Geochemical constraints on provenance and source area weathering of metasedimentary rocks from the Paleoproterozoic (~2.1 Ga) Wa-Lawra Belt, southeastern margin of the West African Craton

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1. Introduction

The West African craton (WAC) is divided into the Reguibat shield and Leo-man shield to the north and south respectively, comprising Archaean rocks of Liberian age (3.0–2.5 Ga) to the west and the Birimian Paleoproterozoic age to the east of the Leo-Man shield, respectively (Figure 1). The Birimian is made up of four metasedimentary basins and six volcanic belts. The volcanics within the belts comprise low grade metamorphosed lavas that are mainly tholeiitic in composition, ‘belt type’ tonalite-granodiorite intrusions as well as minor felsic volcaniclastics (Hirdes, Davis, & Eisenlohr, 1992). The basins consist of volcaniclastics, argillites intruded by extensive, late-kinematic ‘basin type’ granitoid plutons which vary from tonalite to peraluminous granite in composition and wackes which are isoclinally folded (Davis, Hirdes, Schaltegger, & Nunoo, 1994; Hirdes et al., 1992; Leube, Hirdes, Mauer, & Kesse, 1990).

Geochronological as well as geochemical studies of igneous rocks indicate that the main Paleoproterozoic crustal growth events in the WAC are characterised by the formation of huge volumes of juvenile material with the involvement of a significantly small Archaean crust component (Abouchami, Boher, Michel, & Albarède, 1990; Taylor, Moorbath, Leube, & Hirdes, 1992). The processes involved in the growth of the Paleoproterozoic continental crust have always aroused debate amongst various researchers. Workers such as Abouchami et al. (1990) and Boher, Abouchami, Michard, Albarède, and Arndt (1992) have suggested that within the Birimian, a relationship does exist between the tholeiitic magmatism and an oceanic plateau environment whereas several others have proposed that the entire Birimian crust grew in an island arc environment (Ama Salah, Liégeois, & Pouclet, 1996; Beziat et al., 2000; Sylvester & Attoh, 1992). It has further been indicated that the Birimian of the Haute-Comoé was deposited in an intracontinental trans-tensional back-arc basin (Vidal & Alric, 1994). This suggests a pre-Birimian basement existed.

The Birimian Supergroup in Ghana consists of narrow sedimentary basins that trend northeasterly as well as linear greenstone belts consisting mainly of volcanic, volcaniclastic to clastic series. Both the sedimentary basins and the greenstone belts (one of which is the Lawra belt – the study area) are intruded by various generations of granitoids (Figure 2). These volcanic and metasedimentary supracrustal rocks occurred during an accretionary period around 2.1 Ga (Abouchami et al., 1990; Taylor et al., 1992) during the 2.1–2.0 Ga Eburnean orogeny (Bonhomme, 1962). The supracrustal sequence was folded and
metamorphosed under predominantly greenschist facies conditions. To the east of the Birimian Supergroup is a relatively younger surrounding unit which is the Voltaian Supergroup (Figures 1 and 2, insert). The Voltaian Supergroup fills the Volta Basin (Figure 2, insert) which is made up of Neoproterozoic to early Paleozoic strata up to ~5 km thick. The strata consist of a succession of sandstones, mudstones, and few proportions of limestone (Affaton, Sougy, & Trompette, 1980; Anani, Mahamuda, Kwayisi, & Asiedu, 2017; Kalsbeek, Frei, & Affaton, 2008). It covers a surface area of ~115,000 km².

In Ghana, the basement rocks to the Birimian are not known. Extensive geochemical and isotopic studies of igneous rocks (i.e. volcanic rocks and associated granitoids) indicate that the Birimian constitutes a huge addition of materials from the mantle (e.g. Dampare et al., 2009; Sakyi et al., 2018, 2014) although the terrane may be underlain substantially by Archaean basement. In Ghana, the metasedimentary rocks in the Birimian Supergroup have received relatively less attention, even though they form the dominant component of the overall Birimian rocks. The crustal evolution of this segment...
of the continental crust may be derived by important information from these metasedimentary rocks. Siliciclastic sedimentary rocks provide an abundance of data about the evolution of the crust. Siliciclastic rock compositions have served as the source of valuable information regarding source-area and tectonic setting (e.g. Bhatia & Crook, 1986), paleoclimate (e.g. Fedo, Eriksson, & Krogstad, 1996; Fedo, Young, & Nesbitt, 1997), as well as average composition estimates of the upper crust (e.g. Condie, 1993; Taylor & McLennan, 1985). This paper presents the outcome of a bulk-rock geochemical study of Birimian metasediments of the Lawra belt, northwestern Ghana; the scanty geochemical studies of the metasedimentary rocks of the Birimian Supergroup in Ghana have been restricted to southwestern Ghana (Asiedu et al., 2017, 2004). This study aims at (i) defining the geochemical features of the

Figure 2. Geological map of the study area modified after Amponsah et al. (2016), showing the various gold camps (where the samples were collected). Insert showing a map of northwestern Ghana showing the surrounding rock units modified after Petersson, Scherstén, and Gerdes (2018).
metasedimentary rocks, (ii) discussing conditions that prevailed at the source area regarding paleoweathering, and (iii) constraining their tectonic setting and provenance.

2. Geological setting

The Wa-Lawra greenstone belt in NW Ghana forms a section of the Eastern Paleoproterozoic Birimian terrane within the WAC (Amponsah et al., 2016; Block et al., 2015; Griffis, Barning, Agezo, & Akosah, 2002). This Paleoproterozoic Birimian geology extends into countries such as Burkina Faso, Ivory Coast, Mali, Niger and Ghana. The Wa-Lawra greenstone belt trends N-S (Kesse, 1985; Somakin and Lashmanov, 1991) in Ghana whilst all other belts trends NE-SW. It is the southern extension of the N-S trending Bromo belt which runs from Burkina Faso into Ghana (Amponsah et al., 2016; Baratoux et al., 2011). The Wa-Lawra belt in Ghana is bounded by the Diebougou-Bouna granitoid domain to the west in Ivory Coast. It is fault bounded (i.e. Jang Fault which is a NNW-S splay of the main Jirapa fault) by the 2162 ± 1Ma to 2134 ± 1Ma Koudougou-Tumu granitoid terrane composed of gabbro and gneisses. These have porphyritic granite intrusions of 2128 Ma to the east (Block et al., 2015). In the south, it is bounded by the Bole-Nagondi belt and the Bole-Bulenga domain. According to Block et al. (2015) and Amponsah et al. (2015, 2016), the Wa-Lawra belt is divided into two halves, with each half juxtaposed by the crustal-scale transcurrent sinistral Jirapa fault. Jirapa faults crosscuts the Bole-Bolenga domain and integrates with the Bole-Nagondi belt in the south (Block et al., 2015; DeKock et al., 2012). The western portion consists mainly of basalts (2200–2160 Ma; Baratoux et al., 2011), (2139 ± 2 Ma detrital zircon ages; Agyei Duodu et al., 2012), (2139 ± 2 Ma detrital zircon ages; Agyei Duodu et al., 2009), sediments (intercalated suites of meta-shales, meta-siltstone and meta-arenites), volcaniclastic rocks and intrusive granitoids of varying ages (i.e. 2212 ± 1 Ma; Sakyi et al., 2014). All the rocks in this half have experienced greenshist metamorphism. P-T conditions obtained from mica schist in the eastern half from a chlorite-quartz-water (Chl-Qz-H₂O) and phengite-quartz-water (Ph-Qz-H₂O) equilibria defined a P-T space of 310-380°C at 2 kbar (Block et al., 2015). Based on micro-thermometric analysis done, CH₄-H₂O ± SO₂ and H₂O-CH₄ -CO₂-SO₂ fluid inclusions by Amponsah et al. (2016) indicated that greenshist facies hydrothermal fluids circulated in the rock at temperatures 310 to 370°C. The eastern half of the Wa-Lawra belt is composed of amphibolite, para and ortho-gneisses, granitoids and rhyolites (Amponsah et al., 2016; Block et al., 2015). The amphibolite facies metamorphism in the eastern half is defined by the mineral assemblage hornblende, clinopyroxene and plagioclase (Block et al., 2015).

A multiphase deformational episode has been recognised on the Wa-Lawra belt by several workers (Amponsah et al., 2016; Baratoux et al., 2011; Block et al., 2015). The first deformation event on the belt is recognised as a result of a sinistral anastomosing transcurrent shear zone showing steep dips. It is oriented N to NNW (left lateral sinistral jog) or fault (along the Jirapa and Jang fault) and denotes an ESE-WNW and E-W shortening (Amponsah et al., 2016). This structural grain resulted from a long-protracted deformation episode from 2128Ma to 2086Ma. This affected all the volcaniclastic sediments, sedimentary and volcanic rocks within the belt (Baratoux et al., 2011). A N-NNW striking and vertically dipping penetrative foliation (S1) is evidence of this structural grain. Further evidence is a sub-horizontal stretching lineation which trends northwards and plunges 20° and parallel to the S0 bedding planes. The second deformational episode is marked by E-W tension gashes. They crosscut S1 shear zones and are mostly quartz filled with E-W direct shortening. The 2020 Ma to 2000 Ma last deformational episode in the belt is marked by F3 isoclinal fold and crenulation cleavages. Vertical fold axes mark the F3 folds as well as axial planar S3 foliation which is ENE-WSW. This deformational episode is assumed to indicate N-S shortening.

3. Sampling and analytical methods

Forty-one (41) samples were collected from thirty (30) drill holes from the following areas in the western part of the Wa-Lawra belt: Basabli, Duri, Yagha, Benkpang, Kunche and Butele (Figure 2). Twenty-two (22) shale samples devoid of weathering and alterations were selected. These were subjected to whole-rock geochemical analysis. The whole-rock major and trace element (including REE) analysis was performed by ALS laboratory in Vancouver, Canada. Sample preparation was done by placing sample (1.0 g) in an oven at 1000°C for 1 hour, cooled and then weighed. The percent loss on ignition was calculated from the difference in weight.

The major elements were analysed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). This was first achieved by dissolution of the grounded samples by lithium metaborate/lithium tetraborate (LiBO₂/Li₂B₄O₇) fusion method. This involved mixing lithium metaborate/lithium tetraborate flux with a prepared sample (0.200 g) and fused in a furnace at 1025°C. An acid mixture containing nitric, hydrochloric and hydrofluoric acids was then used to cool and dissolve the mixture. The solution was then analysed by ICP-AES. The results were corrected for spectral inter-element interferences. 0.01% was the
The trace element analyses were performed observing the protocols as for the major element analyses. However, the prepared sample weighed 0.100 g and the analysis was done by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). The base metals were analysed using the ICP-AES by sample (about 0.25 g) digestion with perchloric, nitric, hydrochloric and hydrofluoric acids and addition of dilute hydrochloric acid. The detection limits (ppm) for the trace elements are as follows: 1 (Co, Cu, Mo, Ni, Sc, Sn, W), 5 (As, V), 2 (Pb, Zn, Zr) 10 (Li, Ti, Cr), 0.05 (Th, U, Dy, Cd), 0.1 (Sr, Ta, Ca, Nd), 0.2 (Rb, Hf, Nb), 0.5 (Ag, Cd, Y, Ba, Ce, La), 0.03 (Pr, Sm, Yb, Er, Eu), 0.01 (Tm, Tb, Cs, Ho).

4. Results

The results of the geochemical analysis and their corresponding sample locations are shown in Tables 1 and 2 respectively.

4.1. Major elements

The studied metasedimentary rocks generally have SiO₂ (53.9 to 68.6) wt.%, Al₂O₃ (14.5 to 20.5) wt.%, TiO₂ (0.55 to 1.0) wt.% and P₂O₅ (0.11 to 0.21) wt.% contents similar to that of PAAS (Figure 3). However, Fe₂O₃ (6.39 to 10.15) wt.%, MgO (2.2 to 4.5) wt.% and Na₂O (0.94 to 3.63) wt.% contents are enriched whereas CaO (0.24 to 2.21) wt.% and K₂O (1.17 to 3.70) wt.% contents are generally depleted compared to that of PAAS (Figure 3). They have low SiO₂/Al₂O₃ values (2.73 to 4.73) indicative of their low maturity. SiO₂ correlates negatively with Al₂O₃ (r = -0.88), TiO₂ (r = -0.81), MgO (r = -0.88), and Fe₂O₃ (r = -0.81) (Figure 4). P₂O₅, K₂O, MnO and CaO do not systematically vary with SiO₂. However, Na₂O (r = 0.19) shows weak positive correlation with SiO₂ (Figure 4).

Several workers have used major element whole-rock geochemistry to classify siliciclastic sedimentary rocks (e.g. Blatt, Middleton, & Murray, 1980; Crook, 1974; Herron, 1988; Pettijohn, Potter, & Siever, 1972). By their Fe₂O₃/K₂O versus SiO₂/Al₂O₃ the studied samples classify as both Fe-shales and shales (Figure 5). The Fe-shales have comparable SiO₂, moderately lower Al₂O₃ and higher Fe₂O₃ contents than the shales.

4.2. Trace elements

The concentrations of the large ion lithosphere elements (LILE) Cs, Rb, Ba and Sr range from 2.59 to 12.1 ppm, 45.8 to 110 ppm, 218 to 879 ppm, and 110 to 394 ppm, respectively (Table 1). In comparison to PAAS, the studied shales exhibit slight to strong depletion in Rb, Ba and Cs and enrichment in Sr. Rb/Sr ratios (0.2 to 0.93) are lower than that of PAAS (Rb/Sr = 1.25; Taylor & McLennan, 1985).

The studied shales have high so-called transition metals Ni (73 to 120 ppm, average of 94.5 ppm), Co (21 to 35, average of 27.4 ppm), Cr (150 to 260 ppm, with an average of 190 ppm), V (110 to 180 ppm, with an average of 151 ppm), and Sc (16 to 24 ppm, with an average of 19.8 ppm). Generally, the studied shales are enriched in these transition metals relative to PAAS (Figure 6).

The concentrations of the high field strength elements (HFSE), Zr, Hf, Ta, Nb, Th, U, Y, La range from 103 to 163 ppm, 2.8 to 4.1 ppm, 0.2 to 0.4 ppm, 4.6 to 7.1 ppm, 2.26 to 3.86 ppm, 0.9 to 1.45 ppm, 9.2 to 22.2 ppm, 11.8 to 23 ppm, respectively. Relative to PAAS the studied shales exhibit depletion in the HFSE (Figure 6). The average Zr/Hf value of 36.6 is suggestive of zircon control (Zr ≈ 40). Th/U values (2.33 to 3.14) are consistently lower than that of the continental upper crust (Th/U = 3.8; McLennan, Hemming, McDaniel, & Hanson, 1993).

4.3. Rare earth elements

The rare earth element (REE) data for the studied shales are somewhat variable with total REE (ΣREE) values of 65.7 to 127 ppm, averaging of 101 ppm, which is lower than that of PAAS value of 184.8 ppm (Taylor & McLennan, 1985). The shales display REE patterns that are similar when normalised to PAAS with slightly depleted Light REE (LREE) (Figure 7). On a chondrite-normalised diagram (not shown) the studied shales display fractionated LREE patterns (average LaN/SmN = 2.81), small negative Eu (average Eu/Eu* = 0.79) and fairly flat HREE patterns (average GdN/YbN = 1.51) which are characteristic of sediments derived from upper continental crust (Taylor & McLennan, 1985).

5. Discussion

5.1. Heavy mineral accumulation and metamorphism

The degree of sorting and recycling may be deduced by evaluating the accumulation of weathering-resistant phases such as zircon and monazite in siliciclastic sedimentary rocks (McLennan et al., 1993). Enrichment of zircon, and therefore recycling and sorting, can be inferred from the Th/Sc versus Zr/Sc diagram; the ratio Zr/Sc is an effective index of zircon enrichment while the ratio Th/Sc is a good indicator of igneous chemical differentiation processes (McLennan et al., 1993). The studied samples on this diagram trend in the general provenance-dependent compositional variation pattern with none of the
Table 1. Geochemical data for the metasedimentary rocks of the Wa-Lawra belt.

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samples plotting in the high Zr/Sc range which is characteristic of zircon accumulation associated with sediment sorting and recycling (Figure 8(a)).

Zircon is rich in HREE and its accumulation will result in the decrease in the chondrite-normalised La\textsubscript{N}/Yb\textsubscript{N} ratio. Therefore, a negative correlation between Zr and La\textsubscript{N}/Yb\textsubscript{N} would be expected if zircon is concentrated in the samples. However, there is no such negative correlation between the two (Figure 8(b)), and it, therefore, rules out preferential zircon accumulation in the samples. A very steep chondrite-normalised HREE pattern is characteristic of monazite which has very high REE abundances, and even small amounts (<0.01%) result in significant increases in the chondrite-normalised Gd\textsubscript{N}/Yb\textsubscript{N} ratio (McLennan et al., 1993). The fairly flat HREE pattern of the studied shales (Figure 7) rules out preferential monazite accumulation in the samples.

Some major and trace elements in metamorphic rocks are mobilised by interaction with fluids. To a lesser extent, by solid-state diffusion and melt generation (Rollinson, 1993). The rocks of the Lawra Belt have been subjected to up to greenschist facies metamorphism and therefore there is the possibility that some of the elements may have been preferentially remobilized (Rollinson, 1993; Taylor & McLennan, 1985). Such element remobilization would obviously reduce the effectiveness of using them in provenance discrimination.

To minimise the effect of remobilization, samples containing any visible hydrous fluid transfer veinlets were avoided for this study. Nevertheless, some authentic proofs have been used against large-scale remobilization of the elements in the studied metasedimentary rocks: All the samples have similar and smooth REE patterns which would not be expected during remobilization. In addition, although it is

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<td>Dy</td>
<td>3.35</td>
<td>3.50</td>
<td>3.56</td>
<td>3.14</td>
<td>3.68</td>
<td>3.20</td>
<td>3.06</td>
<td>2.61</td>
<td>3.25</td>
<td>3.87</td>
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</tr>
<tr>
<td>Ho</td>
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<td>0.72</td>
<td>0.78</td>
<td>0.66</td>
<td>0.69</td>
<td>0.58</td>
<td>0.70</td>
<td>0.89</td>
<td>0.64</td>
<td></td>
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</tr>
<tr>
<td>Er</td>
<td>2.18</td>
<td>2.20</td>
<td>2.29</td>
<td>2.03</td>
<td>2.06</td>
<td>1.99</td>
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<td>1.65</td>
<td>1.99</td>
<td>2.42</td>
<td>1.85</td>
</tr>
<tr>
<td>Tm</td>
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<td>0.31</td>
<td>0.34</td>
<td>0.29</td>
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<td>0.23</td>
<td>0.29</td>
<td>0.39</td>
<td>0.30</td>
</tr>
<tr>
<td>Yb</td>
<td>1.93</td>
<td>2.05</td>
<td>2.05</td>
<td>2.12</td>
<td>2.01</td>
<td>1.80</td>
<td>1.47</td>
<td>2.01</td>
<td>2.35</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>Lu</td>
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<td>0.33</td>
<td>0.34</td>
<td>0.31</td>
<td>0.34</td>
<td>0.33</td>
<td>0.28</td>
<td>0.26</td>
<td>0.32</td>
<td>0.37</td>
<td>0.29</td>
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</tbody>
</table>

Table 2. Sample locations of the metasedimentary rocks (Table 1) of the Wa-Lawra Belt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1D/Depth</th>
<th>Easting</th>
<th>Northing</th>
<th>Rock name</th>
<th>Sample type</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVA038a</td>
<td>(211.0–211.5 m)</td>
<td>524,468</td>
<td>1,166,276</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>AVA038b</td>
<td>(217.5–218.0 m)</td>
<td>524,468</td>
<td>1,166,276</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>AVA042a</td>
<td>(194.0–194.5 m)</td>
<td>524,420</td>
<td>1,166,079</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>AVA042b</td>
<td>(201.1–201.6 m)</td>
<td>524,420</td>
<td>1,166,079</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>BR203</td>
<td>(251.5–252.0 m)</td>
<td>527,047</td>
<td>1,152,225</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
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<td>(84.4–85.0 m)</td>
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<td>1,151,474</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>BR258</td>
<td>(117.5–118.0 m)</td>
<td>527,046</td>
<td>1,152,173</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>BR263</td>
<td>(144.5–145.0 m)</td>
<td>527,076</td>
<td>1,152,123</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>BR265</td>
<td>(147.7–148.2 m)</td>
<td>527,050</td>
<td>1,152,095</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>BR302</td>
<td>(185.5–186.0 m)</td>
<td>527,022</td>
<td>1,152,224</td>
<td>SHALE</td>
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<tr>
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<td>(228.0–228.5 m)</td>
<td>527,052</td>
<td>1,152,351</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>BR450b</td>
<td>(234.0–234.5 m)</td>
<td>527,052</td>
<td>1,152,351</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>KR080a</td>
<td>(150.0–151.0 m)</td>
<td>527,028</td>
<td>1,149,108</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>KR080b</td>
<td>(156.0–156.5 m)</td>
<td>527,028</td>
<td>1,149,108</td>
<td>SHALE</td>
<td>CORE</td>
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<tr>
<td>KR565</td>
<td>(163.0–163.5 m)</td>
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<td>1,149,499</td>
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<td>CORE</td>
</tr>
<tr>
<td>KR699</td>
<td>(276.0–276.5 m)</td>
<td>526,992</td>
<td>1,148,575</td>
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<tr>
<td>KR700a</td>
<td>(229.0–229.5 m)</td>
<td>524,765</td>
<td>1,166,074</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>KR700a</td>
<td>(261.0–261.5 m)</td>
<td>526,925</td>
<td>1,149,247</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>KR700b</td>
<td>(264.0–264.5 m)</td>
<td>526,925</td>
<td>1,149,247</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
<tr>
<td>KR700b</td>
<td>(299.0–299.5 m)</td>
<td>526,925</td>
<td>1,149,247</td>
<td>SHALE</td>
<td>CORE</td>
</tr>
</tbody>
</table>
possible that some elements such as the LILE may have been remobilized, the covariance among the HFSE such as Zr, Hf, Nb, Ta, Th, U, V, Cr, Ni, Co, and REEs suggests that these elements have the same degree of low mobility during metamorphism.

**5.2. Source area weathering and diagenesis**

For most rocks, the Rb/Sr ratio increases with increasing degree of chemical weathering. This is so because Rb\(^+\), a large alkali trace element, remains fixed in the...
weathered residue, in preference to the smaller Sr$^{2+}$ which is selectively leached (McLennan et al., 1993; Nesbitt et al., 1980). As a result, the Rb/Sr ratio has been used to evaluate the intensity of chemical weathering at the source area; Rb/Sr > 1 is an indication of high degree of chemical weathering whereas Rb/Sr < 1 indicates moderate to low degree of chemical weathering. The studied shales have range of Rb/Sr from 0.20 to 0.93 (average, 0.43) suggesting low degree of chemical weathering at the sediment source area.

For most upper crustal igneous rocks, the Th/U is typically about 3.5 to 4.0 (McLennan et al., 1993). Weathering typically results in the oxidation and subsequent dissolution of U thereby elevating the Th/U ratios above the upper crustal values, especially for shales (Taylor & McLennan, 1985). However, other sedimentary processes may result in U enrichment thereby lowering the Th/U ratio; in such cases the low Th/U will be accompanied by high U content. The Th/U values in the studied shales range from 2.33 to 3.14 (average 2.73) which is well below upper crustal values, and the U concentrations range from 0.9 to 1.45 ppm (average 1.15 ppm) well below that of typical shales (U ~ 3.1) and upper continental crust (U ~ 2.7) (Taylor & McLennan, 1985). This suggests a low degree of chemical weathering at the sediment source area.

The Chemical Index of Alteration (CIA) has been used to quantify the weathering history of sedimentary rocks, primarily to understand paleoclimate conditions (Nesbitt & Young, 1982, 1984). Unweathered igneous rocks have CIA values less than 50, typical shales average about 70 to 75, and intensely weathered rocks have CIA values that approaches 100 (Fedo et al., 1996; McLennan et al., 1993). The studied shales have CIA values that range from 58 to 78 (average, 67.6), which ranges from those of unweathered igneous rocks to typical shales, indicating low to moderate degree of weathering at the sediment source area.

The weathering history for the studied shales may be evaluated using the A-CN-K diagram (Figure 9). In this diagram, it is expected that the samples will plot in a trend parallel to the A-CN join if weathering is the control of the composition (Fedo et al., 1996; Fedo, Nesbitt, & Young, 1995; McLennan et al., 1993). The studied samples, however, indicate a linear trend (Trend 1). It is not comparable with simple weathering being the sole control of the composition (Trend 2). The plots suggest the effects of K addition to the samples as a result of metasomatism (Fedo et al., 1996, 1995). The pre-metasomatized CIA values of the studied samples may be estimated from the diagram using the method outlined by Fedo et al. (1995). This puts the pre-metasomatized CIA range from 60 to 85 (Figure 9) indicating low to moderate degree of chemical weathering in the source area of the sediments.

The occurrence of K enrichment is widespread in Precambrian sedimentary rocks and therefore, Fedo
et al. (1996) proposed the Plagioclase Index of Alteration (PIA) to evaluate weathering histories it takes care of the influence of K-feldspar. The maximum PIA value is 100 and unweathered plagioclase has a PIA value of 50. The studied shales have a range of PIA values from 59 to 88 (average, 72) suggesting weak to moderate weathering in the source area of the sediments.

### 5.3. Source rock composition

The compositions of fine-grained siliciclastic sedimentary rocks, such as shales, are particularly characteristic of the bulk composition of the source region. The abundances of HFSE and the transition metals, and REEs have particularly proved useful in discriminating the source composition of fine-grained metasedimentary rocks (e.g. Asiedu et al., 2017; Roddaz, Debat, & Nikiéma, 2007; Yang, Kyser, & Ansdell, 1998). Compared to PAAS the studied shales show depletion in HFSE such as La, Zr, Hf, Th, Ta, and Nb, and enrichment in transition metals such as Cr, Ni, Co, Sc, and V, suggesting a significant contribution from mafic sources (Figure 6). Compared to PAAS the studied shales show less LREE enrichments and less pronounced europium anomalies (Figure 7) also suggesting significant input from mafic sources.

Co-Th-Sc-La systematics can reveal the mixing between felsic and mafic sources for sedimentary rocks (Taylor & McLennan, 1985; Yang et al., 1998). On La/Sc versus Co/Th and Sc/Th versus Co/Th diagrams (Figure 10(a and b)), the studied Birimian shales plot between the basalt and granite end-members with cluster towards the mafic end (high La/Sc and Co/Th, and low La/Sc). The geochemistry of the studied shales can, therefore, be explained as having been derived from a mixture of basaltic rocks (mainly) and granitic rocks (subordinately).

Following the establishment of diverse possible source components, we seek to indicate the relative contribution of three rock types with distinct REE patterns. These are basalt (BAS), granite (GRA) and tonalite–trondhjemite–granodiorite (TTG). Kasanzu, Makenya, and Manya (2008) were adopted to achieve the mixing calculations. Modelling for the average studied Birimian shale accomplished using the following REE parameters: Gd$_N$/Yb$_N$, Eu/Eu*, and La$_N$/Yb$_N$. The mixing calculations were set in a matrix form as:

$$
\begin{bmatrix}
\text{Eu}^* / \text{Eu} \\
\text{La}_N / \text{Yb}_N \\
\text{La}_N / \text{Sm}_N
\end{bmatrix}
= \begin{bmatrix}
0.93 & 0.36 & 0.99 \\
11.62 & 9.19 & 2.73 \\
3.61 & 3.44 & 1.81
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix}
$$

where $x = $ TTG, $y = $ granite (GRA) and $z = $ basalt (BAS). The ratios La$_N$/Yb$_N$ and Gd$_N$/Yb$_N$ are chondrite-normalised (Normalising values from Taylor & McLennan, 1985).

---

**Figure 9.** $\text{Al}_2\text{O}_3-(\text{CaO}^*+\text{Na}_2\text{O})-\text{K}_2\text{O}$ diagram for the metasedimentary rocks of the Wa-Lawra Belt.

**Figure 10.** Plots of (A) Co/Th versus La/Sc and (B) Co/Th versus Sc/Th for the metasedimentary rocks of the Wa-Lawra Belt. Also plotted are average Paleoproterozoic volcanic and plutonic rocks from Condie (1993). BSH, studied shales; BAS, basalt; AND, Andesite; GRA, granite; TTG, tonalite–trondhjemite–granodiorite; FVO, felsic volcanic rock.
The results obtained from the mixing calculations have shown that a mixture having 16% TTG, 35% granite and 49% basalt is best for the modelling of the studied Birimian shale.

5.4. Tectonic settings and location of sources

The geochemical compositions of siliciclastic sedimentary rocks have been used to discriminate the tectonic settings of sedimentary basins (e.g. Bhatia, 1983; Roser & Korsch, 1986). Particularly useful for Precambrian metasedimentary rocks are tectonic discrimination diagrams that utilise immobile trace elements (e.g. Bhatia & Crook, 1986). On the Th–Sc–Zr and the Th–La–Sc diagrams, the samples of the Birimian shales fall exclusively in the oceanic island arc field (Figure 11(a and b)).

McLennan et al. (1993) defined four different types of terrane that can be identified from geochemical data: Young Differentiated Arc, Old Upper Continental Crust, Young Undifferentiated Arc, and Recycled Sedimentary Rocks. Compared to PAAS and upper crustal values the studied shales have (i) relatively low but variable SiO₂/Al₂O₃, K₂O/Na₂O, and CIA values, (ii) lower ratios of incompatible to compatible elements, such as Th/Sc and Zr/Sc (Figure 3), and (iii) lack of substantial Eu anomalies and low LREE enrichment (Figure 7). These geochemical features indicate young undifferentiated arc provenance for the studied shales (McLennan et al., 1993). The Th/U ratio is typically about 3.5 to 4.0 for most upper crustal rocks (McLennan et al., 1993; Taylor & McLennan, 1985). Sediments from active margin tectonic settings, which consist of young undifferentiated crust, typically have Th/U significantly below 3.5 accompanied by low Th and U abundances (McLennan and Taylor, 1991; McLennan et al., 1993). On Th/U versus Th diagram (Figure 12), the studied shales mainly plot in the depleted mantle sources field reflecting geochemically depleted mantle sources of the arc provenance. The low Th/U values of the studied shales (Th/U = 2.33 to 3.14) and the relatively low Th and U concentrations compared to upper crustal values and PAAS also suggest that the shales have young undifferentiated arc provenance (Figure 12; McLennan et al., 1993). The above geochemical characteristics, therefore, suggest that the studied Birimian shales are juvenile crustal material derived from local sources, most probably the adjacent volcanic rocks and their associated granitoids.

Our inference that the Birimian shales of the Lawra greenstone belt represent juvenile crustal materials derived locally from the volcanic and associated granitic rocks places constraints on the evolution of the Birimian crust. Our present work, together with previous provenance studies on the Birimian metasedimentary rocks (e.g. Asiedu et al., 2017, 2004) shows juvenile geochemical signatures with only minor contribution of an older crustal component. The lack of evidence for incorporation of substantial Archaean

![Figure 11. Plots of (A) Th – Co – Zr, and (B) Th – La – Sc for the tectonic setting discrimination of the shales from the Wa-Lawra belt (after Bhatia & Crook, 1986). A, Oceanic Island Arc; B, Continental Island Arc; C, Active Continental Margin; D, Passive Continental Margin.](image1)

![Figure 12. Plot of Th/U versus Th for the shales of the Wa-Lawra belt (after McLennan et al., 1993).](image2)
detritus, therefore, rules out an intra-cratonic origin of the sediments as previously proposed by Ledru, Pons, Milesi, Feybesse, and Johan (1991).

6. Conclusions

A whole-rock geochemical study was undertaken on fine-grained metasedimentary rocks from the Birimian Wa-Lawra Belt of northern Ghana in order to constrain the provenance and source area weathering. The following deductions were made:

1. The fine-grained metasedimentary rocks are classified as shales on the basis of their major element compositions.
2. The shales are first cycle in origin and obtained from materials of mixed mafic and felsic compositions. Mixing calculations using the REEs suggest a provenance with mixture having 16% TTG, 35% granite and 49% basalt.
3. The shales represent juvenile crustal materials derived locally from the associated granitic and volcanic rocks.
4. The shales were deposited in an oceanic island arc setting.

Acknowledgments

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References


