Geochemical and mineralogical characteristic of the VHMS alteration pipe, major elements variations and peraluminous ratio, in high grade metamorphosed rocks

R. Ghavami-Riabi 1*, H.F.J. Theart 2

1. Faculty of Mining, Petroleum and Geophysics, Shahrood University of Technology, Shahrood, Iran
2. SRK Consulting Engineers and Scientists, 265 Oxford Road, Illovo, Johannesburg, South Africa

Received 23 March 2010; received in revised form 3 November 2010; accepted 1 March 2011

*Corresponding author: rghavami2@yahoo.com (R. Ghavami-Riabi).

Abstract
The massive sulphide deposit at Kantienpan Cu-Zn mine is hosted by volcano sedimentary succession known as the Areachap Group, in the eastern part of Namaqua Metamorphic Province, South Africa. The deposits were affected by a complex deformation and metamorphic history and represent examples of upper amphibolite to granulite grade metamorphosed volcanic-hosted massive sulphide (VHMS) deposits. The principal purpose of this research is to characterise the primary geochemical halo’s related to VHMS deposits in this mine. Lithogeochemical characterization of the primary haloes is based on borehole samples of the footwall, ore zone and hanging wall successions. Geochemically, the ore zone and alteration zones at Kantienpan VHMS ore deposit display a high peraluminous ratio confirming the peraluminous nature of these zones as indicated mineralogically and lithologically. The intervals identified in sampled borehole core with low CaO and Na2O and with high MgO and K2O contents represent the alteration zone in the original footwall rocks of the deposit.

Keywords: VHMS, peraluminous ratio, probability plot, lithogeochemistry.

1. Introduction
Massive sulphide deposits consist of 60% or more sulphide minerals [1]. Two main groups were suggested for these deposits based on the host rock lithology. The first group is composed of sedimentary-exhalative (SEDEX) or shale-hosted stratiform massive sulphides [2, 3, 4, 5] e.g. Sullivan, Broken Hill, Mt. Isa and Rammelsberg. The volcanic-hosted massive sulphide (VHMS) deposit forms the second group [2, 6, 7, 8, 9, 10]. The origin of the immediate host rocks of VHMS deposits are thought to be either derived directly from volcanic activity such as lava or pyroclastic rocks, or have no direct volcanic affiliation e.g. shales or greywackes [2].

The location of massive sulphide lenses seem to be strongly related to structural controls of the ocean floor e.g. synvolcanic faults with vertical displacements [11]. Hodgson and Lydon [12] documented that most of VHMS deposits are related to the fracture systems produced by subvolcanic intrusions or resurgent calderas. This relationship shows that particular hydrologic, topographic and geothermal features of the ocean floor are required to form VHMS deposits [2]. In the study area, Theart [13] suggested that the metamorphosed stratiform massive sulphide deposits of the Namaqua Province be divided into the SEDEX and the VHMS deposits. Rossouw
[14] provides a geological description and ore evaluation of the Kantienpan deposit (5 mt@ 0.49% Cu and 4.09% Zn) and classifies it as a VHMS deposit. Chlorite and sericite are the two major alteration products that form due to the reaction between the hydrothermal fluid and the wall rocks [15]. The nature of the alteration assemblage does however also depend on the composition of the original wall rocks. In most cases the primary calcium and sodium rich silicate minerals such as pyroxenes and feldspars are the first to be destroyed during alteration resulting in a depletion of Ca and Na which is removed from the system in the escaping hydrothermal fluid [16]. The remaining rock becomes enriched in Al, Mg, and Fe, and in some cases K; since the conditions are favourable for the formation of chlorite [17]. Silica released in the solution precipitates as soon as the temperature of the fluid decreases and this may commence in the zone immediately below the massive sulphide zone, and also trends to seal the conduit during the warning stages of the ore forming process. The abundance of Al in the altered rocks results in displaying a peraluminous character, indicating that the percentage of Al₂O₃ is higher than the sum of Na₂O, CaO, and K₂O in these rocks [18]. The variation of major elements concentrations may be used as an index of compositional changes caused by alteration at the time of ore formation [19].

The objective of this article is to identify zones in the successions immediately enclosing the sulphide mineralization displaying compositional variation that is characteristic of hydrothermal alteration at the time of ore formation. For this purpose, the variations of major elements contents in one borehole were selected from the Kantienpan mine (KN11) to locate the alteration zones and to define their geochemical characteristics.

2. Regional geology

The Kibaran Supercrustal Sequence (1600 to 1300Ma) was deposited on the Eburnian basement (2000 Ma) in the western Namaqua Terrane [20]. The lithology of this sequence may indicate that there was an oceanic basin between the Kaapvaal and the older parts of the Namaqua Province at approximately 1600 Ma [13]. The oceanic basin was affected by calc-alkaline and tholeiite volcanism until 1285 ± 14 Ma [21] in the area now preserved in the east-central Namaqua-Natal Province (Figure 1). These extrusive rocks and associated sediments were preserved in the Areachap Group of the eastern part of the Namaqua Province and in the Mfongosi Group of Natal Province [20]. During the period of volcanism, volcanogenic massive sulphide deposits formed on the sea floor due to reactions between the hydrothermal fluids and seawater [21]. This was followed by plate convergence, thrusting, ductile transient shearing, thickening of the crustal sequence, and intensive deformation from 1200 Ma to 1000 Ma due to a northwest-southeast-directed stress regime [20]. The Koras and Sinclair Groups consisting of calc-alkaline volcanic and sedimentary rocks, were formed during the late syn-collision event at ~1150Ma[22].

Figure 1. The location of Namaqua-Natal Province [23] and study area.
The collision of cratons and the related events led to high-grade metamorphism and widespread melting and generation of voluminous granitoid batholiths magma (I-type granites) between 1200 to 1000 Ma [24].

The study area considered here falls within the Gordonia Sub Province of the Namaqua Province [23]. Supercrustal rocks in this Sub Province belong to the Areachap Group comprising the Jannelsepan, Boksputs and Copperton Formations [14, 21, 25]. Rossouw [14] described the Kantienpan deposit in the Boksputs Formation as a VHMS deposit.

3. Geographical situation and geology of the ore zone

The area investigated in this research is located in the Northern Cape Province of the Republic of South Africa. The Kantienpan Cu-Zn deposit is situated on the farms Kantienpan 119 and Gemsbok Bult 120, about 85 km southeast of Upington in the Kenhardt district.

In the current investigation two boreholes were selected for sampling, but the data for one of them was used to illustrate the concepts of hydrothermal alteration. The cross-section as drawn from borehole KN11 (Figuer. 2) was selected because this borehole intersects the hanging wall, ore zone and footwall. In KN11, the ore is overlain by biotite-gneiss or biotite-hornblende-gneiss (unit number 5 in Figuer. 2).

Whereas, the gneisses below the ore zone contain cordierite, sillimanite and biotite reflecting its peraluminous character, the gneisses intercalated with the massive sulphide towards the upper contact of the ore zone contain hornblende and biotite indicating the progressively more calcareous composition of the hangingwall rock succession. The opaque minerals described in the assumed footwall of this deposit include pyrrhotite, chalcopyrite, and pyrite. Magnetite, pyrite and sphalerite are present in the assumed hanging wall successions at this deposit.

Samples were taken at sampling intervals of 2 to 5 m in the ore zone and 5 to 10 m, away from the ore zone. These samples were analysed by x-ray fluorescence as whole rock analysis. For this purpose, press powder and glass bead were made to analyze trace and major elements of the samples. In borehole KN11, K$_2$O contents (0.8-1.2 %) are higher between samples KN11/38 and KN11/43, and decreases from sample KN11/38 (0.35-0.81 %) towards KN11/31 (Figuer. 5). Unlike in the case for Na and Ca (i.e. low contents), the high K$_2$O bearing zones are ascribed to the footwall alteration zone. The MgO contents are generally high (2.5-7 % MgO) between samples KN11/38 and KN11/43, when compared with the samples from KN11/38 to KN11/30 (3.5-5.2 % MgO) in this borehole (Figuer. 6). Samples KN11/30 to KN11/32 are biotite-hornblende-gneisses, which explain the high MgO contents in these samples.

![Figure 2. Cross-section of borehole KN11 in the Kantienpan area (Sil: sillimanite, Crd: cordierite and Hbl: hornblende).](image-url)
5. Identification of Peraluminous rocks close to the ore zone

The peraluminous ratio ($\frac{Al_2O_3}{(Na_2O+K_2O+CaO)}$) may be used to define the peraluminous character of samples in the rock succession. This calculation was done based on the XRF results of the whole rock analysis for borehole KN11 samples (Table 1). Seven samples from KN11 have exceptionally high percentages of peraluminous ratio. The cumulative frequency versus probability behaviour of the peraluminous ratios in all of the samples identifies an anomalous sub-population. This principal is utilized in the Prob Plot software [26, 27] to estimate the threshold values between different sub-populations within a polymodal distribution. These estimates are then entered into a maximum likelihood procedure to calculate a theoretical distribution of a mixture resulting from up to five different sub-populations. The resultant theoretical curve is compared with the original distribution and if the comparison is satisfactory, the threshold values of the underlying sub-population may be used in estimating the threshold value of the anomalous sub-population in the data set, as well as its mean and standard deviation [23, 26, 28]. It is suggesting that there are three sub-populations in the peraluminous value data set depicted in Figure 7. The first of these sub-populations has a cumulative frequency of less than 37.4%, the second is between 37.4% and 83.8% and the third is located at higher than 83.8%. The statistical results of these calculations for anomalous values are summarized in Table 2. Based on the threshold value of the peraluminous ratio for the third sub-population ($\geq$4), seven samples (KN11/33 and KN11/38 to KN11/43)
Figure 5. Variation of K2O through the lithological successions adjacent to the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

Figure 6. Variation of MgO through the lithological successions hosting the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

Table 1. Peraluminous ratio and minerals present in KN11

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Depth(m)</th>
<th>Per.1 Ratio</th>
<th>Minerals present</th>
</tr>
</thead>
<tbody>
<tr>
<td>KN11/30</td>
<td>195.35</td>
<td>1</td>
<td>Pl, Hbl, Bt, Qtz</td>
</tr>
<tr>
<td>KN11/31</td>
<td>196.85</td>
<td>1</td>
<td>Pl, Hbl, Cpx, Bt, Qtz</td>
</tr>
<tr>
<td>KN11/32</td>
<td>198.80</td>
<td>1</td>
<td>Pl, Hbl, Qtz</td>
</tr>
<tr>
<td>KN11/33*</td>
<td>205.00</td>
<td>6</td>
<td>Qtz, Crd, Sil, Bt</td>
</tr>
<tr>
<td>KN11/34*</td>
<td>206.57</td>
<td>3</td>
<td>Qtz, Crd, opaque min., Grt, Bt</td>
</tr>
<tr>
<td>KN11/35*</td>
<td>206.95</td>
<td>1</td>
<td>opaque min., Qtz, Crd (alt.)</td>
</tr>
<tr>
<td>KN11/36*</td>
<td>208.25</td>
<td>1</td>
<td>opaque min., Qtz, Crd (alt.)</td>
</tr>
<tr>
<td>KN11/37*</td>
<td>209.20</td>
<td>1</td>
<td>opaque min., Qtz, Crd (alt.)</td>
</tr>
<tr>
<td>KN11/38*</td>
<td>210.66</td>
<td>12</td>
<td>Qtz, Crd, Bt</td>
</tr>
<tr>
<td>KN11/39</td>
<td>212.16</td>
<td>10</td>
<td>Qtz, Crd, Bt, Opx</td>
</tr>
<tr>
<td>KN11/40</td>
<td>216.23</td>
<td>7</td>
<td>Qtz, Opx, Bt, Crd</td>
</tr>
<tr>
<td>KN11/41</td>
<td>217.73</td>
<td>8</td>
<td>Qtz, Crd, Sil, Bt</td>
</tr>
<tr>
<td>KN11/42</td>
<td>217.80</td>
<td>7</td>
<td>Qtz, Bt, Hercynite, Crd, Sil</td>
</tr>
<tr>
<td>KN11/43</td>
<td>218.19</td>
<td>7</td>
<td>Qtz, Crd, Sil</td>
</tr>
</tbody>
</table>

1. Per.: Peraluminous  
Bt=biotite; Chl: chlorite; Pl=plagioclases;  
Qtz=quartz; Crd=cordierite; Sil=sillimanite;  
Opx=ortho-pyroxene; Cpx=clino-pyroxene;  
Hbl=hornblende; alt=altered; Kfs= k-feldspar;  
Grt=garnet; Ms=muscovite; Min=mineral  
KN11/35*: Samples in the ore zone
were identified as anomalous (Table 1). Mineralogically and lithologically all these samples (except sample KN11/33 from the ore zone of borehole KN11) belong to the garnet-sillimanite-cordierite-gneiss that has been identified as the rock type reflecting a hydrothermal footwall alteration zone in previous sections. Sample number KN11/33 might be considered as altered sample in the hanging wall near the ore zone.

In Figure 8, the variation in the peraluminous ratio is demonstrated versus depth near the Kantienpan ore zone in borehole KN11. In this graph, those samples with high peraluminous values (>6.7, between 212 to 218 meter depth) also belong to the gneissic rocks, which contain cordierite and sillimanite. It is suggested that this depth interval represents the footwall alteration zone of the Kantienpan deposit. Samples with low peraluminous values (<2) are assumed to be located in the original hangingwall of the ore deposit.

![Figure 7. The probability plot of peraluminous ratio based on AP5 and KN11 data set (AP5 is a borehole at Areachap VHMS Cu-Zn deposit in Areachap Group)](image1)

![Figure 8. The variation of peraluminous ratio near the ore zone in borehole KN11 (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)](image2)
6. Conclusions

Geochemically, the peraluminous ratio \( (\text{AI}_2\text{O}_3 / (\text{Na}_2\text{O+K}_2\text{O+CaO}) \) is high for the samples adjacent to the ore zone in Kantienpan VHMS ore deposit. Mineralogically and lithologically these samples represent to the garnet-sillimanite-cordierite-gneiss, identified as the rock type representing metamorphic equivalent of the originally formed in the hydrothermal footwall alteration zone.

Based on the major oxides variation, the borehole sampling intervals with low CaO and Na2O and high MgO and K2O represent the alteration zone in the original footwall rocks of the deposit. This interpretation requires that the ore body in borehole KN11 were not structurally overturned in acquiring its present habit confirming the conclusion based on the interpretation of the peraluminous ratio.

Mineralogically, a silisification occurred near the ore zone in the stringer zone, which is a characteristic of VHMS deposits. The lithogeochemical and mineralogical characteristics of these alteration zones may now be used in exploration in this and similar terranes to identify concealed VHMS mineralization.

Acknowledgements

We are grateful to Prof S.A. de Waal for the financial support from the Centre for the Research of Magmatic Ore Deposits. Thanks are also due to Kumba Resources Limited for providing access to the borehole samples and field visits with Mr. D. Rossouw. M Classen and P Sibiya are thanked for their assistance with making of the thin sections. Thanks must also be given to Mrs. M. Loubser for analyzing samples by XRF. I also wish to thank Miss. I. Chimeloa for drafting some of the geological maps.

References


<table>
<thead>
<tr>
<th>Variable</th>
<th>No. of popul.</th>
<th>Means (M)</th>
<th>Stan. Dev. (SD)</th>
<th>%</th>
<th>Threshold values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peraluminous Ratio</td>
<td>1</td>
<td>1</td>
<td>-0.80</td>
<td>1.34</td>
<td>37.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4</td>
<td>-2.68</td>
<td>6.69</td>
<td>46.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8</td>
<td>-5.86</td>
<td>11.41</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Note: No. of popul.: Number of population, SD: Standard deviation


