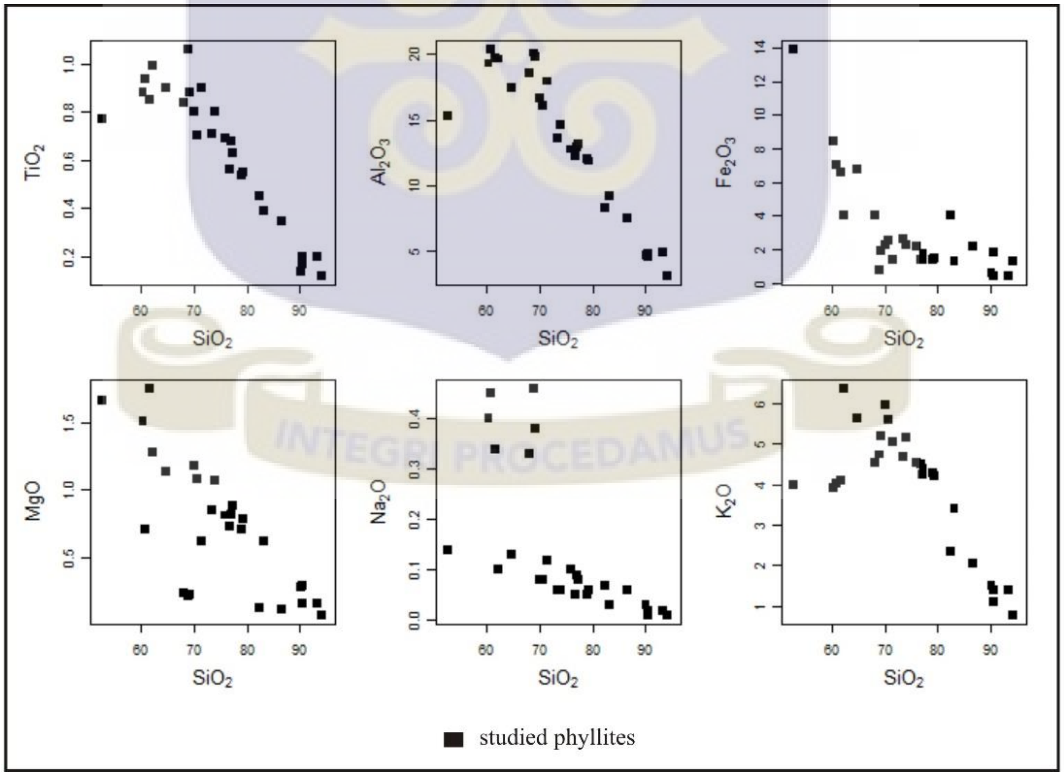

Figure 4.14 Binary plots of SiO_2 versus other major elements for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana.

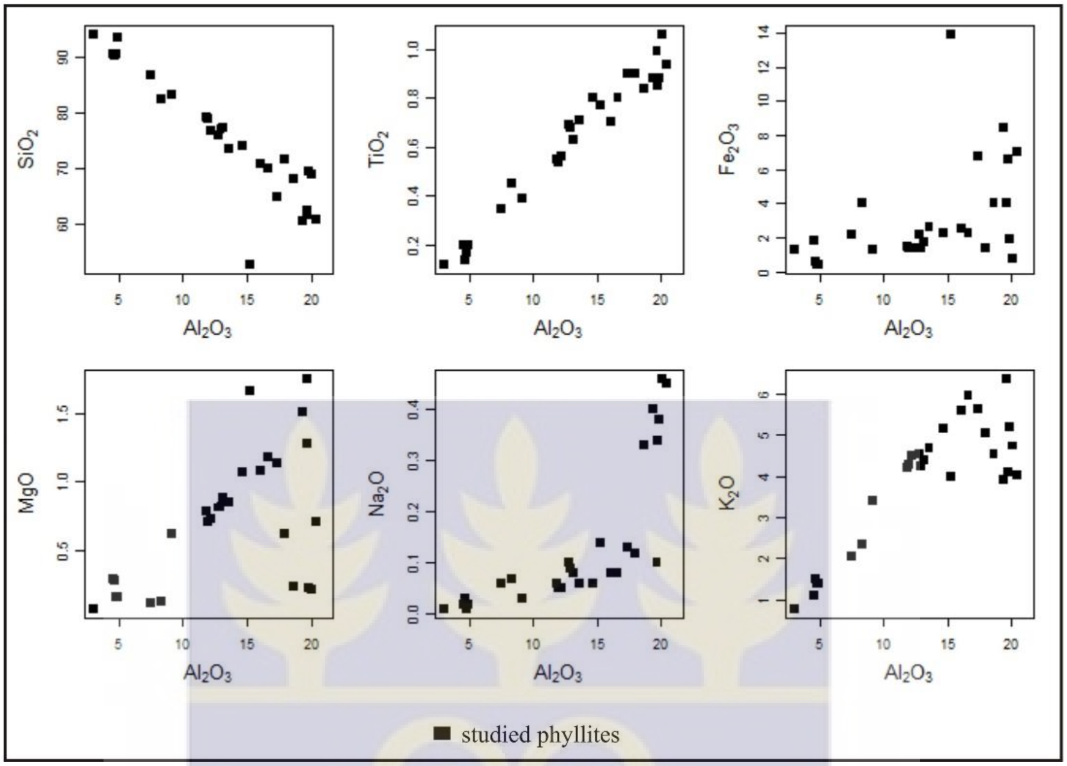

Figure 4.15 Binary plots of Al_2O_3 versus other major elements for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana.

Table 4.3 Linear correlation coefficients for selected elements

Elements	Linear correlation
K_2O-Al_2O_3	0.85
K_2O – Ba	0.86
K_2O – Cs	0.65
K_2O – Rb	0.87
K_2O – Th	0.77
K_2O – U	0.87
K_2O – Ta	0.8
K_2O – Nb	0.87
K_2O – Ba	0.86
K_2O-total REE	0.19
Al_2O_3-Fe_2O_3 + MgO	0.49
Al_2O_3-TiO_2	0.98
P_2O_5 – Cs	0.55
P_2O_5 – Ni	0.68
P_2O_5 – Co	0.68
Th – Cs	0.88
Th-total REE	0.34
Al_2O_3-total REE	0.29
Zr-total REE	-0.32
La-Al_2O_3	0.24
Yb – Zr	0.31
Yb-Al_2O_3	0.9
La – Zr	-0.35
Zr-Eu/Eu*	0.1
Fe_2O_3-Al_2O_3	0.46
Sc-Al_2O_3	0.96
V-Al_2O_3	0.94
Cr-Al_2O_3	0.93
Ni-Al_2O_3	0.3
Co-Al_2O_3	0.26
Cu-Al_2O_3	0.37
Rb-Al_2O_3	0.97
Sr-Al_2O_3	0.58
Cs-Al_2O_3	0.86
Ba-Al_2O_3	0.78
Y-Al_2O_3	0.84
Nb-Al_2O_3	0.98
Ta-Al_2O_3	0.98
Th-Al_2O_3	0.97
U-Al_2O_3	0.84
Cr – Ni	0.23
Cr – Co	0.23
Ni – Co	0.8
Zr – Hf	0.99
Ta – Nb	0.98
Nb – Th	0.97
Nb – U	0.88
Th – U	0.79

CHAPTER FIVE

DISCUSSION

5.1 IMPLICATION OF MINERALOGICAL CONTENT

According to Armstrong-Altrin et al (2004), increasing compositional maturity of clastic sediments leads to an increase in the quartz content with respect to clay-size materials. This is because the transport of sediments usually leads to the removal of less stable minerals such as clay minerals and the enrichment of more stable minerals such as quartz. The phyllites have relatively high quartz content of 30-49 wt% and low content of clay size materials such as chlorite and muscovite (average = 17.2 wt%; 17.8 wt%, respectively) suggesting compositional maturity of sediments.

In addition, Bhatia (1985) showed that sediment maturity may be determined by the maturity index which is defined as the ratio of total phyllosilicates to phyllosilicates + tectosilicates (mainly feldspar and quartz). The phyllites have high quartz/feldspar ratios [average (quartz/quartz + feldspar) = 0.71] further confirming the compositional maturity of the sediments (Cullers, 2000). The maturity of clastic sediments have been associated with sedimentary sorting (Veizer and Jansen, 1979; McLennan, 1989). Therefore, the maturity of the sediments may suggest sedimentary sorting of the phyllites probably during transportation of sediments.

The ratios between quartz and feldspar of clastic sediments have been shown to give useful clues on the source rock composition (Cullers, 2000). According to Cullers (2000), high ratios between quartz and feldspar is indicative of a probable sediment production by weathering of crystalline rocks and/or by recycling of sedimentary deposits. The phyllites exhibit high quartz/feldspar ratios (average = 2.61) which suggest derivation of sediments from crystalline rocks and/or recycled sedimentary rocks.

The relative quartz, feldspar and phyllosilicate proportions in fine-grained sediments is indicative of their tectonic setting (Bhatia, 1985). According to Bhatia (1985), oceanic island arc rocks are characterised by high feldspar and low phyllosilicate content. They are derived from calc-alkaline andesitic mudrocks of magmatic arcs. Again, mudrocks of the continental island arc and active continental margins (Andean type and strike-slip basins) are characterised by a higher phyllosilicate content. Passive margin mudrocks are characterised by extremely high phyllosilicate and low feldspar contents, suggesting their recycled nature. The analysed phyllites have relatively low feldspar content (average = 14.6 wt%) and relatively high quartz content (average = 35.5 wt%) which are characteristic of sediments derived from passive margin tectonic setting.

Furthermore, the maturity of sediments has been related to the tectonic setting of siliciclastic sedimentary rocks (Roser and Korsch, 1986). The high proportion of quartz and compositional maturity of the sediments indicate that the source rocks were probably exposed to prolonged weathering conditions. A passive continental margin is the most probable geotectonic setting for the source rocks as it allows for the exposure of sediments to long episodes of weathering due to slow input of sediments and less tectonic activity. The long episode of weathering leads to the removal of less stable minerals and subsequent enrichment in more stable minerals such as quartz. The maturity of the Neoproterozoic phyllites suggest a passive continental margin geotectonic setting for the source rocks (Roser and Korsch, 1986).

5.2 SEDIMENTARY SORTING AND RECYCLING

Sorting is one of the most important sedimentary processes from which the energy and type of medium of transport, distance, duration of transport and tectonics of the source area can be deduced (Kuenen, 1955; 1956). Sorting is generally determined by analysing the textural maturity, grain sizes and shapes and mineralogical composition of sedimentary rocks (McLennan et al., 1993). However, chemical composition of sedimentary and metasedimentary rocks may be used to evaluate sedimentary sorting (McLennan et al., 1993; Kasanzu et al., 2008). Sedimentary sorting is usually inferred from the compositional maturity which is determined by the relative concentrations of major elements in sediments. This is based on the mobility of major elements during sedimentary processes such as sorting, and therefore, the effect of this process can be determined by the relative concentration of major elements that remain in the sediments. Sedimentary sorting usually leads to the destruction and removal of less stable elements (e.g., plagioclase) and subsequent enrichment of more stable elements (e.g., quartz).

The phyllites have SiO_2 concentrations (average = 75.14 wt%) which are relatively higher than that of the average Upper Continental Crust (UCC, SiO_2 = 66 wt%; Taylor and McLennan, 1985) and Post-Archean Australian (average) Shale(PAAS, SiO_2 = 64.8 wt%; Taylor and McLennan, 1985). The high SiO_2 concentrations is indicative of sediment maturity probably due to sedimentary sorting and/or sedimentary recycling as a result of progressive weathering which led to the removal of plagioclase, alkali and alkaline earth elements and enrichment of more stable components (McLennan, 1989). Also, the phyllites show high SiO_2/Al_2O_3 values (average = 8.17) supporting sediment maturity and therefore, sedimentary sorting (Pettijohn et al., 1972; Armstrong-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. 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 phyllites exhibit high K_2O/Na_2O values (average = 54.31) indicative of high K-feldspar content and low Na-plagioclase which suggest that the sediments are mature and highly 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 phyllites as a function of climate. On this plot (Figure 5.1), the phyllites plot in a trend indicating increasing chemical maturity of sediments in semi-arid to semi-humid region. The chemical maturity supports the interpretation of sedimentary sorting of the sediments.

Geochemical studies by various workers such as McLennan et al. (1993) and Akarish and El-Gohary (2008) have shown that the degree of sedimentary sorting may be inferred from the accumulation of heavy minerals especially zircon (McLennan et al., 1993; Akarish and El-Gohary, 2008). 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 ($ZrSiO_2$), therefore, the geochemical characteristics of zirconium can be used to evaluate the degree of sorting in clastic sediments. The phyllites show high concentrations of Zr (range = 184-719 ppm, average = 408.08 pp) indicating enrichment in zircon which suggest sedimentary sorting.

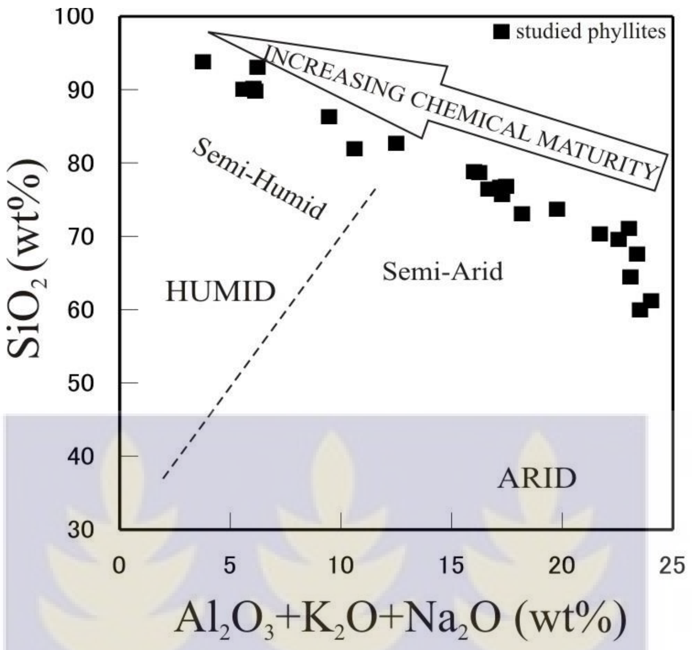

Figure 5.1 Bivariate plot of SiO_2 versus Al_2O_3+ K_2O + Na_2O for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Suttner and Dutta, 1986).

Sedimentary recycling usually leads to high degree of sorting in clastic sediments (e.g., Veizer and Jansen, 1979; Johnsson, 1993) and it results in changes in the major element composition of sediments as recycled minerals have differing susceptibilities to weathering and alteration (Cox and Lowe, 1995b). As a result, K_2O tend to be enriched in recycled sediments (Potter et al., 1975; Potter et al., 1980; Cox and Lowe, 1995b). The phyllites show enrichment of K_2O (average = 3.90) as compared to that of the average Upper Continental Crust (UCC, 3.39; Taylor and McLennan, 1985) which may suggest sedimentary recycling.

However, Cox and Lowe (1995b) suggested that high concentrations of K_2O may also be related to first-cycle, feldspar bearing mudrocks which are rich in potassium. The recycled sediments may be distinguished from the first-cycle, feldspar bearing sediments by their relative proportion of potassium and alumina which is given by the K_2O/Al_2O_3 ratio (Cox and

Lowe, 1995b). First-cycle, feldspar bearing mudrocks have K_2O/Al_2O_3 values greater than 0.4 whereas recycled mudrocks have values less than 0.3 (Cox, 1993). The phyllites generally show K_2O/Al_2O_3 values between 0.2 and 0.37 with an average of 0.3 which are within the range for recycled mudrocks confirming sedimentary recycling.

The plot of Th/Sc against Zr/Sc proposed by McLennan et al. (1993) can be used to depict the direct correlation between Zr enrichment in sediments and sedimentary recycling. On the plot of Th/Sc versus Zr/Sc (Figure 5.2), the phyllites plot in a region and in a trend which support zircon addition revealing the relative Zr enrichment and sedimentary sorting. This plot supports that the sediments were probably derived from recycled sediments of felsic composition.

Rare-earth element (REEs) are generally immobile but they also exhibit gradation in aqueous solubility as the heavy REE (HREE) form soluble complexes more easily than the light REE (LREE) (Brookins, 1989). As a result, sedimentary recycling will lead to an increase in the light relative to the heavy REE (LREE/HREE) (Cox and Lowe, 1995b). The phyllites show LREE enrichment relative to the HREE (average La_N/Yb_N = 1.46) confirming sedimentary recycling.

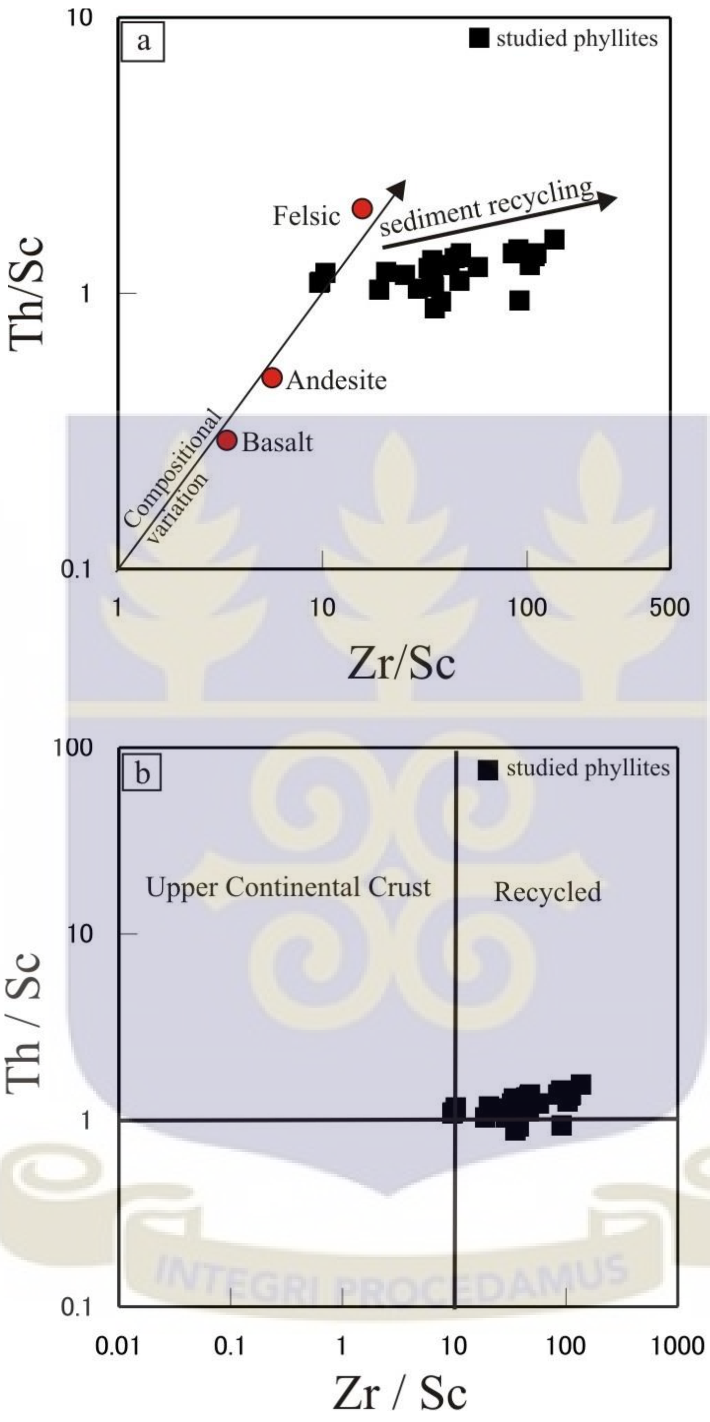

Figure 5.2 Plot of Th/Sc versus Zr/Sc for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after McLennan et al., 1993). Values for felsic, andesites and basalts are from Condie (1993).

5.3 PROVENANCE

5.3.1 Source-area weathering and diagenesis

The major element composition of sedimentary and metasedimentary rocks reflects their mineralogy, which is sensitive to chemical weathering (Harris and Adams, 1966; Middleburg et al., 1988). Chemical signatures imparted upon the sediments by chemical weathering may be transferred to the sedimentary record (e.g., Nesbitt and Young, 1982; Wronkiewicz and Condie, 1987), and therefore provide a useful tool for determining source-area weathering conditions. Chemical weathering generally leads to the depletion of alkalis (e.g., Na) and alkaline earth elements (e.g., Ca) and preferential enrichment of SiO_2 and $A1_2O_3$ (Cox et al., 1995).

The phyllites show relative depletion of Na_2O and CaO (average = 0.14 wt%, 0.02 wt%, respectively) and enrichment of SiO_2 and $A1_2O_3$ (average = 75.14 wt%; 13.25 wt%) indicative of the depletion of alkalis and alkaline earth elements suggesting high chemical weathering in the phyllites. Additionally, compositionally more complex clays such as smectites and chlorites, which contain Ca, Na, Fe, and Mn, degrade quickly during weathering as compared to illite containing K_2O which is stable and resistant to weathering (Cox et al., 1995). Therefore, the relationship between these major elements may be used to infer the chemical weathering of sediments (Nesbitt and Young, 1982). The phyllites have relatively high K_2O/Na_2O (range = 8.93-113.67, average = 54.31) which support a high intensity of chemical weathering at the source area.

The intensity of chemical weathering of sedimentary and metasedimentary rocks can be quantified using indices proposed by various workers (Nesbitt and Young, 1982; Harnois, 1988; Cox et al., 1995; Fedo et al., 1995). One of these indices is the chemical index of alteration (CIA) which measures the extent of conversion of feldspars (which dominate the upper crust) to clays and is defined as (Nesbitt and Young, 1982):

CIA = $[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$; In molecular proportions. Where the 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 overall low LOI contents suggest that carbonates were rather rare in the analysed sediments (Table 4.1). Therefore, CaO concentrations were used as CaO* for the calculation (Bock et al., 1998). CIA values of 45-55% indicate weak weathering and values of 56-65% indicate moderate weathering whereas values greater than 65% 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., 1995). The phyllites have relatively high CIA values (average = 74.73 %) which are significantly greater than that of PAAS (70; Taylor and McLennan, 1985) and falls within the range for intensive chemical weathering. This indicates that the source rocks of these sediments may have been subjected to intense weathering conditions under a warm humid climate, for a shorter period or moderate degree of chemical weathering for an extended period of time.

During diagenesis, K-metasomatsism (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. Accordingly, K-free indices such as plagioclase index of alteration (PIA) and the chemical index of weathering (CIW) have been calculated to determine the intensity of chemical weathering for the phyllites. Plagioclase Index of Alteration (PIA) is defined as:

PIA = 100 x [(Al_2O_3-K_2O)/(Al_2O_3+CaO*+Na_2O-K_2O)] (after Fedo et l., 1995); and

Chemical index of weathering (CIW) is defined as:

CIW = [Al_2O_3/(Al_2O_3+CaO∗+Na_2O)] x 100 (after Harnois, 1988); In molecular proportions. Where CaO* represents the CaO in silicates only.

CaO concentrations were used as CaO* for the calculation as explained earlier. High PIA values (> 90%) indicate complete conversion of plagioclase into aluminous clay minerals such as kaolinite, illite and gibbsite and low PIA values (≤ 50%) indicate unweathered plagioclase (Fedo et al., 1995). Also, high CIW values (90-98%) indicate intense weathering at source area (Condie, 1993). The phyllites show high PIA (average = 97.68 %) values higher than 90% which indicate complete conversion of plagioclase into aluminous clay minerals suggesting high intensity of chemical weathering at source area. Additionally, the phyllites exhibit high CIW values (range = 96.20-99.28 %; average = 98.36 %) which fall within the range for sediments derived from highly weathered source terrains supporting high intensity of chemical weathering at the source area.

The CIA data are plotted on an A-CN-K diagram (Nesbitt and Young, 1982), to give a graphic representation which allows for the evaluation of the extent of chemical weathering (Nesbitt and Young, 1984). On this plot (Figure 5.3), the phyllites clusters along the A-K edge suggesting an intense chemical weathering. According to Barbera et al. (2006), this trend is indicative of sediment derivation from crystalline basement rocks subjected to an alteration process leading to the significant loss of Na, Ca. The source rock composition can also be determined from this ternary plot by backward extrapolation of the weathered samples, parallel to the A-CN line (Fedo et al., 1996). The backward extrapolation of the line from the weathered sample points indicates the provenance of the phyllites to be originated from average granite (Figure 5.4).

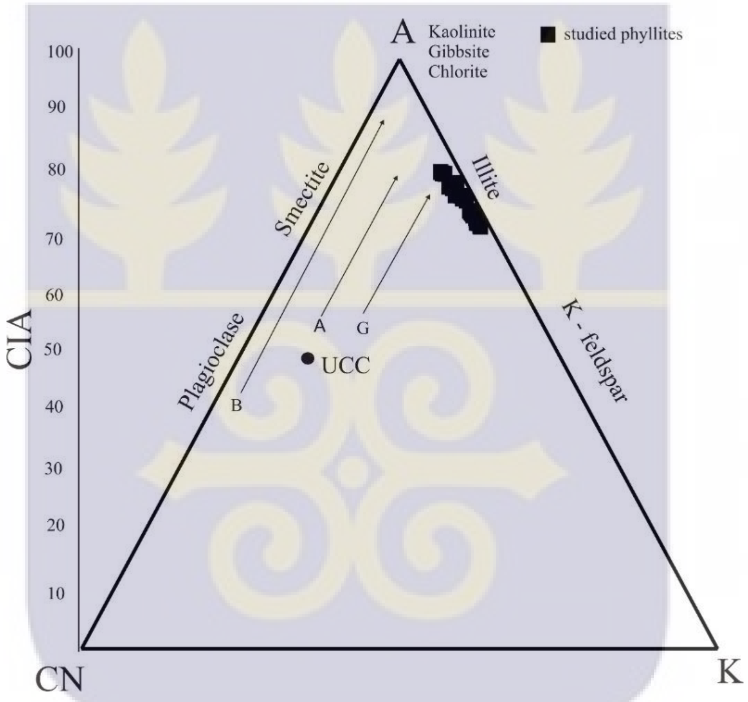

Figure 5.3 Ternary A-CN-K (Al_2O_3-$CaO+Na_2O$-K_2O) for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Nesbitt and Young, 1984; 1989). Average values of G: granite; A: andesite; B: basalt; values taken from Condie (1993). Upper Continental Crust (UCC) plotted for comparison (values taken from Taylor and McLennan, 1985).

CIA, PIA and CIW indices generally reflect the amount of feldspar and plagioclase relative to clay minerals respectively, and therefore are not strongly sensitive to the composition of source rock (Potter, 2005). The index of compositional variability (ICV) proposed by Cox et al. (1995) was calculated for the phyllites as it includes Fe and Mg which gives a better insight on the source rock composition (Potter, 2005). Index of compositional variability (ICV) measures the abundance of alumina relative to the other major cations in the sediments excluding SiO_2 and therefore eliminating the effect of quartz dilution. ICV is defined by:

ICV = $[CaO+K_2O+Na_2O+Fe_2O_3(t)+MgO+MnO+TiO_2]/Al_2O_3$; In weight percents (wt%). Where $Fe_2O_3(t)$ = total iron and CaO includes all sources of Ca.

In general, ICV values decrease with increasing degree of weathering. ICV values for average basalt and average granite are 2.20 and 0.95 respectively (Li, 2000). The phyllites have low ICV values (average = 0.64) indicating high intensity of chemical weathering at the source area. Also, the low ICV values reflect compositionally mature sediments which describe intracratonic environments (Weaver, 1989), where the recycling of old sediments is an active process, or provenance from intensely weathered crystalline basements (Barshad, 1966). The ICV values of the phyllites are close to that of granite suggesting a probable component of provenance of granitic composition. A binary plot of CIA index versus ICV index (after Potter, 2005), which may provide relevant clues on the source rock composition based on the intensity chemical weathering was plotted for the phyllites. On this plot (Figure 5.4), the phyllites mostly plot close to the trend for granite composition suggesting a granitic source rock composition as inferred from the ICV values.

Even though trace elements are generally less mobile during chemical weathering, some trace elements, such as Ba and Sr may be efficiently removed from soils (Wedepohl, 1978). During chemical weathering, Rb is preferentially incorporated into clays and divalent Sr undergoes leaching leading to the relative high concentrations of Rb and low Sr concentrations in sediments (Camiré et al., 1993). As a result, the Rb/Sr values of sediments may infer the degree of source area weathering (McLennan et al., 1983). The phyllites have high Rb/Sr values (average = 4.22) which are significantly higher than that of UCC (0.32; Taylor and McLennan, 1985) and PAAS (0.88; Taylor and McLennan, 1985) suggesting high intensity of chemical weathering at the source area.

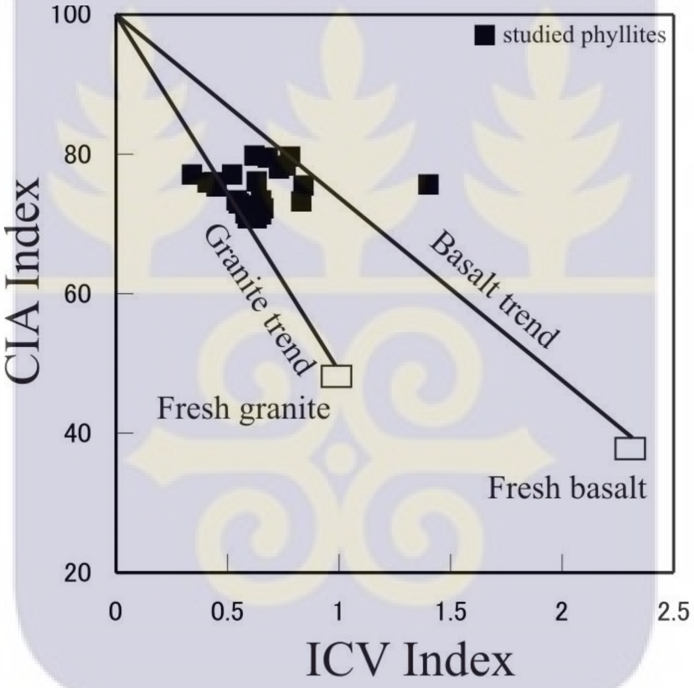

Figure 5.4 Plot of CIA index versus ICV index for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Potter, 2005).

Also, McLennan et al. (1993) showed that intensive chemical weathering leads to the elevation of Th/U due to the oxidation of U^{4+} to U^{6+}, decreasing the abundance of U in sediments and therefore resulting in Th/U ratios higher than those of upper crustal igneous rocks (about 3.5-4.0, McLennan et al., 1993). The phyllites have high Th/U values (average = 4.09) higher than those of upper crustal igneous rocks suggesting high intensity of chemical weathering.

Additionally, on a plot of Th/U versus Th (Figure 5.5; after McLennan et al., 1993), the phyllites plot in a trend indicative of recycled sediments which might have undergone some degree of weathering.

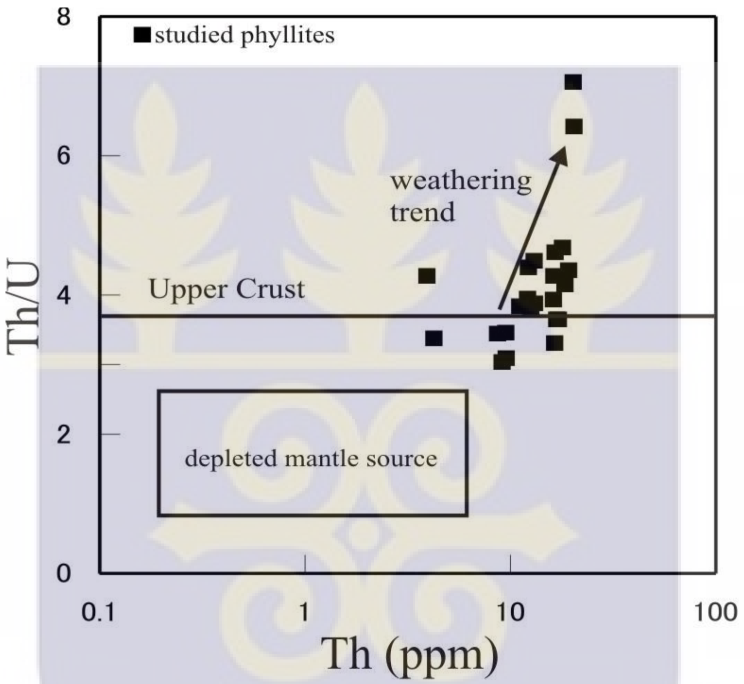

Figure 5.5 Plot of Th/U versus Th for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after McLennan et al., 1993).

The effect of diagenesis in the phyllites may be inferred from the geochemical modifications to major element (such as K_2O) composition of the sediments (Wintsch and Kvale, 1994). The phyllites have high K_2O concentrations (average = 3.90 wt%) which are slightly lower than that of Post-Archean Australian (average) Shale(PAAS: 3.97 wt%; Taylor and McLennan, 1985). This may suggest that the sediments have not undergone significant post-depositional K-metasomatism (Roddaz et al., 2007). The A-CN-K diagram may be used to infer the effect of post-depositional K-metasomatism in sediments (Fedo et al., 1997). According to Fedo et al. (1997), trends resulting from the chemical weathering of crystalline bedrock are roughly parallel to the A-CN boundary; however, K-metasomatism may result in significant departure from the predicted weathering trend. On this diagram (Figure 5.3), the analysed phyllites data plot along the A-K line instead of A-CN line. This type of trend shown in the A-CN-K diagram indicate that the phyllites have not undergone K-metasomatism supporting the interpretation by the low K_2O content relative to PAAS.

5.3.2 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).

The phyllites have high SiO_2 concentrations (average = 75.14 wt%) suggesting derivation of sediments from a granitic source or acidic high-grade metamorphic rocks (Crook, 1974). According to Cox et al. (1995), sediments derived by weathering of progressively more granitic source materials have high concentrations of Al_2O_3 and K_2O. The phyllites show relatively high concentrations of Al_2O_3 and K_2O (average = 13.25 wt%, 3.9 wt%) which support the interpretation that they were probably derived from granitic/felsic source rocks (Cox et al., 1995).

The ratio of TiO_2 and Al_2O_3 in sediments have been used to infer their source rock composition (Hayashi et al., 1997; Nagarajan, 2007). TiO_2 is relatively enriched in mafic rocks than in felsic rocks and Al_2O_3 which resides in feldspars is relatively enriched in more felsic/granitic source rock. Al_2O_3/TiO_2 ratios increases from 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks, and from 21 to 70 for felsic igneous rocks (Hayashi et al., 1997). The phyllites have high Al_2O_3/TiO_2 values (average = 21.87) characteristic of sediments derived from felsic source rocks.

The plot of K_2O versus Rb proposed by Floyd and Leveridge (1987) can be used to distinguish sediments of acid to intermediate rock composition from those derived from basic composition. On this plot (Figure 5.6), all the phyllites plot close to the typical differentiated magmatic suite with ratio of 230 (Shaw, 1968) and fall within the acid to intermediate composition range suggesting that the sediments were probably derived from magmatic rocks, predominantly acidic to intermediate in composition.

In addition, on a ternary diagram of $SiO_2/20$-K_2O+Na_2O-$MgO+FeO+TiO_2$ (Figure 5.7) proposed by (Roser and Korsch, 1988), majority of the phyllites plot near rhyolite with few plotting near dacite, andesite and basalt regions suggesting a major component of provenance of felsic composition.

Discriminant function diagram of Roser and Korsch (1988) is another method that can be used to further constrain the source rock composition of the phyllites. The discriminant functions of Roser and Korsch (1988) discriminate between four sedimentary provenance fields. These are: mafic igneous provenance (P1)-first cycle basaltic and lesser andesitic detritus; intermediate igneous provenance (P2)-dominantly andesitic detritus; felsic igneous provenance (P3)-acid plutonic and volcanic detritus; and quartzose sedimentary provenance/recycled (P4)-mature polycyclic quartzose detritus (indicate sedimentary maturity). On this diagram (Figure 5.8), the phyllites plot in the P4 field, supporting derivation of mature sediments from recycled sedimentary sources, similar to passive margin-derived sediments (Roser and Korsh, 1988).

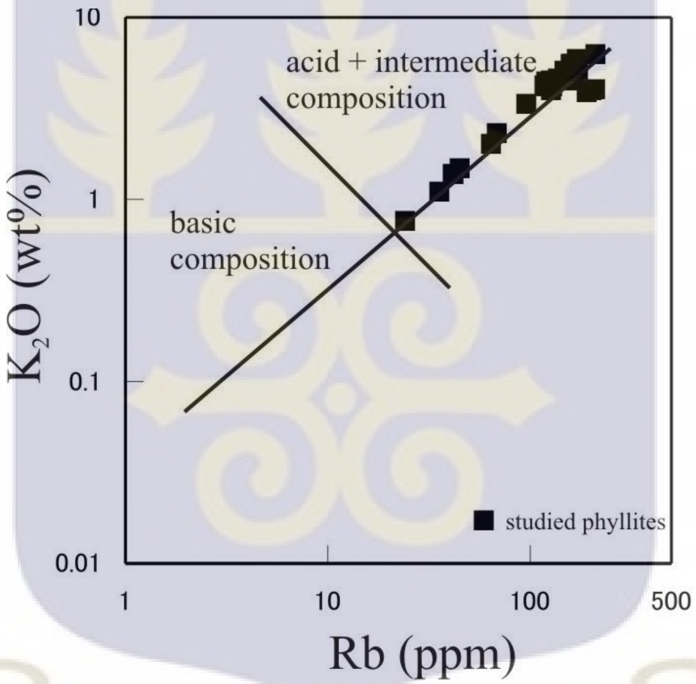

Figure 5.6 Distribution of K_2O and Rb in the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana, relative to a K_2O-Rb ratio of 230 (values for K_2O-Rb ratio are from Shaw, 1968) (after Floyd and Leveridge, 1987).

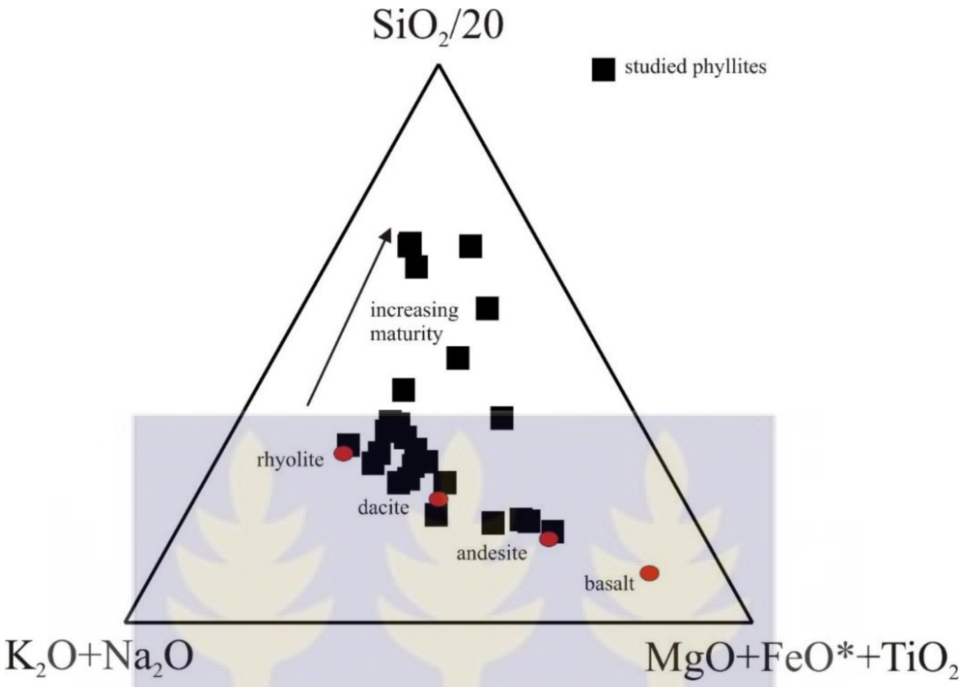

Figure 5.7 A ternary plot of $SiO_2/20$-K_2O+Na_2O-$MgO+Fe^*+TiO_2$ for the Neoproterozoic phyllites from the akuapim range. Southeastern Ghana (after Roser and Korsch, 1988).

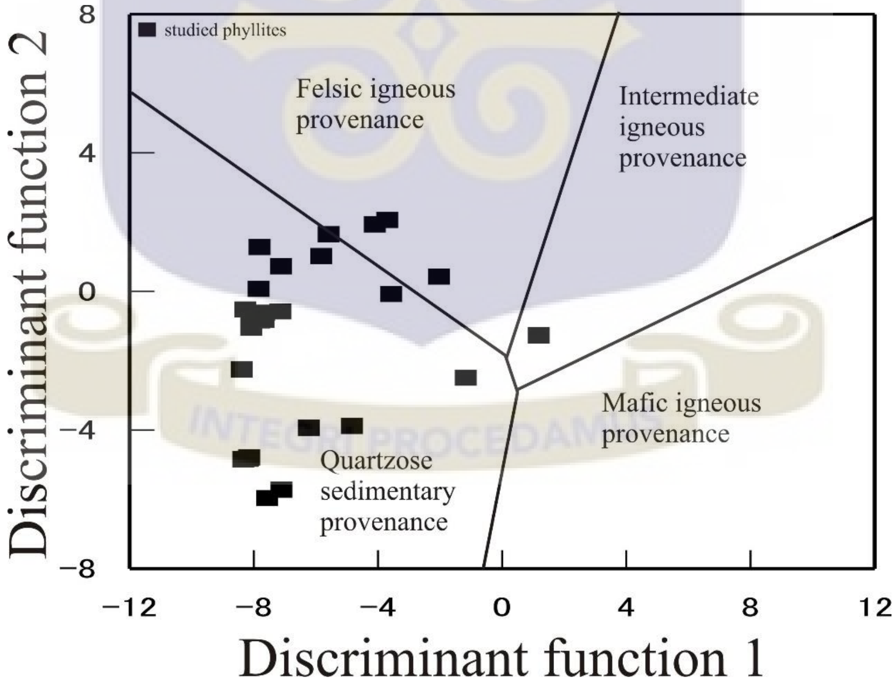

Figure 5.8 Discriminant function diagram for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Roser and Korsch, 1988).

Source rock composition of sedimentary and metasedimentary rocks is best determined using trace elements, especially the immobile elements, such as REE, Th, Cr, Co, Zr, and Y. This is because their distribution is not significantly affected by sedimentary processes, diagenesis and metamorphism (Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987; McLennan, 1989; Cox et al., 1995). Trace elements are generally concentrated in clay minerals as sorbed particles on surfaces or included in interlayer cation sites, and are transferred nearly quantitatively and unfractionated into the sedimentary record during sedimentary processes (Goldberg, 1954; Ermolenko, 1972; Roaldset, 1973, 1978; Davies, 1980; Salomons and Forstner, 1984; Taylor and McLennan, 1985; Horowitz and Elrick, 1987; McLennan, 1989; McBride, 1991; Horowitz, 1991; Keizer and Bruggenwert, 1991; Cox and Lowe, 1995). As a result, their abundance in sedimentary and metasedimentary rocks generally reflect the composition of their source rocks (Cullers et al., 1975; Taylor and McLennan, 1985; McLennan, 1989; Asiedu et al., 2004; Manu et al., 2013).

Trace elements usually occur as sorbed particles on the surfaces of clay minerals (Goldberg, 1954; Ermolenko, 1972; Roaldset, 1973, 1978; Davies, 1980). The geochemical characteristics of the phyllites show strong correlations between Sc, V, Cr, Rb, Cs, Ba, Y, Nb, Ta, Th, U and Al_2O_3 (linear correlation coefficient, r = 0.97, 0.94, 0.93. 0.97, 0.86, 0.78, 0.85, 0.98, 0.98, 0.97, 0.84, respectively) indicating that these elements are hosted in clay minerals and their chemical signatures can be used to infer the source rock composition of the sediments.

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 phyllites show low concentrations of Cr, Ni, V and Sc with slight enrichment of Co compared to the Post-Archean Australian (average) Shale (PAAS) (Figure 4.9). This suggests that very minimal mafic rocks were exposed in the source area suggesting a felsic provenance (Wrafter and Graham, 1989). The slight enrichment of Co is probably be due to post-depositional alterations in the sediments (Osae et al., 2006).

According to Feng and Kerrich (1990), high field strength elements (HFSE) such as Zr, Nb, Hf, Ta, Y, Th and U are preferentially incorporated into melts during crystallization and anatexis and therefore, these elements are enriched in felsic rather than mafic rocks. The phyllites show relatively high concentrations of Zr, Y, Hf and Th as compared to the Post-Archean Australian (average) Shale (PAAS) (Figure 4.12), suggesting felsic source rock composition for the sediments.

Studies by McLennan and Taylor (1991) have shown that Th/U ratios serves as a good indicator of provenance of sediments. According to McLennan and Taylor (1991), sediments derived from oceanic island arcs and oceanic basalts have low Th/U ratios. The phyllites have relatively high Th/U (average = 4.09) values which suggest no or low input of sediments of basaltic composition supporting felsic provenance for the sediments.

In addition, the relative distribution of immobile elements such as La and Th in felsic and basic rocks may be used to infer the relative contribution of felsic and basic sources in sediments from different source rock terranes (Wronkiewicz and Condie, 1990). According to Floyd and Leveridge (1987), low and uniform La/Th ratios of less than 5 and Hf abundances of about 3-

7 ppm are characteristic of sediments derived from felsic composition-dominated arcs. The phyllites reveal La/Th values averaging 3.82 which is considerably less than 5 which shows derivation of sediments from felsic composition-dominated arcs. The phyllites also show Hf (average = 10.52) abundances which are close to the ranges proposed by Floyd and Leveridge (1987) for sediments derived from felsic composition-dominated arcs.

The Cr/Th ratio has been used to discriminate basic sediments from felsic sediments (McLennan et al., 1993; Cullers, 1994a, 1994b; Roddaz et al., 2005, 2006). According to Cullers (2000), sediments derived from silicic sources have Cr/Th ratios ranging from 0 to 15 whereas sediments of basic origin have higher Cr/Th ratios that ranges from 22 to 500. The phyllites have Cr/Th (average = 3.73) values which are significantly lower than that of PAAS (7.5; Taylor and McLennan, 1985) and fall within the range for felsic sediments (Cullers, 2000), indicating a significant contribution of felsic component.

Numerous workers have shown that discrimination diagrams of trace elements may also be used to deduce source rock compositions of clastic sediments (e.g., Bhatia, 1983; Taylor and McLennan, 1985; Bhatia and Crook, 1986; Jahn and Condie, 1995; Bracciali et al., 2007). The plot of Th/Co vs. La/Sc has been used to distinguish between sediments derived from felsic rocks and those from basic rocks. On this diagram (Figure 5.9; after Cullers, 2002), the phyllites plot close to felsic rocks which shows derivation of sediments from felsic source rocks. Also, on a ternary plot of V-Ni-Th*10 (Figure 5.10; after Bracciali et al., 2007), the phyllites mainly plot within and close to felsic rocks supporting the interpretation that the sediments were derived from felsic source rocks.

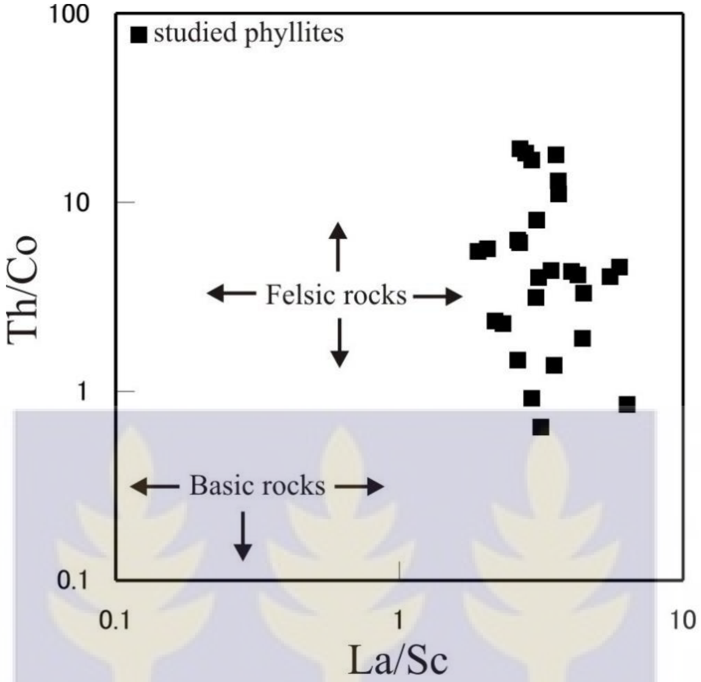

Figure 5.9 Th/Co versus La/Sc for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (fields are after Cullers, 2000).

Various workers have shown that the ternary diagrams of Th-Hf-Co and La-Th-Co are very important in deducing the source rock composition of clastic sediments (Bhatia, 1983; Taylor and McLennan, 1985; Bhatia and Crook, 1986; Jahn and Condie, 1995). On the ternary diagram of Th-Hf-Co (Figure 5.11a), the phyllites plot close to continental crust and far from average oceanic crust composition, indicating derivation of sediments from a felsic source rock. Also, on the plot ternary plot of La-Th-Sc (Figure 5.11b), the samples plot in a trend showing abundances of La, Th and Sc similar to that of granite and granodiorite, which suggests a felsic source rock composition for the sediments. Cr/Th and Th/Sc ratios are very useful tools in constraining the composition of sediment sources (Taylor and McLennan, 1985; McLennan et al., 1993; Cullers, 2000). The plot of Cr/Th versus Th/Sc (Figure 5.12) shows that the phyllites cluster close to the felsic volcanics further supporting the interpretation that the sediments were derived from felsic source rocks.

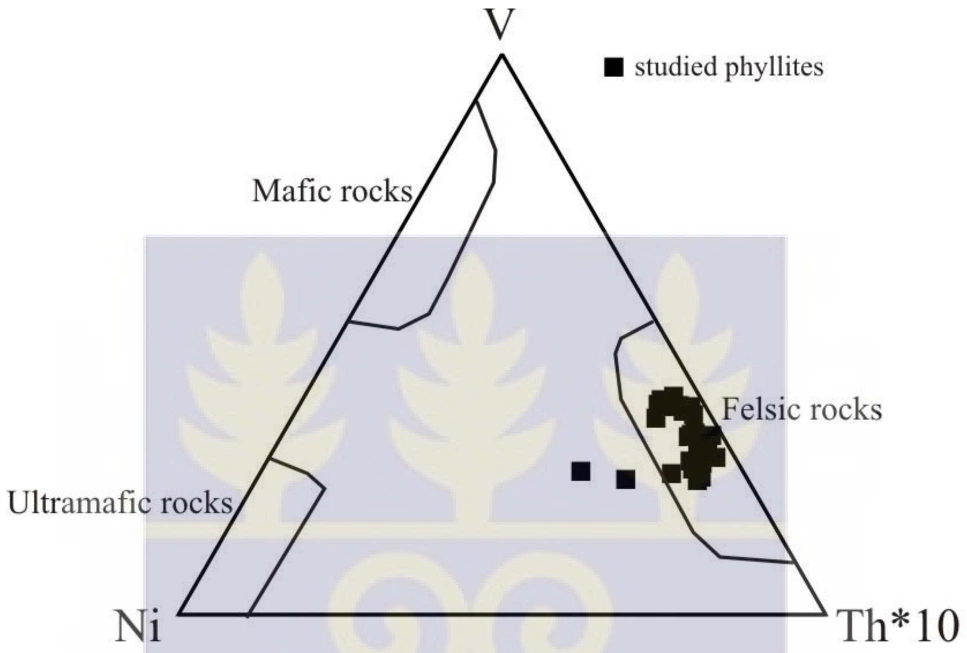

Figure 5.10 A ternary plot of V-Ni-Th*10 for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (fields are after Bracciali et al., 2007).

In Figure 5.14, plot of La/Th versus Hf (after Floyd and Leveridge, 1987), the phyllites plot around the felsic source region and in a trend of increasing old sediment component close to the passive margin source. This may be characteristic of mature sediments derived from old/recycled sedimentary sources. Furthermore, the ratio Th/Sc probably best reflects the overall bulk composition of provenance, therefore making Th/Sc ratio a very important tool in deducing source rock compositions (Taylor and McLennan 1985). In Figure 5.2a, the plot of Th/Sc versus Zr/Sc (after McLennan et al., 1993), the phyllites cluster close to average granite and in a trend characteristic of recycled sediments. This may suggest derivation of sediments from recycled sedimentary rocks.

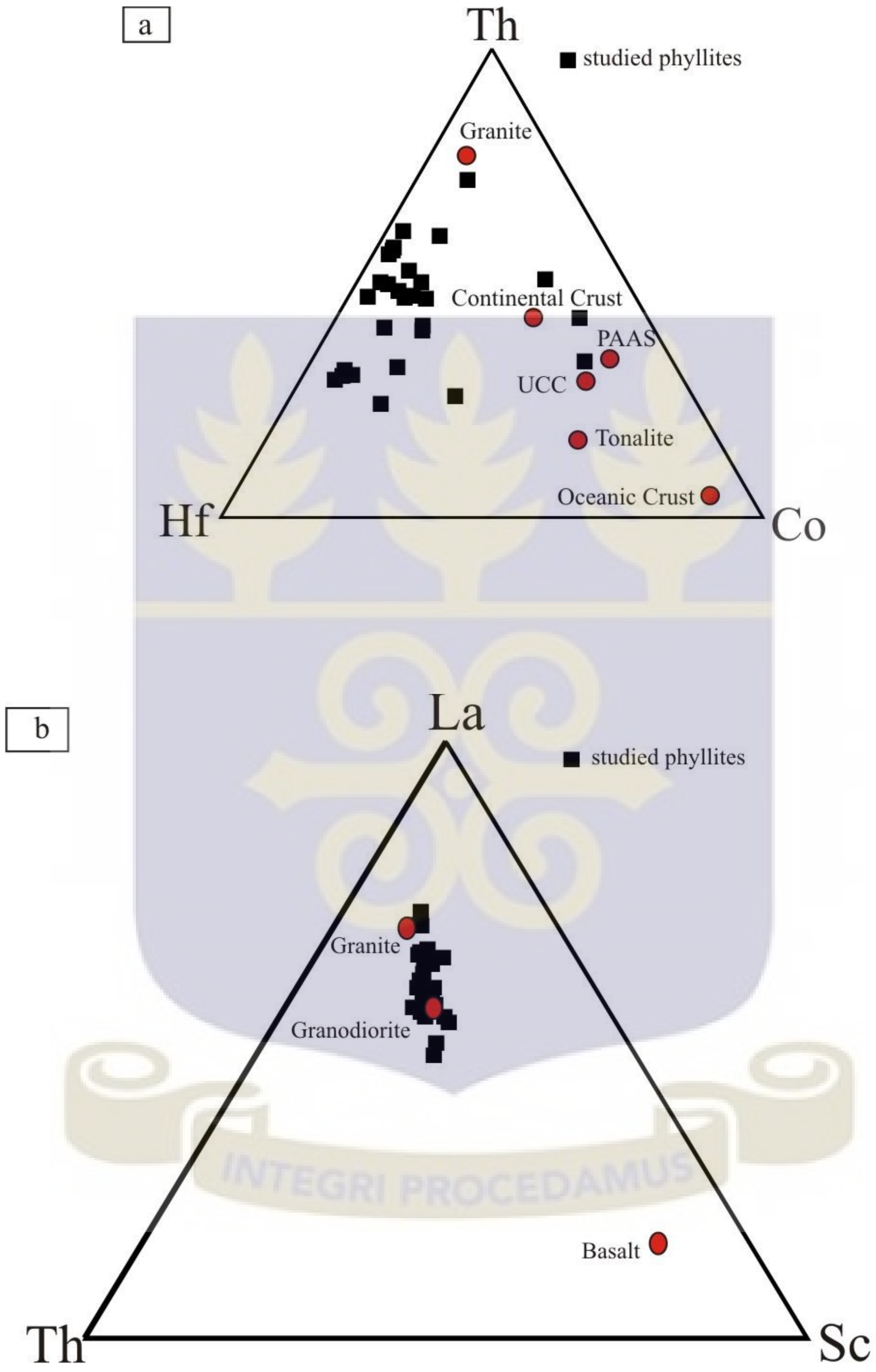

Figure 5.11 (a) Th-Hf-Co ternary diagram and (b) La-Th-Sc ternary diagram, for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (compositional fields are after Roddaz et al., 2007). Post-Archean Australian (average) Shale(PAAS) and Upper Continental Crust (UCC) are plotted for comparison (values are from Condie, 1993).

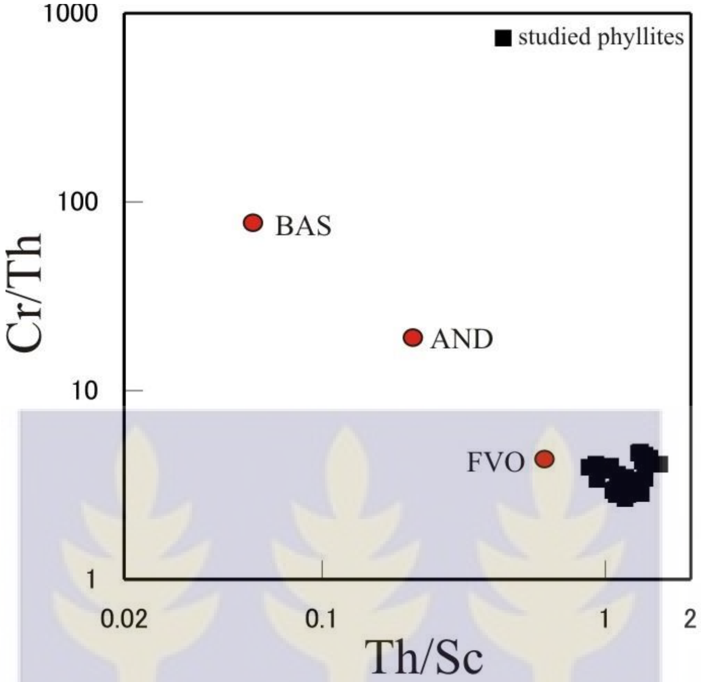

Figure 5.12 A plot of Cr/Th versus Th/Sc for the distribution of Neoproterozoic phyllites from Akuapim range, southeastern Ghana. Values for FVO: felsic volcanics; AND: andesites; BAS: basalts are from Condie (1993).

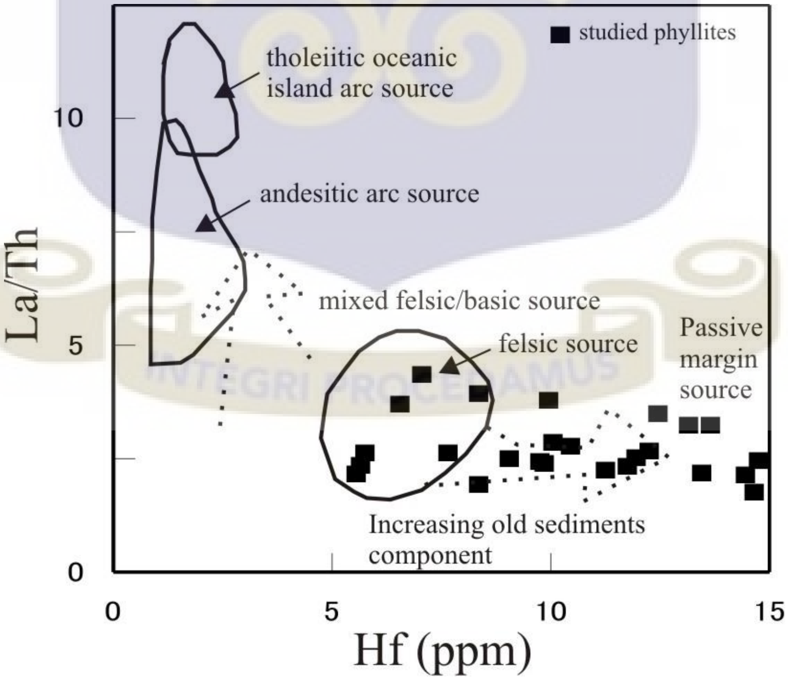

Figure 5.13 A plot of La/Th versus Hf for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (compositional fields are after Floyd and Leveridge, 1987).

The ratios of Th/Sc, Th/Co, Th/Cr, Cr/Th, and La/Sc ratios are significantly different in felsic and basic rocks and may allow constraints on the average provenance composition (Wronkiewicz and Condie, 1990; Cox et al., 1995; Cullers, 1995, 2000; Armstrong-Altrin et al., 2004). The elemental ratios deduced from composition of the phyllites have been compared with those sediments derived from felsic and basic rocks (fine fraction) as well as to Upper Continental Crust (UCC) and Post-Archean Australian (average) Shale (PAAS) values (Table 5.1).

From Table 5.1, the Neoproterozoic phyllites from the Akuapim range of the Togo Structural Unit show elemental ratios which are close to or within the range of sediments derived from felsic source rock further confirming provenance of felsic composition.

Table 5.1 Range of elemental ratios of Togo Phyllite compared to the ratios in similar fractions derived from felsic rocks, mafic rocks, Upper Continental Crust, (UCC) and Post-Archean Australian (average) Shale (PAAS)

Elemental ratios	Togo Phyllite	Range of sediments		UCC	PAAS
		Felsic rocks	Mafic rocks		
Th/Sc	0.89-1.58	0.84-20.5	0.05-0.22	0.79	0.9
Th/Co	0.67-19.85	0.67-19.4	0.04-1.4	0.63	0.63
Th/Cr	0.20-0.36	0.13-2.7	0.02-0.05	0.13	0.13
Cr/Th	2.79-4.93	4.00-15.00	25-500	7.76	7.53
La/Sc	1.93-6.47	2.5-16.3	0.43-0.86	2.21	2.4

The range of values for sediments from felsic and mafic rock sources are from Cullers et al. (1988), Cullers (1994; 2000) and Cullers and Podkovyrov (2000).
Upper Continental Crust and Post-Archean Australian (average) Shale values are from Taylor and McLennan (1985).

The enrichment of incompatible elements relative to compatible elements and Eu anomaly of the elemental composition provide important information about the source rock composition of sediments (Taylor and McLennan, 1985). The light rare-earth elements (LREE) which are incompatible elements preferentially go into melt phases during partial melting and therefore are relatively enriched in Upper Continental Crust and/or felsic rocks. The heavy rare-earth elements (HREE) are preferentially incorporated into the structures of principal minerals during magmatic crystallization due to their smaller ionic radius and therefore are enriched in mantle and/or basic rocks (Potter, 2005). As a result, the ratio of LREE to the HREE which is given by La_N/Yb_N may be used to distinguish sediments derived from felsic and mafic sources. Sediments derived from basic source rocks have low $\Sigma LREE/\Sigma HREE$ (La_N/Yb_N) ratios and insignificant Eu anomalies, whereas felsic source rocks usually contain higher $\Sigma LREE/\Sigma HREE$ (La_N/Yb_N) ratios (Cullers and Graf, 1984; Cullers, 1994). The phyllites exhibit chondite-normalised REE patterns which are similar to that of PAAS (Figure 4.10), with a general enrichment of LREE relative to HREE (average $La_N/Yb_N = 7.56$) characteristic of sediments derived from Upper Continental Crust and/or felsic rocks.

The anomalous behaviour of Eu is generally inherited from sediment sources and therefore makes it an important tool in distinguishing 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 source rocks (Cullers, 1994; Gao and Wedepohl, 1995). The phyllites have negative Eu anomalies (average $Eu/Eu^* = 0.61$) which are generally close to that of PAAS (0.66; Taylor and McLennan, 1985). This is indicative of the present Upper Continental Crust suggesting sediment derivation from intracrustal sources, and therefore, felsic source rocks.

McLennan et al. (1993, 1995) described five major provenance types on the basis of geochemistry, the characteristics of which are summarized in Table 5.2. Comparing the geochemical characteristics of the Togo phyllites to that of the major provenances given in Table 5.2, the sediments are likely dominated by sources representative of Recycled Sedimentary Rocks (RSR). This assertion is supported by the following evidences:

1) The high heavy mineral concentrations (e.g., Zr, Hf, for zircon, REE for monazite);
2) The general lack of significant negative Eu anomalies (average Eu/Eu* = 0.61);
3) Relatively high Th/Sc ratios (average Th/Sc = 1.22); and
4) In general, phyllites have average to above-average REE abundances with LREE enrichment relative to PAAS.

From the geochemical characteristics, the Togo phyllites were predominantly derived from Old/Recycled Upper Continental Crust.

In an attempt to model the source rock composition for the phyllites, the lithological units which are more likely to produce the sediments were considered. These include: Upper Continental Crust (UCC), average granites, and tonalite-trondhjenite-granodiorite (TTG). The average chemical compositions of Proterozoic Upper Continental Crust, granite and tonalite-trondhjenite-granodiorite (TTG) from Condie (1993) were used as potential sources for the phyllites. The phyllites were modeled using the Fedo et al. (1996) modelling method which attempt to conserve mass balance amongst the relatively immobile REEs and in the Th/Sc ratios which is a sensitive index of bulk composition (Taylor and McLennan, 1985).

The model REE values were achieved by following the mass balance equation of Albarède (2000): $WR^{mix} = \alpha C_1 + \beta C_2 + \gamma C_3$, where WR^{mix} represents the calculated whole rock compositions, α, β and γ represent the proportion of UCC, granite and TTG obtained from the modeling of the source rocks, respectively whereas C_1, C_2 and C_3 represent the rare-earth element in UCC, granite and TTG.

Using the source compositions listed in Table 5.3, average Togo phyllites is composed by a mixture of 80% Upper Continental Crust and 20% granite. The modeled chondrite-normalized REE patterns for the phyllites are similar to the average phyllites (Figure 5.16) which supports the results obtained for the mixing calculations for the source rocks of the Togo phyllites.

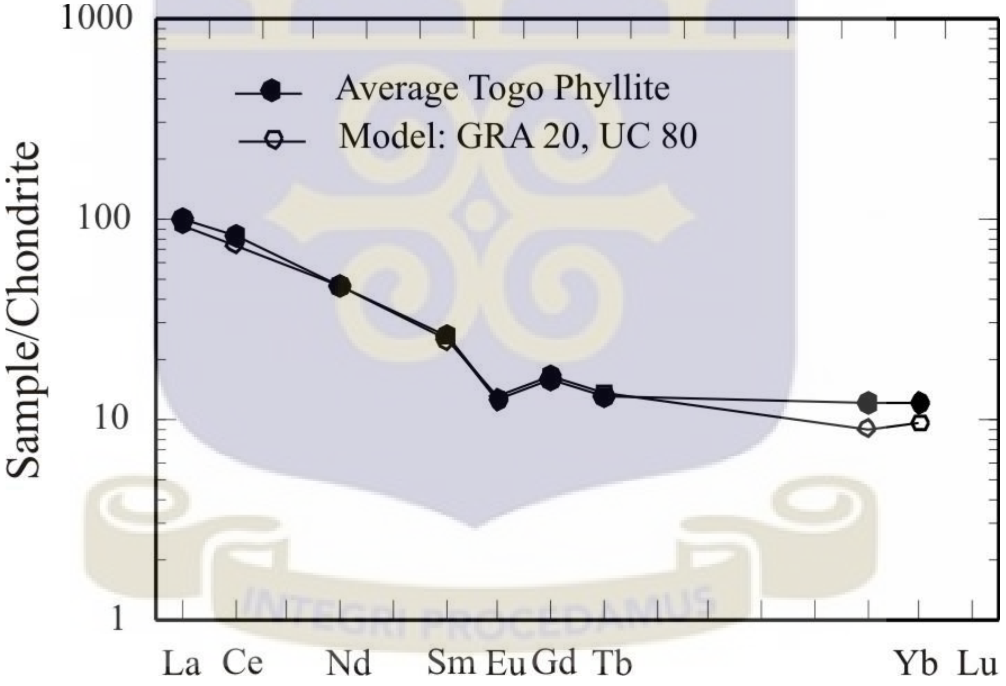

Figure 5.14 Comparison of Chondrite – normalized REE patterns of average Togo phyllites and model Togo phyllites (Parameters are in Table 5.3).

Table 5.2 Summary of geochemical characteristics of provenance types

Terrane	Eu/Eu*	Th/Sc	Other geochemical features	Description
Old Upper Continental Crust (OUC)	~0.60-7.0	-1.0	Evolved major element composition (e.g., high Si/Al, CIA); High LILE abundance; uniform compositions	Old igneous/metamorphic/sedimentary terranes affected by intracrustal differentiation. Stable cratons, old foundation of active setting.
Recycled Sedimentary Rocks (RSR)	~0.60-0.70	≥1.0	Evidence of heavy mineral concentrations in trace elements (e.g., Zr, Hf, for zircon, REE for monazite)	Recycled sedimentary/metasedimentary rocks specifically identified. If not separately identified, part of OUC.
Young Undifferentiated Volcanic Arc (YUA)	~1.0	<1.0	Unevolved major element compositions (e.g., low Si/Al, CIA); Low LILE abundances; variable compositions	Young mantle-derived volcanic/plutonic arc rocks. Dominates forearcs, components in continental arcs, back arcs
Young Differentiated Volcanic Arc (YDA)	~0.50-0.90	Variable	Evolved major element composition (e.g., high Si/Al, CIA); High LILE abundances; variable composition	Young mantle-derived volcanic/plutonic arc rocks affected by intracrustal differentiation. Similar environment YUA but more mature arcs or more discussion.
This Study Togo Phyllite	0.61	1.22	High SiO_2/Al_2O_3 and CIA values. Evidence of heavy mineral concentrations (Zr).	Recycled sedimentary/metasedimentary/metamorphic and/or igneous rocks derived from stable cratons.

(after McLennan et al., 1993, 1995)

Table 5.3 Results from mixing calculation

Elements	Average Togo Phyllite		Mixing end members						Mixing results
			Upper Continental Crust		Granite		TTG		Model Phyllite
									80: 20: 0
	Ppm	N	ppm	N	ppm	N	ppm	N	N
La	36.87	99.64	30.9	83.51	50	135.14	26	70.27	93.84
Ce	78.71	82.25	65.3	68.23	95	99.27	45	47.02	74.44
Nd	33.13	46.59	29.8	41.91	46	64.7	20	28.13	46.47
Sm	6.1	26.4	5.59	24.2	6.3	27.27	4.5	19.48	24.81
Eu	1.09	12.5	1.19	13.68	0.85	9.77	1.3	14.94	12.9
Gd	4.67	15.87	5.24	17.12	4.67	15.26	4.09	13.37	16.75
Tb	0.65	12.99	0.82	14.14	0.65	11.21	0.63	10.86	13.55
Yb	3.03	12.21	2.32	9.35	2	8.06	1.5	6.05	9.1
Lu	0.46	12.17	0.38	9.97	0.32	8.4	0.23	6.04	9.66
(La/Sm)$_N$		3.77		3.45		4.95		3.61	3.75
(Gd/Yb)$_N$		1.3		1.83		1.89		2.21	1.84
(La/Yb)$_N$		8.16		8.93		16.76		11.62	10.49
Eu/Eu*		0.61		0.67		0.48		0.93	0.63
Th/Sc		1.25		0.72		3.75		0.83	1.32

$_N$ denotes chondrite-normalized value.

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

5.3.3 Tectonic setting of source area

Geochemistry of clastic rocks have been shown to furnish vital information about the tectonic setting of source rocks (Bhatia and Crook, 1986; McLennan et al., 1993). This 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) greywackes 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 phyllites have average SiO_2 concentration of 75.14 wt% which is characteristic of quartz-rich sediments (> 65% quartz) which shows derivation of sediments from a passive continental margin.

Additionally, the major role of sedimentary recycling in the phyllites which is shown by high SiO_2 and Al_2O_3 contents and high Th/U ratios may suggest a passive margin tectonic setting for the source rock (Veizer and Jansen, 1985). This is supported by the lesser diversity in chemical composition of the analysed phyllites which is an expected consequence of sediments derived from passive margin tectonic setting (Bhatia 1985; McLennan et al. 1990).

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). On the plot of K_2O/Na_2O versus SiO_2 (Figure 5.15), the phyllites predominantly plot in the passive continental margin. This supports the interpretation of the compositional maturity of the sediments which suggest that the sediments were probably derived from passive margin setting.

In addition, Maynard et al. (1982) used a similar plot of SiO_2/Al_2O_3 versus K_2O/ Na_2O to discriminate different tectonic settings, in their study of modern sediments. On this plot (Figure 5.16), the phyllites plot mainly in the passive margin setting supporting the derivation of sediments from a passive continental margin.

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 plot above line = 1). From the plot of Th/Sc versus Sc (Figure 5.17), almost all the phyllites show Sc values more than 10 and Th/Sc ratios higher than 1 characteristic of recycled sediments deposited on a stable crust.

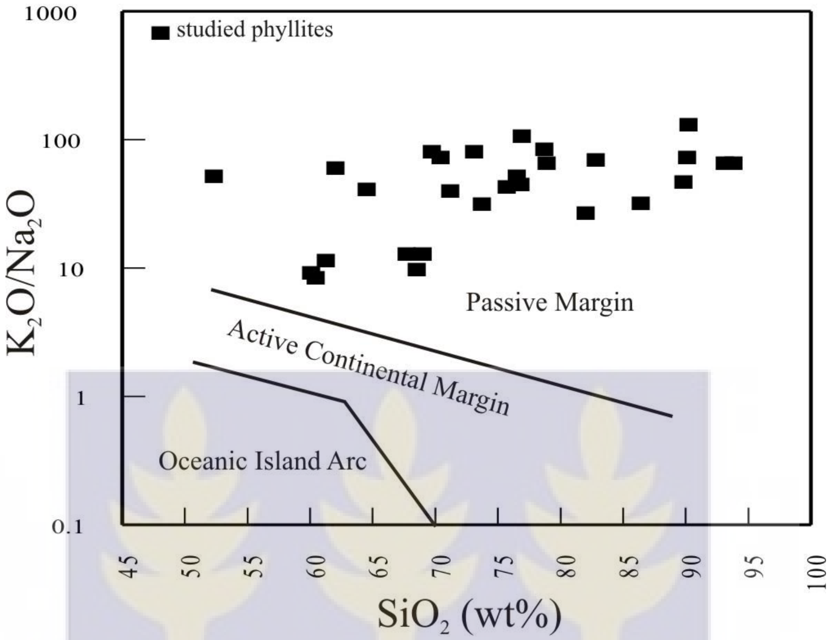

Figure 5.15 K_2O/Na_2O versus SiO_2 diagram for the Neoproterozoic phyllites from Akuapim range, southeastern Ghana (fields are after Roser and Korsch, 1986).

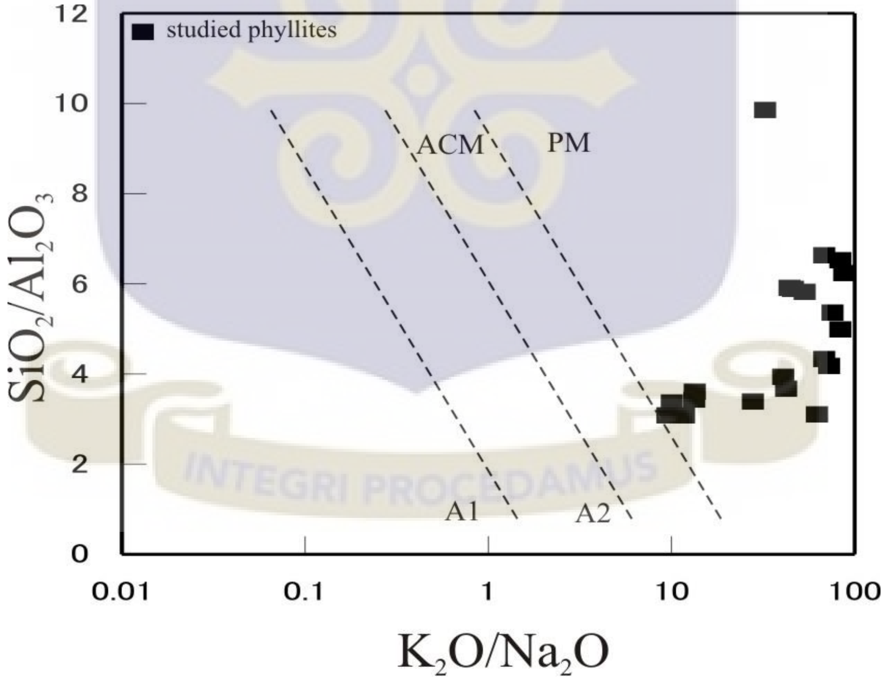

Figure 5.16 Plot of SiO_2/Al_2O_3 versus K_2O/Na_2O for the Neoproterozoic phyllites from Akuapim range, southeastern Ghana. Boundary lines for different tectonic settings from Roser and Korsch (1986). ACM, active continental margin; PM, passive margin; A1, arc setting, basaltic and andesitic detritus; A2, evolved arc setting, felsitic-plutonic detritus.

On the plot of La/Y versus Sc/Cr (Figure 5.18; after Bhatia and Crook, 1986) the phyllites plot dominantly within passive continental margin with few straddling the active continental margin supporting passive margin tectonic setting at the source rock area.

Additionally, the La-Th-Sc ternary plot (Bhatia and Crook, 1986) shows that arc-derived sediments and passive margin sediments can be effectively differentiated from each other. This plot successfully discriminates between the different arc settings except for the distinction between the active continental margin and passive continental margin. The distinction between tectonic settings is based on an increase in the La/Sc ratio as the sands become more mature (quartz rich). On the ternary plot of La-Th-Sc (Figure 5.19), the phyllites dominantly plot within the continental margin (active and passive) with few straddling the continental island arc.

Th-Co-Zr/10 and Th-Sc-Zr/10 ternary diagrams (Bhatia and Crook, 1986) have been used to differentiate between oceanic island arc (OIA), continental island arc (CIA), active continental margin (ACM) and passive margin (PM) setting. On the plots of Th-Co-Zr/10 and Th-Sc-Zr/10 (Figure 5.20), majority of the phyllites plot within the passive margin confirming derivation of sediments from passive continental margin.

In general, the geochemical characteristics of the phyllites indicate that the Neoproterozoic phyllites from the Akuapim range were predominantly derived from sediments deposited in a passive continental margin and/or intra-cratonic terranes.

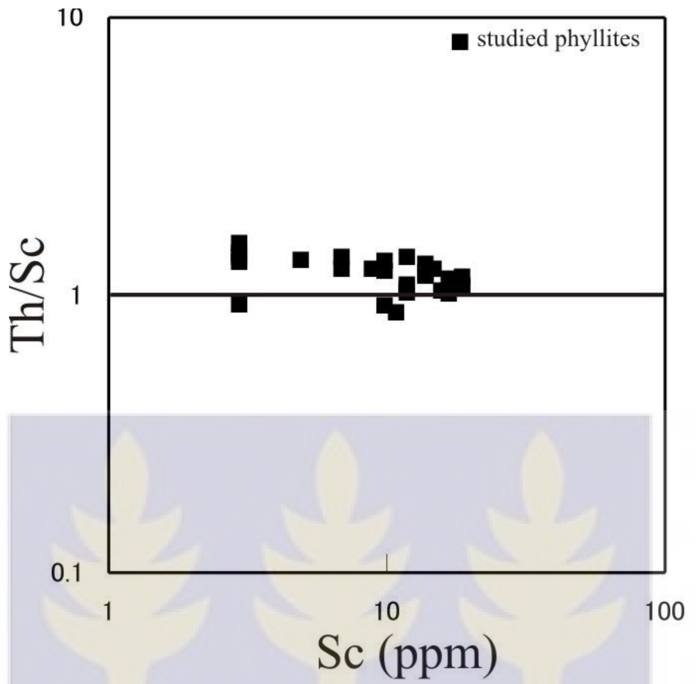

Figure 5.17 Plot of Th/Sc versus Sc for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after McLennan and Taylor, 1991).

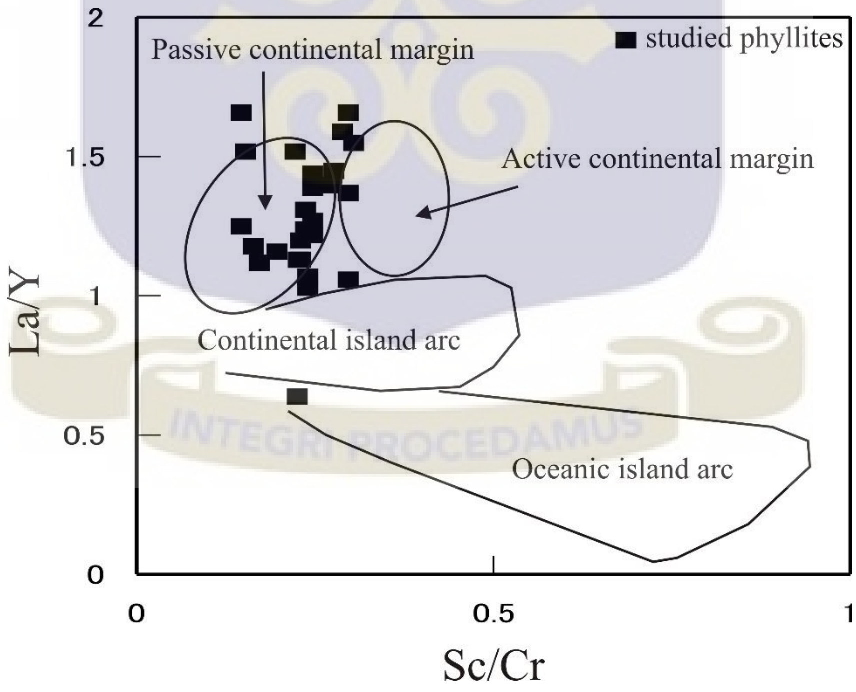

Figure 5.18 Plot of La/Y versus Sc/Cr for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Bhatia and Crook 1986).

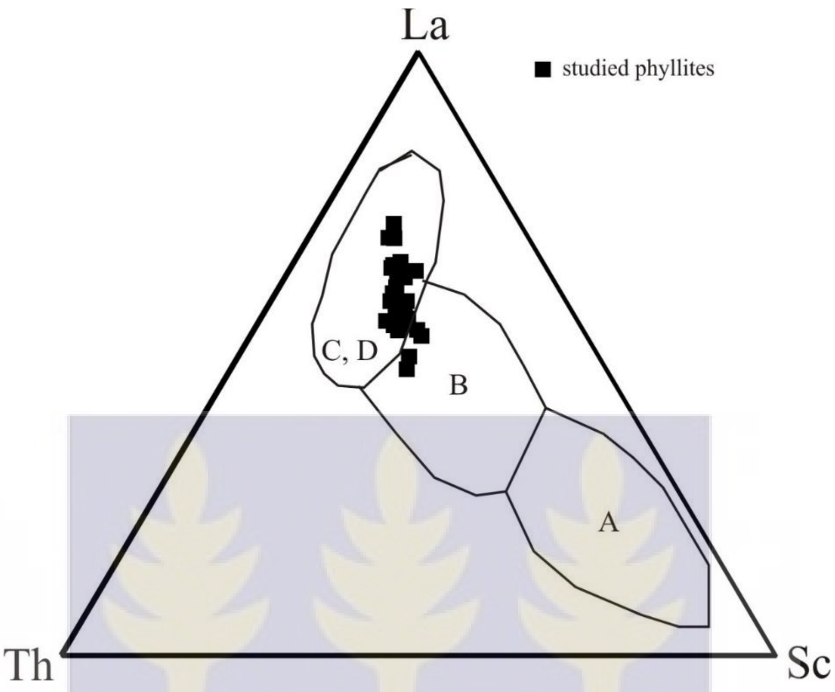

Figure 5.19 La-Th-Sc ternary diagram for the Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (modified after Bhatia and Crook, 1986). A: oceanic island arc; B: continental island arc; C, D: active continental margin and passive margin.

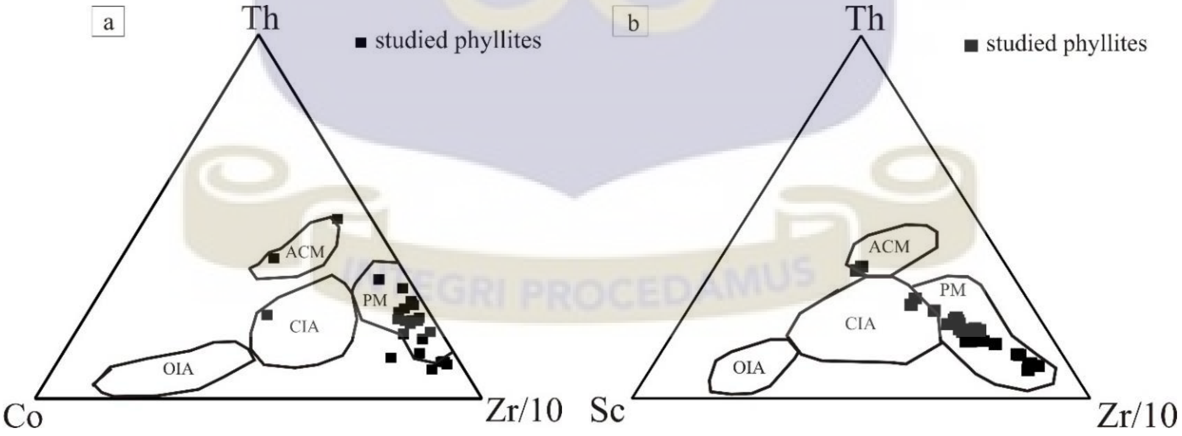

Figure 5.20 (a) Th-Co-Zr/10 and (b) Th-Sc-Zr/10 ternary diagrams for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after Bhatia and Crook, 1986). PM: passive margin; ACM: active continental margin; CIA: Continental island arc; OIA: oceanic island arc.

5.4 CRUSTAL EVOLUTION

Numerous workers have investigated surface samples from various Precambrian shields in North America, Western Europe, Australia, India, South Africa and West Africa (Condie, 1993; McLennan and Xiao, 1998; Asiedu et al., 2004). These studies have helped in the estimation of the chemical composition of the upper continental crust which is now well known. However, 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). Taylor and McLennan (1985) suggested that these variations were as a result of sedimentary processes and Plank and Langmuir (1996) suggested that the dilution of marine terrigeneous sediments with low trace elements bearing siliceous and carbonate sediments probably lead to the variation in chemical composition of the upper crust. McLennan and Xiao (1998) proposed that the cause of this variation may be due to combination of regional variations, difficulties in formulating averages and analytical difficulties.

These hypothetical variations in trace element compositions of rocks between Archean and post-Archean Upper Crust can be observed by the following geochemical signatures (Condie, 1993):

1) A decrease in Eu anomalies;
2) A decrease in Gd_N/Yb_N values from > 2 to 1.0 – 2.0;
3) A decrease in Sm/Nd ratio from about 0.21 to 0.19;
4) A decrease in Cr/Th values from about 20.0 to 5.7;
5) A decrease in the Cr/Sc values from about 13 to 4.1; and

6) An increase in the Th/Sc values from about 0.5 to 1.0.

Studies by Asiedu et al. (2004) on metagraywackes and metapelites from the Paleoproterozoic Birimian Supergroup in the Birim diamondiferous field, southern Ghana, one of the Precambrian shields, 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 characteristic features suggest that the continental crust of the region in Ghana (and possibly for West Africa) during the early Proterozoic had chemical compositions similar to those of the Archean crust (Abouchami et al., 1990; Leube et al., 1990; Sylvester and Attoh, 1992; Taylor et al., 1992).

However, the Neoproterozoic phyllites from the Akuapim range show trace element variations which are typical of post-Archean sedimentary rocks. These variations include the relatively low average Eu anomalies (average Eu/Eu* = 0.61), decrease in Gd_N/Yb_N values (average = 1.46), a decrease in Sm/Nd ratio (average = 0.19) a decrease in Cr/Sc (average = 4.56) and increase in Th/Sc values (average = 1.22), suggesting a significant compositional variation through time. The phyllites show relatively low Gd_N/Yb_N ratios (average = 1.46) which are significantly lower than 2 characteristic of sedimentary rocks of post-Archean age (McLennan and Taylor, 1991). A plot of Eu/Eu* against $Gd_N/Yb_N = 2.0$ (after McLennan and Taylor, 1991) is very useful in the evaluation of trace element variation of the Upper Continental Crust composition through time. On this plot (Figure 5.21), the phyllites compares favourably with Post-Archean sedimentary rocks and further away from the Birimian metasediments which suggests compositional variation in their trace elements through time.

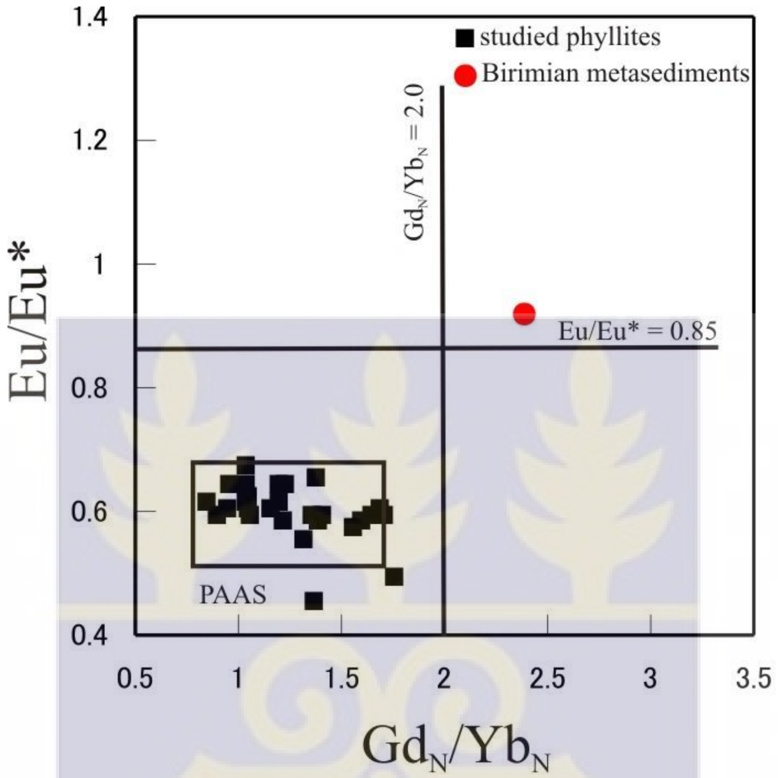

Figure 5.21 Plot of Eu/Eu* versus Gd_N/Yb_N for Neoproterozoic phyllites from the Akuapim range, southeastern Ghana (after McLennan and Taylor, 1991). Birimian metasediments and Post-Archean Australian (average) Shale (PAAS) are plotted for comparison (values are from Asiedu et al., 2004; Taylor and McLennan, 1985, respectively).

5.5 LOCATION OF SOURCE AREA

Grant (1969) and Affaton et al. (1980) suggested that the Buem Structural Unit is a laterally equivalent of the Middle Voltaian, which is, the Afram and Oti Group in Ghana and the Pendjari Group in Togo, Benin and Burkina Faso. In addition, Affaton et al. (1980) suggested that the Togo Structural Unit is a lateral equivalent of the Kwahu/Bombouka Group of the Voltaian Basin. However, studies by Kalsbeek et al. (2008), which involved Pb-Pb zircon dating of rocks from the Voltaian, Buem Structural Unit and Togo Structural Unit revealed that the Lower Voltaian (Kwahu/Bombouaka Group), the Buem Structural Unit and the Togo Structural Unit have similar ages and were probably derived from same source. They interpreted that the Togo Structural Unit and some parts of the Buem Structural Unit correlate with the Kwahu/Bombouaka Group (Figure 5.22).

The rocks of the Kwahu/Bombouaka Group are believed to have been deposited on a passive margin associated with the opening of a Pan-African ocean (Kaslbeek et al., 2008). Also, studies by Osae et al. (2006), showed that the rocks of Buem Structural Unit were deposited on a passive margin that received large amounts of mature detritus from the hinterland areas. In this study, the provenance characteristics of the Togo Phyllites indicate that the rocks were probably deposited on a passive margin. These conclusions support the interpretation that the Kwahu/Bombouaka Group, Buem Structural Unit and Togo Structural Unit are lateral equivalents and were probably derived from the same source.

The rocks of the Kwahu/Bomabouaka Group, Togo Structural Unit and Buem Structural Unit reveal zircons ages of 1000-1300 Ma (Kalsbeek et al. 2008). From the geology of Ghana, no rocks of this age range had been observed in Ghana. According to Kalsbeek et al. (2008), this age range is typical of rocks derived from sources outside the West African Craton and probably from sources in the Amazonian Craton. This assertion was supported by the following evidences:

1) The Amazonian craton was situated close to the West African Craton during the supercontinent Rodinia around 1000-1200 Ma;
2) The prevalence of rocks with ages between 1000-2000Ma in the Amazonian Craton. (e.g. Santos et al., 2000; Tassinari et al., 2000);
3) The predominance of northerly paleocurrent directions in the rocks of the Kwahu/Bombouaka Group (Junner, 1940).

Kalsbeek et al. (2008) concluded that sediments from the Kwahu/Bombouaka Group rocks were probably derived from sources in the Amazonian Craton. Considering the similar tectonic setting and depositional ages as well as the lateral correlation between the Kwahu/Bombouaka Group and the Togo Structural Unit, the Togo Phyllites were probably derived from sources in the Amazonian Craton. However, detailed geochemistry such as zircon dating of the Togo Phyllites must be carried out in order to ascertain this assertion.

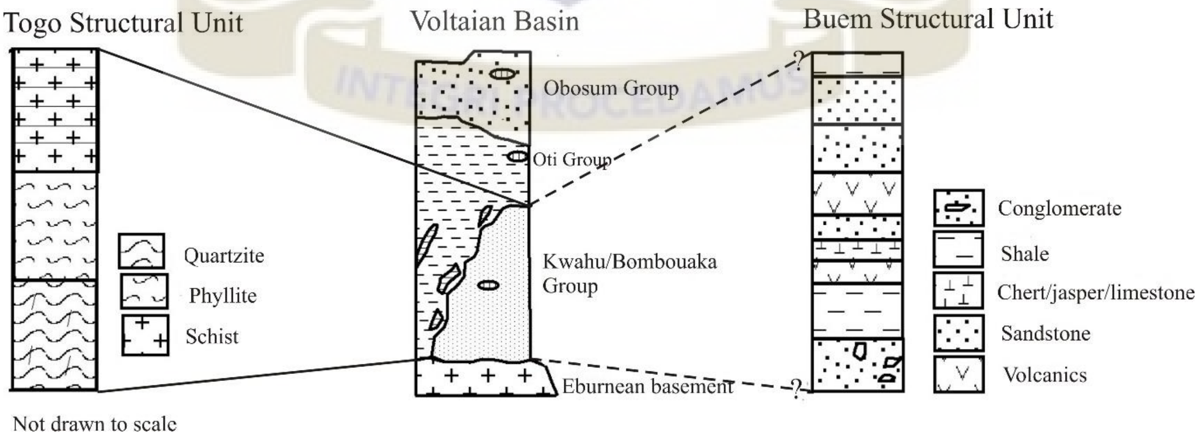

Figure 5. 22 Correlation between the lithological logs of the Togo Structural Unit (after Blay, 1991), the Voltaian (after Affaton, 1990) and the Buem Structural Unit (after Osae et al., 2006).

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The Neoproterozoic phyllites from the Akuapim range have been for their mineralogy and geochemistry. The results are broadly in agreement and the main conclusions are:

1) From geochemical data, the phyllites can be classified mostly as quartz-rich with few quartz-intermediate.
2) The phyllites show geochemical characteristics typical of mature sediments probably derived from an intensely weathered source.
3) The mineralogical and geochemical characteristics of the phyllites indicate that the sediments are mainly derived from an old Recycled Upper Continental Crust. Provenance modeling of the Togo Phyllites shows that the phyllites are composed of a mixture of ~80% Upper Continental Crust and 20% granite.
4) The phyllites exhibit mineralogical and geochemical characteristics indicative of sediments derived from stable continental areas and deposited on a passive continental margin.
5) Trace element data of the phyllites show characteristics that closely resemble those of post-Archean sediments suggesting that, the chemical composition of the continental crust in the study area during the Proterozoic are different from the Archean crust.
6) The phyllites show provenance characteristics similar to that of the Lower Voltaian (Kwahu/Bombouaka Group) and Buem Structural Unit which suggest that the sediments were possibly derived from the same sources in the Amazonian craton.

6.2 RECOMMENDATIONS

The Neoproterozoic phyllites from the Akuapim range show coherent mineralogical and geochemical characteristics which indicate derivation of sediments from one source. It is therefore recommended that single-grain analyses such as Sensitive High Resolution Ion Micro-Probe (SHRIMP) determinations of $^{207}Pb/^{206}Pb$ to determine ages of detrital zircons should be carried out to compare with known ages of possible source rocks to test this hypothesis.

Also, Sm-Nd isotopic composition of the phyllites should be carried out to provide more information on the composition of the source terrane and age at which the source igneous rocks separated from the mantle.

In addition, further petrographical and geochemical studies are recommended in other areas of the Togo Structural Unit to give a better and broad understanding of the provenance of this unit.

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APPENDIX

LIST OF SAMPLE LOCATIONS

Sample station	Latitude (N/degree)	Longitude (W/degree)
KP1	5.80025	-0.18419
KP2	5.800083	-0.1845
KP3	5.799083	-0.18469
KP4	5.798944	-0.18422
KP5	5.795417	-0.18428
KP6	5.795222	-0.18467
KP7	5.79475	-0.18603
KP8	5.79475	-0.18672
KP9	5.793861	-0.18647
KP10	5.792778	-0.18647
KP11	5.788861	-0.18617
KP12	5.788889	-0.18578
KP13	5.788806	-0.18536
KP14	5.766417	-0.19664
KP15	5.768	-0.19514
KP16	5.792139	-0.18447
KP17	5.786611	-0.20775
KP18	5.779000	-0.186000
KP19	5.776000	-0.190000
NP11	5.780000	-0.187000
NP12	5.779000	-0.186000
NP13	5.777000	-0.186000