Geochemistry of Birimian phyllites from the Obuasi and Prestea Mines, Southwestern Ghana: Implications for provenance and source-area weathering

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Abstract

Phyllites from the Ashanti Belt of the Paleoproterozoic Birimian rocks of Ghana were analyzed for their major and trace element geochemistry in order to constrain their provenance and source area weathering. The analyses of the phyllites generally define a single geochemical group by their major- and trace-element abundances. The metamorphosed sediments may be classified as immature by their high index of compositional variability values of mostly > 1. High field strength elements are generally depleted whereas transition metals are typically enriched relative to average Proterozoic upper crust. Such geochemical characteristics suggest that the source of the phyllites dominantly consisted of mafic rocks. Average Cr and Ni abundances and Cr/Ni ratios of average phyllites of the Birimian metasediments indicate that the source consisted of basaltic material. Major element data, plotted in Al₂O₃ – (CaO+Na₂O) – K₂O ternary diagram indicate that the phyllites have undergone significant post-depositional K metasomatism. Low to moderately high chemical weathering of the source terrane is indicated by premetasomatized chemical index of alteration values of 55 – 85. The geochemical data further suggest that the sediments were deposited within an active continental margin setting and mostly supplied by the adjacent volcanic belts.

Keywords: Birimian, Geochemistry, Ghana, Phyllites, Provenance

1 Introduction

The notion that there is a record of geologic history within the chemical composition of sedimentary rocks is well established. Geochemical studies of terrigenous sedimentary rocks have provided critical information regarding provenance, source-area weathering conditions, and estimates of average upper crustal composition through time [1, 2, 3]. This observation has been especially true for Precambrian terranes for which, in many cases, source areas have been eroded away or remain conjectural. In addition, geochemical studies have added much to the understanding of the growth of the continental crusts through time [4, 5].

Owing to their grain size homogeneity and post-depositional impermeability, the chemical composition of fine-grained siliciclastic sedimentary rocks have proved very useful in evaluating the nature of their source lithology and paleoclimate conditions, in the identification of tectonic and crustal extraction events, and in the understanding of crustal and mantle evolution. Indeed, the present level of understanding of crustal evolution comes mainly from geochemical and isotopic data gathered on fine-grained sedimentary rocks [4, 6].

Of the major Precambrian cratons exposed on Earth, only the sedimentary rocks of the West African Craton (Fig. 1) remain to be subjected to detailed geochemical and isotopic studies despite earlier attempts by Boher et al. [7], Taylor et al. [8], Asiedu et al. [9, 10], Karikari et al. [11] and Roddaz et al. [12]. It is therefore not surprising that sedimentary rocks from the West African Craton, one of the most extensive outcrops of Paleoproterozoic rocks on earth [13], by and large remain unrepresented in any computed model for crustal composition.

In order to contribute to the study of Precambrian sedimentary rocks of the West African craton that can be used for the computation of crustal composition we present a paper on Birimian phyllites from the Obuasi and Prestea mines (Fig. 2). This paper discusses the nature of source rocks and the paleoclimatic conditions in the source area and at the time of deposition. In addition, the geochemical data generated can be useful for future computation of the crustal composition of the West African Craton at ~ 2.1 Ga.
2 Materials and methods

The samples for this study were taken from the Obuasi and Prestea mines which fall within the Birimian terrane recognised in Ghana as northeasterly striking belts of metasedimentary-volcanic rocks, which are intruded by syntectonic and late-tectonic suites of granitoids. The Birimian assemblage formed around 2100 Ma during the early Proterozoic [14] and is 10-15 km thick [15]. The rocks dip steeply and are isoclinally folded. Subdivisions of the Birimian are the Lower Birimian and the Upper Birimian which represent mainly metasedimentary and metavolcanic sequences respectively. The rock units of the metasediments (i.e. Lower Birimian) are primarily phyllites and greywackes. There are also weakly metamorphosed tuffs, feldspathic sandstones and Mn- and Si-rich chemical sediments. Carbonaceous matter is present in most of the phyllites. The rock units of the metavolcanics (i.e. Upper Birimian) are predominantly tholeiitic basalt and pyroclastic rocks. There are also some mafic to ultramafic intrusions.
3 Petrography

Megascopically, the phyllites have a planar to crumple foliation. The grey-green to light-green pure phyllites and ankerite phyllites are evenly foliated with “dull” pronounced lustre whereas the graphite phyllites are black and have silky lustre. The phyllitic rocks, particularly the graphite ankerite phyllites occasionally contain pyrites. In thin section, fine sericite flakes form bundles and together with fine quartz grains define the foliation. Small tabular muscovite crystals (40 x 10µm) are rare. Big quartz grains can occur sub-rounded (400µm), longitudinal (1.4 mm) or lens-shaped. Occasionally, there is recrystallisation and re-orientation of the quartz gains. Fine- to medium grained Carlsbad-twinned albite and polysynthetic oligoclase are also sub-rounded (100 µm) and tend to be fresh. The mica bend round or are pushed aside slightly by the quartz and feldspar grains which indicate quartz and feldspar formation before or during the matrix development.

Ankerite (100 µm) occurs as irregular aggregates which are intergrown with tiny quartz grains or as small occasionally being replaced by opaques (or leucoxene)? Accessories are epidote, tourmaline and deep-blue interference colour chlorite (Fe-rich chlorite) which occurs after the sericite. The modal estimate of the pure phyllite is mica (50%), quartz (45%), ankerite (2%) and accessories (3%).

In the chlorite phyllite, the chlorite, as single tabular forms (150 x 20 µm) or aggregated big flakes has a light grey-green interference colour. It occurs within or across the foliation. The chlorite phyllite can be enriched in opaques. Sometimes the accessory epidote shows zoning.

In the graphite phyllite (modal estimate: quartz, 45%; mica, 30%; graphite, 18%; ankerite, 5%; accessories, 2%), the increased amount of graphite is finely distributed in the foliation plane. Often the graphitic material forms bands which intercalate with quartz ± sericite ± ankerite and occasionally light grey interference colour chlorite (Mg-rich chlorite) bands. There can be abundance of chlorite giving graphite-chlorite phyllite.

The foliation bands are often folded and such phyllites have previously been described as contorted (carbonaceous) phyllites. The graphite phyllite shows such strong deformation especially at the contact to the metavolcanics. Most often adjacent to the quartz reef is a very fragile graphite phyllite often referred to by the local geologists as “fissure zone”. Here the quartz gains show extreme deformational effects as deformation lamellae or granulation.

The quartz ± ankerite ± sericite ± opaques ± apatite ± apatite paragenesis form lensoid pockets or short layers. The foliation bands are distorted and mainly marked by graphite. Quartz ± sericite ± Fe-rich chlorite can also form bands in the foliation. The graphite phyllites intercalates with pure phyllites.

4 Geochemical analysis

Crushing and pulverization of samples was done using standard procedures in the preparation of samples for whole-rock geochemical analysis. The samples were analysed for the elements presented (except for LOI, Au and Si) using a BAUSCH & LOMB induced couple plasma emissions spectrometer (Type 3520). LOI (Loss on ignition) was determined thermogravimetrically. The analyses were performed by D. Zachman at Geochronological Laboratory, Technical University, Braunschweig, Germany. Si was determined on a PHILIPS X-ray fluorescence spectrometer (Type PW 1410/10) using fused glass discs (2700mg lithium tetraborate (Li2B407), 300mg lanthan oxide (La203) and 300mg fused sample).

5 Results and discussion

5.1 Results

The bulk-rock chemical data is shown in Table 1. The samples of the Birimian phyllites are characterized by low to moderate SiO2 concentrations (range from 44 to 72 wt. %) and moderate to high Fe2O3 (total Fe as Fe2O3) + MgO contents 6 to 15wt. %. SiO2/Al2O3 ratios are fairly constant (range from 0.13 to 0.34), but K2O/Na2O ratios are variable, ranging from 0.3 to 8.7. Using the geochemical classification diagram of Herron [16], the Birimian phyllites are classified as shale or wacke; one sample, however, fall in Fe-sand field (Fig. 3). This differentiation is due to high SiO2/Al2O3 ratios on the average for some of the graphite phyllites.

The K2O/Al2O3 ratio of sediments can be used as an indicator of the original composition of ancient sediments. The K2O/Al2O3 ratios for clay minerals and feldspars are different (0.0 to 0.3, 0.3 to 0.9, respectively; [17]. In most of the samples the K2O/Al2O3 ratios are close to the upper limit of the clay mineral range, which suggest that the illite is the dominant clay mineral in these phyllites. Cox et al. [17] indicates that the compositional trends in muds derived by weathering of progressively more granitic source material are similar to those in recycled muds; both become richer in
Al$_2$O$_3$ and K$_2$O. This assertion is not the case in the Birimian phyllites as the averages of both Al$_2$O$_3$ and K$_2$O are 13.7 and 2.2 respectively, as compared to EPUC being 14.9 and 3.2. Compared to average estimates of early Proterozoic crust [6] the Birimian phyllites have lower abundances of both large-ion lithophile elements (LILE) and high field strength elements (HFS), but higher abundances of first series transition metals (Fig. 4). The so-called ferromagnesian trace elements, Cr, Sc, V and Ni show moderately strong correlation with Al$_2$O$_3$. This may suggest that these ferromagnesian elements are chiefly controlled by the clay mineral chlorite.

The abundance of Cr and Ni in siliciclastic sediments are considered as a useful indicator in provenance studies. Average Cr and Ni abundances and Cr/Ni ratios of average phyllites of the Birimian metasediments are 104.6 p.p.m., 68.8 p.p.m. and 1.52 respectively (Table 1), and for early Proterozoic upper crust are 59 p.p.m., 31p.p.m and 1.90 [6]. According to Wrafter and Graham [18] a low concentration of Cr indicates a felsic provenance, and Bock et al. [19] have indicated that Ferromagnesian elements (e.g., Fe, Cr, Ni) are enriched in mafic and ultramafic igneous rocks and elevated abundances of these elements in the sediments and sedimentary rocks may indicate the addition of components derived from mafic lithologies. Elevated Cr and Ni abundances with low Cr/Ni (between 1.3 and 1.5) were further suggested to be indicative of ultramafic rocks in source area of shales by Garver et al. [20]. The Cr, Ni and Cr/Ni data above suggest therefore a mafic source for the Birimian Phyllites.

Table 1: Major and trace elements of selected phyllite samples from the Obuasi and Prestea mines of the Birimian Supergroup, Ghana.


**5.2 Paleoweathering conditions and metasomatism**

The Chemical Index of Alteration (CIA) is widely used to quantify the degree of source-area weathering and to constrain the paleoweathering conditions of ancient shales [21, 22, 23]. This index, defined as Nesbitt and Young [21]: CIA = [$\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})] \times 100$ (in molar proportions), where CaO* represents the CaO content in the silicate fraction, measures the degree of feldspar alteration to aluminous clay minerals. Values of about 50 indicate fresh bedrock (no chemical weathering), and values close to 100 indicate complete conversion of feldspars to clay minerals (intense chemical weathering; [22, 23]). CIA values for the analyzed phylites are variable and typically range from 57.6 to 80.1 (average 66.7).

Paleoweathering conditions as well as post-depositional K metasomatism can be visualized in an Al$_2$O$_3$-CaO +Na$_2$O-K$_2$O (A-CN-K) diagram (Fig. 5). From this diagram, 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 [24]. The analyzed Birimian phyllites, plotted in A-CN-K diagram (Fig. 5), define a linear array that is distinctly different from the expected weathering trend. A straight line through the data intersects the feldspar join at a point indicating the fresh composition of potential bedrock; in this case the bedrock source is dominantly basaltic in composition. The weathering trend as depicted in the A-CN-K diagram (Fig. 5) indicate that the analyzed phyllites have undergone post-depositional K metasomatism (due possibly to K-metasomatism of kaolinite to illite). This observation is consistent with earlier provenance studies on the Birimian metasediments [12, 10]. From Fig. 5 it is possible to calculate the pre-K metasomatism CIA following the method of Fedo et al. [22]. The calculated pre-K metasomatism CIA values for the analyzed samples range from 55 to 85 (Fig. 5) suggesting low to moderately high degree of source area weathering.

<table>
<thead>
<tr>
<th>Test</th>
<th>CIA</th>
<th>Chemical Index of Alteration; PIA, Plagioclase Index of Alteration; ICV, Index of Compositional Variability</th>
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</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>57.3</td>
<td>53.3 67.3 67.1 61.0 58.3 71.7 62.6 65.4 44.4 56.0 62.4 62.9 57.1 61.6 62.9 64.6 54.8 57.2 60.1 57.1 62.9 60 65.4 66.9</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.2</td>
<td>0.2 0.2 0.1 0.2 0.3 0.3 0.2 0.1 0.1 0.3 0.2 0.1 0.1 0.1 0.3 0.2 0.1 0.4 0.3 0.1 0.1 0.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>16.2</td>
<td>17.1 15.2 15.2 14.8 16.4 9.1 11.0 9.2 3.8 15.5 14.5 11.3 16.7 13.0 12.5 11.3 18.6 16.7 15.5 16.5 12.7 12.9 14.9</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>8.7</td>
<td>7.0 6.8 6.3 4.7 5.7 5.1 4.2 4.6 7.8 5.2 3.9 6.1 7.0 5.4 5.9 4.9 7.0 6.7 5.9 6.6 5.9 7.0 6.7 4.5</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.10 0.06 0.20 0.10 0.30 0.30 0.20 0.30 0.20 0.10 0.08 0.05 0.09 0.07 0.09 0.09 0.02 0.06 0.07 0.09 0.10 0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>2.7</td>
<td>2.6 2.6 2.7 2.2 2.4 2.0 2.4 2.5 6.4 2.5 1.9 2.6 3.2 2.3 2.2 2.5 3.0 1.4 2.3 2.5 2.1 2.3 2.3 1.95</td>
</tr>
<tr>
<td>CaO</td>
<td>0.8</td>
<td>3.4 0.6 5.6 2.4 1.1 1.8 4.3 4.8 14.0 1.5 2.2 3.9 0.4 3.1 1.4 2.3 0.9 1.5 2.0 1.9 2.3 2.9 1.6 3.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.4</td>
<td>2.3 0.3 0.7 2.2 2.8 0.5 0.6 1.0 0.3 1.6 0.8 1.2 5.7 2.5 3.9 2.8 5.2 0.9 2.3 2.1 2.1 2.0 4.3 3.3</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.9</td>
<td>2.8 2.6 3.5 2.3 2.0 1.2 1.9 1.3 0.6 3.4 3.3 1.9 2.1 2.0 1.3 1.4 2.2 4.0 2.8 2.5 2.0 1.9 1.8 3.2</td>
</tr>
<tr>
<td>LOI</td>
<td>8.7</td>
<td>9.3 6.0 8.0 9.6 9.3 7.2 12.1 10.6 23.4 13.0 8.9 10.8 8.5 9.0 7.0 8.1 9.4 12.1 8.7 9.2 8.5 10.2 9.2</td>
</tr>
<tr>
<td>Sum</td>
<td>99.0</td>
<td>100.1 101.7 99.4 99.7 98.4 98.1 99.6 99.7 101.1 99.2 98.2 100.9 100.9 99.1 97.3 98.1 101.5 100.7 99.8 98.9 98.4 100.7</td>
</tr>
</tbody>
</table>

CIA, Chemical Index of Alteration; PIA, Plagioclase Index of Alteration; ICV, Index of Compositional Variability
6 Provenance

The geochemical signatures of clastic sediments have been used to find out the provenance characteristics [4, 25, 26, 27].

Based on geochemical data the Birimian phyllites presented here may be compared with clastic rocks from different tectonic setting in Australia and New Zealand [28]. On the binary relation of SiO$_2$ versus K$_2$O/Na$_2$O, the Birimian phyllites dominantly plot in the active continental margin and with some straddling around the passive margin setting (Fig. 6) probably due to K-metasomatism effect in the area (Fig. 5). Therefore, the major element characteristics of the phyllites suggest an active continental margin setting.

The major element data/analysis above indicates illites predominance in the clays. However, the Al$_2$O$_3$ and K$_2$O averages are relatively poor which does not suggest a granitic source or recycled mud but rather a possible source from mafic/volcanic material.

The Birimian phyllites have shown enrichment in Cr and Ni but with low Cr/Ni ratio which is suggestive also of a mafic/ultramafic source material as elaborated above. The CIA values point to this possible mafic source material as composed predominantly of a basaltic parent material.
7 Conclusion

The Proterozoic phyllites of the Birimian Supergroup generally indicate a single geochemical group by their major- and trace-element abundances. Their low to moderately high CIA values suggest that these rocks experienced a relatively weak to moderately high chemical weathering from a basaltic source rock. The transition metal geochemistry as well as SiO$_2$-K$_2$O/Na$_2$O binary plot also support that these phyllites originated from a mafic igneous source and were deposited in an active continental margin setting.

Acknowledgement

We acknowledge D. Zachman at the Geochemical Laboratory of the Technical University at Braunschweig, Germany for the geochemical analysis of the samples and the Deutscher Akademischer Austauschdienst (DAAD) for the financial assistance.

References


