MINERALOGICAL AND GEOCHEMICAL COMPARISON BETWEEN THE SHALES OF BEDUH AND BALUTI FORMATIONS IN THE NORTHERN THRUST ZONE, KURDISTAN REGION, IRAQ: IMPLICATION FOR PROVENANCE AND TECTONIC SETTING

Faraj H. Tobia*, Baran H. Mustafa, Sirwa S. Shangola and Mario U. Kasha

*Department of Geology, College of Science, University of Salahaddin, Erbil, Iraq
*Corresponding author: e-mail: farajabba58@gmail.com

Received: 23 May 2017; accepted: 10 August 2017

ABSTRACT

The mineralogical and geochemical data are employed to determine the provenance, paleoweathering, and depositional setting of the shales from the Beduh (L. Triassic) and Baluti (U. Triassic) formations at Sararu area N of Iraq. The mineralogical data (e.g., high illite content and moderate illite crystallinity index in Beduh shale and kaolinite in Baluti shale) and geochemical parameters of the shales (major, trace, and REE-based discrimination diagrams, Al$_2$O$_3$/TiO$_2$, and LREE/HREE ratios) indicate that both shales were evolved from acidic source rocks. This is inclined by the enrichment of LREEs, depletion of HREEs, and negative Eu anomaly. The paleoweathering parameters (chemical index of alteration and chemical index of weathering), in addition to the A-CN-K (Al$_2$O$_3$-CaO+Na$_2$O-K$_2$O) diagram of the Beduh shale induce that the source terrain was moderately to intensively and for Baluti shale was intensively chemically weathered. The Beduh shale was plot perpendicular to the A-K line indicates the K-metasomatism, and for Baluti shale was fall parallel to the A-K line suggesting intense weathering with no evidence for K-metasomatism. The discriminant diagrams based on major elements in addition to critical trace and REE parameters suggest that the origin of the sediments was probably from passive (Arabian Shield and the Rutba Uplift) tectonic environments for both with the effect of the active (volcanic activity) tectonism on the Beduh shale. The geochemical parameters such as U/Th, V/Cr, and Ni/Co ratios and negative Eu anomalies indicate the study shales were deposited in an oxic environment.

Keywords: Beduh Formation; Baluti Formation; REE; Shale; Provenance
INTRODUCTION

The mineralogical and geochemical data of the clastic rocks have been used to determine the degree of weathering (Fedo et al., 1995; Ghandour et al., 2003; Srivastava et al., 2013), tectonic setting (Bhatia, 1983; Verma and Armstrong-Altrin, 2013), and the diagenesis (Zaid et al., 2015), in addition it reflect the characteristics of their source rocks which some trace elements (e.g., REEs, Th, Zr, and Hf) are transformed from the site of weathering to the sedimentary basin (McLennan and Taylor, 1991; Tawfik et al., 2011; Armstrong-Altrin et al., 2012, 2014; Dai et al., 2016). Therefore, these terrigenous materials can be preserving the characteristics of their parent rocks.

The Triassic formations in the Northern Thrust Zone in Iraq (Fig. 1) receive less attention in relative to other younger rocks. Most of the previous studies were related to structural, tectonic, and facies analyses. In 1997, Numan proposed the tectonic scenario of Iraq and suggested Beduh shale in the Werfenian, marking isolation of the Iranian Plate; and Baluti shale, marking isolation of the Turkish Plate.

The siliciclastic-dominated Beduh Formation described as 60 m thick reddish brown to reddish purple shale and marl with thin beds of limestone and hard sand (Bellen et al., 1959). The shale-dominated Baluti Formation is comprised mainly of shale interbedded with thin beds of dolomitic limestones. It varies in thickness from 35 to 60 m and the age of the formation is decided by its stratigraphic position between the Upper Triassic Kurra Chine Formation and the overlying Liassic Sarki Formation (Fig. 2). However, Hanna (2007) suggested the Carnian age based on the assemblage palynozones.

The current study examines the mineralogy and geochemistry of the Beduh and Baluti shales and the objectives of this study are to compare between these shales to understand the provenance and tectonic setting of the basin during the Lower and Upper Triassic.
Fig. 1: Geological map and the location of the study area, (enlarged from Sissakian, 2000)

Fig. 2: Columnar sections, a) in Beduh Formation and b) in Baluti Formation, in Sararu area
GEOLOGICAL SETTING

At the Late Permian the Neo-Tethys Ocean started opening, then progressively widened during Early Triassic time (Figs. 3a and 4). The Late Permian-Liassic sequence was deposited on the north and east fringes of passive margin of the Arabian Plate. Thermal subsidence causes the formation of a passive margin sequence along these margins and the creating of the Mesopotamian Basin (Jassim et al., 2006). Renewed rifting occurred within this passive margin in Mid-Late Triassic time (Fig. 3b) creating a broad and highly restricted basin in Mesopotamia splitted from the open ocean by a narrow rift with an outer ridge of thinned continental crust and development of an open marine carbonate platform (Numan, 1997; Jassim and Goff, 2006).

The Rutba Basin was gently inverted; forming the Rutba Uplift. The shoreline of the Late Permian basin was located along the eastern fault of the Rutba Uplift (Fig. 3). The Arabian Shield was composed of igneous-metamorphic complexes and was an elevated area at that time, located to the southwest of the basin of deposition.

Fig. 3: a) Late Permian-Early Triassic, b) Mid Triassic-Norian geodynamic development of the Arabian Plate (after Jassim and Goff, 2006)
Fig. 4: Imaginary model for the Permian-Triassic plate tectonic situation of Iraq and surrounding countries: a) intraplate set-up, b) rifting set-up (after Numan, 1997)

The study area lies at 37°14′25″N and 43°18′19″E (Fig. 1). In this area, the Beduh Formation is conformably underlain by the Mirga Mir Formation and overlain by the Geli Khana Formation. The upper boundary of Baluti Formation is conformable with the Liassic Sarki Formation. Hanna (2007) suggested the Carnian (Julian) age for the upper part of Baluti Formation depending on the assemblage palynozones. He proposes the shore zone depositional environment with influence of fresh water for the lower portion of the upper part of the formation.

SAMPLING AND METHODS

Thirty six shale samples were collected from the Sararu area: 21 samples from the Beduh and sixteen samples from Baluti Formation (Fig. 2). The mineralogy of fourteen shale samples (six from Beduh and 8 from Baluti shales) was determined by conventional X-ray diffraction (XRD) method using Philips PM8203 X-ray diffractometer at the Iraqi Geological Survey Laboratories, Baghdad, Iraq. The oriented clay samples were run under three different conditions: air-dried state, ethylene glycolation at 25 °C for 15 h, and after heating to 550°C for 1 h. The area under curve of specific reflections of the clay minerals was calculated for the semiquantitative analysis (Carroll, 1970).

The 36 shale samples were analyzed for major, trace, and rare earth elements. Chemical analyses of Beduh shale were performed at Acme Analytical Laboratories, Vancouver, Canada; and for Baluti shale at ALS international laboratory in Spain. The
major element contents were analyzed by X-ray fluorescence spectrometry. Loss on ignition (LOI) was calculated after ignition at 1000 °C for 2 h. Trace and REE concentrations were measured by inductively coupled plasma mass spectrometer. Chemical analysis for major elements has precisions up to 3%; whereas it varies from 1 to 10% for the trace and REEs.

Based on the standards, the accuracy and the precision of the analyses were within ±2% to ±10%. The Post-Archean Australian shale (PAAS) values were used for comparison. The REE data were normalized to the chondrite values of Taylor and McLennan (1985). The normalized Eu anomaly (Eu/Eu*) was calculated by the following equation: Eu/Eu* = Eu_n/(Sm_n x Gd_n)^1/2, where the subscript n denotes chondrite normalized values (Taylor and McLennan, 1985). CaO was corrected by the method of McLennan et al. (1993).

RESULTS

Mineralogy

XRD analysis of selected Beduh shale samples indicates that clay minerals are mainly represented by illite and kaolinite, with small amounts of chlorite and a mixed layer (illite/smectite and illite/chlorite). On the other hand, calcites and quartz together with minor amounts of albitic feldspar and hematite are the dominant non-clay species (Fig. 5a). The analysis revealed qualitative differences in bulk mineral compositions (Table 1). Illite and kaolinite have an average of 58.07% and 26.05%, respectively. The samples generally showed moderate illite crystallinity index with an average of 0.49° Δ20 (Table 1). All the study shales have illite chemistry index (5Å°/10Å° ratios) of >0.4 (Table 1).

However, the Baluti shales are mainly comprised of clay minerals with calcite, quartz, and minor amounts of muscovite; and the main clay minerals are kaolinite, illite, and mixed layer illite/smectite (Fig. 5b). Illite and kaolinite have an average 32.9% and 32.3%, respectively. The average of Kübler illite index is 1.0 Δ20 (Table 1); the modal illite crystallinity value is 0.69 Δ20 which is typical for a high diagenetic zone (Merriman and Frey, 1999). The average of illite chemistry index is 0.59 and kaolinite crystallinity index is 0.15.
Fig. 5: X-ray diffractograms for selected shale samples from, a) Beduh Formation and b) Baluti Formation

Table 1: Mineralogical composition and crystallographic parameters for the shales from Beduh and Baluti formations

<table>
<thead>
<tr>
<th>Non-clay minerals</th>
<th>Clay minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcite</td>
</tr>
<tr>
<td></td>
<td>%</td>
</tr>
<tr>
<td><strong>Beduh shale</strong></td>
<td></td>
</tr>
<tr>
<td>Ba1</td>
<td>84.9</td>
</tr>
<tr>
<td>Ba5</td>
<td>50.0</td>
</tr>
<tr>
<td>Ba13</td>
<td>79.1</td>
</tr>
<tr>
<td>Ba19</td>
<td>85.0</td>
</tr>
<tr>
<td>Ba20</td>
<td>85.0</td>
</tr>
<tr>
<td>Ba25</td>
<td>50.9</td>
</tr>
<tr>
<td>average</td>
<td>54.8</td>
</tr>
<tr>
<td><strong>Baluti shale</strong></td>
<td></td>
</tr>
<tr>
<td>Ba1</td>
<td>91.4</td>
</tr>
<tr>
<td>Ba3</td>
<td>89.3</td>
</tr>
<tr>
<td>Ba5</td>
<td>95.1</td>
</tr>
<tr>
<td>Ba7</td>
<td>95.1</td>
</tr>
<tr>
<td>Ba9</td>
<td>94.2</td>
</tr>
<tr>
<td>Ba11</td>
<td>91.0</td>
</tr>
<tr>
<td>Ba13</td>
<td>91.2</td>
</tr>
<tr>
<td>Ba15</td>
<td>92.9</td>
</tr>
<tr>
<td>average</td>
<td>92.7</td>
</tr>
</tbody>
</table>
Major element geochemistry

The major element concentrations of the Beduh and Baluti shales are given in Table 2. Both shales have high CaO content. Such content has a great dilution effect on the other oxides. The average of SiO$_2$ content in the Beduh is 36.38%, and 9.12 % in Baluti shale. Al$_2$O$_3$ content is 11.37% in Beduh and 14.60% in the Baluti. The TiO$_2$ content of both shales is relatively low (0.46% in Beduh and 0.48% in Baluti). The average of K$_2$O content is 3.68% for Beduh and 5.64% for Baluti shales. Na$_2$O content is 0.61% for Beduh and 0.09% for Baluti shales. Except for CaO, the study shales show depletion in all elements relative to those of the PAAS (Table 2).

Table 2: Major oxides concentrations (wt %) for the shales from the Beduh and Baluti formations; compared with PAAS and UCC (Taylor and McLennan, 1985)
Trace element geochemistry

The trace element concentrations of the Beduh and Baluti shales are reported in Table 3. The study shales show enrichment in Sr, Ba, and Th; and depletion in Rb, U, Y, Zr, Nb, Hf, V, Cr, Co, Ni, Cu and Zn relative to PAAS (Table 3). The high concentration of Sr (average = 418 ppm) in a few samples is probably linked to the carbonate content (Yan et al., 2007). This is conform to the significant positive correlation between CaO and Sr (r = 0.871) in Beduh and (r = 0.820) in Baluti. Al₂O₃ is positively correlated with HFSEs such as Y, Zr, Nb, and Hf (for Beduh, r = 0.741, 0.586, 0.934, and 0.579; and for Baluti, r = 0.671, 0.525, 0.632, and 0.725) and LILEs such as Th (r = 0.908 for Beduh and 0.737 for Baluti); and to TTEs such as V, Co, and Ni (for Beduh, r = 0.969, 0.932, and 0.964; and for Baluti, r = 0.650, 0.813, and 0.552), suggesting their incorporation in clay fractions and concentrated during weathering (Fedo et al., 1996; Nagarajan et al., 2007) and some of them (such as Zr and Hf) are associated with the heavy minerals.

Table 3: Trace element concentrations (ppm) for the shales from the Beduh and Baluti formations, compared with PAAS and UCC (Taylor and McLennan, 1985)
The average of total rare earth elements (ΣREE) is 146.40 ppm for Beduh shale, and 117.17 ppm for Baluti shale; both are lower than for the PAAS (184.77 ppm; Table 4). The results show the dilution effect caused by carbonate, is a major control over the REE concentrations (correlation coefficient between CaO and ΣREE is -0.875 for Beduh and -0.348 for Baluti). In this regard, the significant correlations of ΣREE with Al₂O₃ and TiO₂ (for Beduh, r = 0.870 and 0.899, and for Baluti r = 0.672 and 0.955, respectively) suggest that clay minerals typically control REE distribution in the shales (McLennan, 1989; Condie, 1991). The chondrite normalized (Taylor and McLennan, 1985) REE patterns of these shales (Fig. 6) exhibit LREE enrichment and negative Eu anomaly (Eu/Eu* = 0.73 for Beduh and 0.68 for Baluti).

Table 4: REE concentrations (ppm) for the shales from the Beduh and Baluti formations

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>REU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beduh</td>
<td>442</td>
<td>372</td>
<td>100</td>
<td>99</td>
<td>364</td>
<td>607</td>
<td>118</td>
<td>478</td>
<td>383</td>
<td>473</td>
<td>398</td>
<td>256</td>
<td>040</td>
<td>247</td>
<td>337</td>
</tr>
<tr>
<td>Baluti</td>
<td>261</td>
<td>369</td>
<td>114</td>
<td>71</td>
<td>405</td>
<td>617</td>
<td>115</td>
<td>476</td>
<td>383</td>
<td>473</td>
<td>398</td>
<td>256</td>
<td>040</td>
<td>247</td>
<td>337</td>
</tr>
</tbody>
</table>

Table 4: REE concentrations (ppm) for the shales from the Beduh and Baluti formations
DISCUSSION

Clay mineralogy

The moderate illite crystallinity index values indicate a moderate-grade chemical degradation in the source area during transportation and sedimentation. According to the illite crystallinity index most of the studied samples plotted in the zone of diagenesis. Both study shales have an illite chemistry index value of $>0.4$ (Table 1), corresponding Al-rich illite (muscovite type) reflecting a granitic provenance. The kaolinite has a low crystallinity index, i.e. high crystallinity, which can be explained by being directly supplied from the rivers (Oliveira et al., 2002). Kaolinite has been accepted for a long time as a product of chemical weathering. Kaolinite formation is, therefore, favored under tropical to subtropical humid climatic conditions (Chamley, 1989; Hallam et al., 1991). Kaolinite may also formed by diagenetic processes indicated by the Al-shale enrichment of the Baluti Formation. Illite is developing in soils with low chemical weathering in cold and/or dry climates, and in areas of high relief where physical erosion is common. Kaolinite was concentrate in sediments of non-marine conditions and marginal marine settings, whereas smectite is proposed to have higher contents in normal marine shales. This could be attributed to the hydraulic separation of clay minerals (Raucsik and Merényi, 2000). Accordingly, it may suggest that the shales of Beduh and Baluti were developed under tropical to subtropical climate.
Source area weathering

The rate of chemical weathering of source rocks and the erosion of the profiles are controlled by climate in addition to the composition of the source rock and tectonics; warm humid climate and stable tectonic settings favor chemical weathering. Absent of chemical alteration results in low CIA values, which may reflect cool and/or arid conditions or alternatively rapid physical weathering and erosion under an active tectonic setting (Fedo et al., 1995; Nesbitt et al., 1997; Absar and Sreenivas, 2015; Tawfik et al., 2015). Different source materials have different initial CIA values. For example, basalts have a CIA of <45 (Sheldon, 2003), felsic rocks 55 – 60, and shales 70 – 75 (Nesbitt and Young, 1982; Maynard, 1992), indicating a moderate to high degree of chemical weathering. The degree of weathering in clastic sediments at the source area can be estimated by the relationships between alkali and alkaline earth elements (Nesbitt and Young, 1996; Nesbitt et al., 1997). This can be deduced through the calculated values of the CIA, CIW, and ICV which are defined as follows:

\[
\text{CIA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})} \times 100 \quad (\text{Nesbitt and Young, 1982})
\]

\[
\text{CIW} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O})} \times 100 \quad (\text{Harnois, 1988})
\]

\[
\text{ICV} = \frac{(\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{Fe}_2\text{O}_3 + \text{MgO} + \text{MnO} + \text{TiO}_2)/\text{Al}_2\text{O}_3}{(\text{Cox et al., 1995})}
\]

where the oxides are expressed as molar proportions and \(\text{CaO}^*\) represent the Ca in silicate fractions only.

The CIA values of the study shales vary from 71.76 to 76.24 (average = 74.32) in the Beduh and from 67.03 to 85.21 (average = 79.82) in the Baluti (Table 5). The former average is nearly similar to PAAS (=75; Taylor and McLennan, 1985) and the latter is higher; this implies that the sediments of Beduh suffered moderate to high degree of weathering and for Baluti are subjected to intense degree of weathering. The CIA values are also plotted on the \(\text{Al}_2\text{O}_3 - (\text{CaO}^*+\text{Na}_2\text{O}) - \text{K}_2\text{O}\) (A-CN-K) diagram (Fig. 7) to evaluate the extent of weathering in the igneous rocks (Nesbitt and Young, 1984) and K-metasomatism (Fedo et al., 1995).

Figure 7 show the Beduh shale forms a weathering trend that is almost perpendicular to the A-K line close to the illite composition, suggesting K-enrichment during diagenesis. The Beduh shale shows a deflection trend from the predicted weathering trend and the pre-metasomatism CIA values of the shales range between 72.5 and 88.0 with an average of 80.25. However, the study samples of Baluti fall parallel and along the A-K line close to illite field suggesting high degree of chemical weathering with no clear evidence of K-metasomatism.
Table 5: Paleoweathering parameters and REE ratios for the shales from Beduh and Baluti formations

<table>
<thead>
<tr>
<th></th>
<th>CIA</th>
<th>CWT</th>
<th>SIV</th>
<th>LICSE</th>
<th>HREE</th>
<th>LREE</th>
<th>REE</th>
<th>Eu-Eu*</th>
<th>Eu/Eu*</th>
<th>REE/REE</th>
<th>Rb/REE</th>
<th>Ba/REE</th>
<th>Yb/REE</th>
<th>Y/REE</th>
<th>Lu/Lu*</th>
<th>Rb/Rb*</th>
<th>Ba/Ba*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bedu</td>
<td>80.34</td>
<td>48.29</td>
<td>0.99</td>
<td>162.95</td>
<td>13.74</td>
<td>0.93</td>
<td>134.54</td>
<td>8.74</td>
<td>137.40</td>
<td>8.08</td>
<td>10.07</td>
<td>4.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balu</td>
<td>71.12</td>
<td>60.16</td>
<td>1.15</td>
<td>148.41</td>
<td>16.74</td>
<td>1.05</td>
<td>137.67</td>
<td>6.00</td>
<td>18.14</td>
<td>6.31</td>
<td>9.14</td>
<td>4.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7: A-CN-K diagram in molecular proportions for the Beduh and Baluti shales (after Nesbitt and Young, 1984); also plotted is the average Upper Continental Crust and Post Archean Australian Shale (Taylor and McLennan, 1985)
Harnois (1988) proposed the CIW index to monitor paleoweathering at the source area. The Beduh shale possesses CIW average values 91.41 similar to the PAAS value (90.56; Table 5), and 98.97 for Baluti higher than PAAS.

The ICV is useful to estimate the chemical weathering degree (Cox et al., 1995), which illustrates the development of aluminous clay minerals over the silicate minerals. Moreover, the sediments with ICV > 1 are immature with the first cycle of sediments that deposited in active tectonic setting. While, those of ICV < 1, are mature and deposited in a quiescent tectonic environment (Weaver, 1989; Cox et al., 1995). The average of ICV values for the Beduh shale is 1.07 and for Baluti is 0.85 (Table 5). According to the average ICV values, it can be interpreted that the shale of the Beduh Formation is compositionally immature and tectonically affected by active setting; whereas, for Baluti is mature and deposited in quiescent tectonic environment. Thus, the variation in ICV values may be due to the diversity in source-rock composition and in the degree of weathering (Potter et al., 2005).

Provenance

The chemical composition of clastic sedimentary rocks can be attributed to the composition of their source rocks (e.g., Madhavaraju and Lee, 2009; Nagarajan et al., 2011; Armstrong-Altrin, 2014; Awadh and Al-Ankaz, 2016). In order to imply the provenance of clastic rocks, different discrimination diagrams based on major, trace, and rare earth elements, have been proposed by several authors (Floyd et al. 1989, 1990; McLennan et al., 1993; Mortazavi et al., 2014).

In the provenance discrimination (TiO$_2$-Ni bivariate) diagram of Floyd et al. (1989), the Beduh and Baluti shales plot in the field of acidic rocks, and the latter are toward more mature (Fig. 8a). However, these study shales are plot in the field of mixed felsic and intermediate rocks on the bivariate diagrams La/Th versus Hf and K$_2$O versus Rb that proposed by Floyd and Leveridge (1987) as shown in Fig. 8b and c.

The Al$_2$O$_3$/TiO$_2$ ratio in clastic rocks is used to determine the source rock compositions, because this ratio increases from 3 to 8 for mafic rocks, 8 to 21 for intermediate rocks, and 21 to 70 for felsic igneous rocks (Hayashi et al., 1997). The values of the Al$_2$O$_3$/TiO$_2$ ratio for Beduh and Baluti shales are ranged from 16.50 to 28.88 and from 17.81 to 38.86, respectively (Table 6). Cullers (1994) proposed that sediments with Cr/Th ratios ranging from 2.5 to 17.5 and Eu/Eu* values from 0.48 to
0.78 are indicative of felsic sources. The values of the Cr/Th and Eu/Eu* in the Beduh and Baluti samples (3.38 and 0.73 and 9.37 and 0.68, respectively; Tables 5 and 6) generally are within the felsic range. The Cr/Th values (Table 6) indicate the Beduh shale are derived from more acidic source rocks relative to Baluti shale, UCC, and PAAS.

Additionally, the REE patterns can also be used for suggesting the sediment sources, meanwhile felsic rocks have high LREE/HREE ratios and negative Eu anomalies, whereas mafic rocks usually contain low LREE/HREE ratios and no Eu anomalies (e.g., Cullers and Graf, 1983; Cullers, 1994; Absar et al., 2009; Absar and Sreenivas, 2015). The high LREE/HREE (for Beduh and Baluti shales are 8.54 and 8.87, respectively; Table 5) and flat HREE patterns are similar to the PAAS, UCC (Fig. 6), and Precambrian Shield of the Arabian-Nubian Plate (Gebreyohannes, 2014), which indicates a felsic source for the both shales. Accordingly, the felsic igneous rocks are suggested as source rocks for the Beduh and Baluti shales as well as they are slightly influenced by intermediate rocks.

Fig. 8: Provenance discrimination diagrams: a) TiO₂ vs. Ni (after Floyd et al., 1989), b) La/Th vs. Hf (after Floyd and Leveridge, 1987), c) K₂O vs. Rb (after Floyd and Leveridge, 1987)
Tectonic setting

Various discrimination diagrams, based on the content of major elements in the clastic sediments, are widely employed to determine the tectonic setting of the basins (Bhatia, 1983; Roser and Korsch, 1986). Although several studies proposed that the results inferred from these diagrams were not confirm with the geology of the areas (Valloni and Maynard, 1981; Dostal and Keppie, 2009). The use of these discrimination diagrams has been prudence against by many researchers (e.g., Armstrong-Altrin and Verma, 2005; Ryan and Williams, 2007; Armstrong-Altrin, 2015; Verma and Armstrong-Altrin, 2016).

Recently, Verma and Armstrong-Altrin (2013) suggest two discriminant diagrams, based on the content of major elements, for the tectonic discrimination of clastic
sediments from three main tectonic settings: island or continental arc, continental rift, and collision, originated for the tectonic discrimination of high-silica \([(\text{SiO}_2)_{\text{adj}} = 63\% - 95\%]\) and low-silica \([(\text{SiO}_2)_{\text{adj}} = 35\% - 63\%]\) types. In addition, Armstrong-Altrin (2015) evaluated these two tectonic diagrams and advice that the two multidimensional diagrams can be considered as a tool for discrimination of the tectonic setting of the old basins. These diagrams were successfully used in recent studies to discriminate the tectonic setting of a source area based on the composition of the clastic sediments (Nagarajan et al., 2015; Tawfik et al., 2015; Zaid et al., 2015).

These diagrams based on the major element compositions were used in this study to determine the tectonic environment of the Beduh and Baluti shales. On the low-silica multidimensional diagram (Fig. 9), most of the Beduh and Baluti shales were plotted in the rift field, which are conform with the geology of the Arabian Shield and the Rutba Uplift (Jassim and Goff, 2006) and some of the Beduh samples fall in collision field, that reveal the possibility that the Beduh shales may consist of sediments derived from active regions of the Mid-Oceanic Ridge to the northeast of Arabian Plate (Fig. 3). In addition it is suggested that the Beduh shale also received sediments by volcanic activity, certitude by the presence of volcaniclastic materials (glass shards and glassy spherules) and smectite as a mixed layer with illite (Hakeem, 2012).

Trace elements especially that are relatively immobile with low residence times in seawater (i.e., La, Nd, Th, Zr, Hf, Nb, and Ti) are assured fingerprints for discrimination of tectonic setting (McLennan et al., 1990; LaMaskin et al., 2008). Several studies have used the REE contents in sediments to identify their plate tectonic settings (e.g., Bhatia and Crook, 1986; McLennan et al., 1990; McLennan and Taylor, 1991; Mader and Neubauer, 2004; Verma and Armstrong-Altrin, 2013). These studies imply the sediments deposited in the continental margin are characterized by LREE enrichment (indicated by high La/Sm) and high total rare earth elements (ΣREE), on the other hand, those from young undifferentiated oceanic arcs have lower La/Sm, lower ΣREE, and lack for Eu anomaly.
Discriminant function equations are:

\[
\begin{align*}
\text{DF1} & = 0.608 \times \ln(\frac{\text{TiO}_2}{\text{SiO}_2})_{\text{adj}} - 1.854 \times \ln(\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2})_{\text{adj}} + 0.299 \times \ln(\frac{\text{Fe}_2\text{O}_3}{\text{SiO}_2})_{\text{adj}} - 0.550 \times \ln(\frac{\text{MnO}}{\text{SiO}_2})_{\text{adj}} + 0.120 \times \ln(\frac{\text{MgO}}{\text{SiO}_2})_{\text{adj}} + 0.299 \times \ln(\frac{\text{Fe}_3\text{O}_4}{\text{SiO}_2})_{\text{adj}} - 1.510 \times \ln(\frac{\text{Na}_2\text{O}}{\text{SiO}_2})_{\text{adj}} + 1.941 \times \ln(\frac{\text{K}_2\text{O}}{\text{SiO}_2})_{\text{adj}} + 0.003 \times \ln(\frac{\text{P}_2\text{O}_5}{\text{SiO}_2})_{\text{adj}} - 0.294. \\
\text{DF2} & = -0.554 \times \ln(\frac{\text{TiO}_2}{\text{SiO}_2})_{\text{adj}} - 0.995 \times \ln(\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2})_{\text{adj}} + 1.765 \times \ln(\frac{\text{Fe}_2\text{O}_3}{\text{SiO}_2})_{\text{adj}} - 1.391 \times \ln(\frac{\text{MnO}}{\text{SiO}_2})_{\text{adj}} - 1.034 \times \ln(\frac{\text{MgO}}{\text{SiO}_2})_{\text{adj}} + 0.225 \times \ln(\frac{\text{CaO}}{\text{SiO}_2})_{\text{adj}} + 0.713 \times \ln(\frac{\text{Na}_2\text{O}}{\text{SiO}_2})_{\text{adj}} + 0.330 \times \ln(\frac{\text{K}_2\text{O}}{\text{SiO}_2})_{\text{adj}} + 0.637 \times \ln(\frac{\text{P}_2\text{O}_5}{\text{SiO}_2})_{\text{adj}} - 3.631. 
\end{align*}
\]

Therefore, the REE patterns of sediments deposited in continental margins can generally be differentiated from those derived from undifferentiated oceanic arcs. Continental margins can be classified into passive and active types. Passive margin provenance is characterized by uniform REE patterns being and similar to PAAS (Bhatia, 1985; McLennan, 1989). Sediments deposited at active continental margins generally show a REE pattern intermediate between a typical andesite pattern and PAAS or in some cases indistinguishable from PAAS itself. Thus, the most active continental margin sediments display intermediate REE abundances, variable LREE enrichments and variable negative Eu anomalies, with Eu/Eu* in the range of 0.6 – 1.0 (McLennan, 1989).
Paleoredox conditions

The redox sensitive elements, such as Cu, Zn, V, Ni, Cr, and U, in the sediments can be used as effective tool for determination of the paleoredox conditions (Jones and Manning, 1994; Madhavaraju and Ramasamy, 1999; Armstrong-Altrin et al., 2015a; Hu et al., 2015).

The U/Th ratio was used as a redox indicator, being higher in organic-rich mudstones (Jones and Manning, 1994). U/Th ratios below 1.25 suggest oxic conditions of deposition, whereas elevated values indicate suboxic and anoxic conditions (Jones and Manning, 1994; Akinyemi et al., 2013). The present study shows a low U/Th ratio (0.17–0.38, average = 0.24, for the Beduh shale; and 0.33–0.82, average = 0.47, for Baluti shale (Table 6), indicating deposition in an oxic environment.

Jones and Manning (1994) and Rimmer (2004) used the elemental ratios (Ni/Co and V/Cr) to deduce the redox conditions during the deposition of the shale. The higher Ni/Co and V/Cr ratios are related to low oxygen levels during the deposition. Jones and Manning (1994) and Sari and Koca (2012) suggested that Ni/Co ratios below 5 indicate oxic environments, whereas ratios of 5–7 indicate dysoxic environments and ratios above 7 suboxic to anoxic. The Beduh shale shows a lower Ni/Co ratio (1.74–2.53, average = 2.10 nearly similar to the UCC and PAAS; Table 6) suggests an oxic environment, and for Baluti shale (3.03–9.18, average = 6.56) reflect the dysoxic depositional environment during deposition of sediments. Jones and Manning (1994) and Armstrong-Altrin et al. (2015a) used the V/Cr ratio to infer the depositional environment. A V/Cr ratio below 2 refers to oxic, 2.0–4.25 to dysoxic, and higher than 4.25 to suboxic to anoxic conditions. V/Cr ratios of the study shales vary from 0.73 to 3.11 with an average ratio value of 1.93 for Beduh; and 1.26 to 2.54 with an average of 2.09 for Baluti which are higher than for UCC and PAAS (Table 6), indicating an oxic condition during deposition.

CONCLUSIONS

1. The clay mineralogy reveals the tropical to sub-tropical climate during the Lower and Upper Triassic.
2. The study shales show high CaO content (due to the high carbonate content), which have dilution effect on the other oxides and trace elements.
3. The mineralogical and geochemical parameters like illite crystallinity, CIA and CIW values, and A-CN-K diagram reveal moderate to intense for Beduh shale and intensive chemical weathering in the source area for Baluti shale.

4. Major, trace, rare earth elements and elemental ratios imply the felsic and intermediate source rocks for the shales of the Beduh and Baluti, probably from the plutonic-metamorphic complex of the Arabian Shield and Rutba Uplift to the southwest of the basin.

5. The tectonic setting discrimination diagram reveals passive tectonic environment for the study shales with influence of volcanic activity on the Beduh shale.

6. The U/Th, V/Cr, and Ni/Co ratios and negative Eu anomaly (Eu/Eu*) suggest the deposition of the shales under an oxic environment.

REFERENCES


Gebreyohannes, G.W., 2014. Geology, geochemistry and geochronology of Neoproterozoic rocks in western Shire, Northern Ethiopia. MSc, University of Oslo, Oslo, Norway.
Hanna, M.T., 2007. Palynology of the upper part of Baluti Formation (Upper Triassic) and the nature of its contact with the Sarki Formation (Lower Jurassic) at Amadiya district, Northern Iraq. PhD, Mosul University, 143p.


