

**Geochemical exploration for base metal sulphide deposits in an arid environment
(eastern Namaqua Metamorphic Province), South Africa**

by

Reza Ghavami-Riabi

Submitted in partial fulfilment of the requirements for the degree

DOCTOR OF PHILOSOPHY

**in the Faculty of Natural & Agricultural Science
University of Pretoria**

Pretoria

August 2006

ABSTRACT

The massive sulphide deposits at Areachap and Kantienpan Cu-Zn Mine are hosted by a ~1600 Ma old 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 host rocks of both ore deposits are peraluminous-gneisses and the dominant sulphide minerals in the ore zone are pyrite, pyrrhotite sphalerite, and chalcopyrite and trace amounts of galena. Other ore related minerals include barite and anhydrite. The metamorphic minerals in the alteration zones at the Areachap and Kantienpan VHMS deposits are characterized by the presence of plagioclase, almandine and pyrope, enstatite and clinoenstatite, cummingtonite and gedrite, cordierite, sillimanite, and retrograde chlorite and chamosite.

Lithogeochemical methods are widely used in exploration geochemistry to identify the primary alteration zones related to VHMS mineralization, as these zones are often exposed, while the massive sulphide ore body itself may be concealed. Especially in areas that were not affected by high grade metamorphism and intensive deformation. Some of these methods include the variation in the relative abundance of major element concentrations throughout the rock successions, mineral chemistry of silicates and spinel minerals near the ore zone, and normative compositions of the rock successions. However, the application of these methods is limited by complex geology in regional metamorphic terranes, such as the Namaqua Metamorphic Province. Therefore, in addition, three of the more advanced lithogeochemical approaches, known as the Isocon method, the Box Plot and Pearce Elemental Ratios, are combined here and adapted for application in such regions.

Based on the mineral chemistry, it is evident that plagioclase is more Ca-rich adjacent to the ore zone, pyroxene has the highest relative Mg* ratio (Mg^* ratio = 100 x cationic ratio of Mg / (Mg + Fe + Ca)), the almandine and pyrope components of garnet are high and the spessartine and grossular components are low. In addition, the Mg-rich variety of mica (phlogopite) is more common near the ore zone and the peraluminous nature of the footwall zone is revealed by the presence of gahnite. Cordierite and retrograde chlorites show the highest Mg#'s ($Mg\# = Mg / (Mg + Fe)$) in the ore zone. In addition to the above, Pearce Element Ratio analyses of cordierite, pyroxene and garnet may be used to define proximity to sulphide mineralization.

Geochemically, the ore zone and alteration zones at Areachap and Kantienpan VHMS ore deposits display a high peraluminous ratio ($Al_2O_3 / (Na_2O + K_2O + CaO)$) confirming the peraluminous nature of these zones as indicated by the mineral chemistry discussed above. 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. Isocon studies have shown that the alteration zones at the Areachap and Kantienpan deposits are enriched in Mg, Fe (total), S, Zn, Si, Co and F and depleted in Na, Ca, Sr, Ni, V and La. Elements that behaved relatively immobile include Zr, Ti, P, Mn, Al, Y, and U.

The box plot, alteration index versus the chlorite-carbonate-pyrite index, was originally proposed to illustrate the combined effects of hydrothermal and diagenetic alteration and is based on characteristic primary mineral reactions in regions not affected by regional metamorphism. It is demonstrated here that these primary mineral reactions are preserved in a unique set of metamorphic minerals, and that the box plot can be modified for high-grade metamorphic rock types. When samples with very high Mg contents ($MgO \gg K_2O$, $AI > 90\%$ and $CCPI > 98\%$) are plotted in the box plot they may be classified as representative of anomalous areas that are highly prospective. Samples with high Mg contents ($MgO > K_2O$, $AI > 64\%$ and $CCPI > 93\%$) may be considered representative of areas that may be classified as of moderate priority in an exploration programme.

The findings of the mineral chemical and geochemical investigations of the footwall alteration at the Kantienpan, Areachap and Prieska Cu-Zn ore bodies are used to

define various statistical factors. The applicability of these factors in lithogeochemical exploration is demonstrated by calculating the respective factor scores for a regional lithogeochemical data set. It is demonstrated how these factors could be used to identify samples collected from localities that are highly prospective for the discovery of concealed VHMS style mineralization.

Based on the statistical analyses of the regional data set, the altered rocks may be distinguished from the metapelitic rocks by their high scores for the alteration factor and low scores for the peraluminous factor. The peraluminous rocks may be separated from the hornblende-gneisses by their high scores for the peraluminous factor, and from the amphibolites by their very low ortho-amphibolite factor scores and high peraluminous factor scores.

The variation, of trace elements in the surface calcrete layer that conceals the mineralization in the studied areas, displays the geochemical signature of mineralization, but the concentrations of Cu, Zn and Pb are much lower at and near surface and increase down depth within the profiles. The absolute concentrations and peak to background ratios of the elements of interest at the surface therefore depend on the thickness of the underlying calcrete layer in the area.

Two methods, a total analysis (x-ray fluorescence, XRF) and partial extraction (NH₄EDTA solution), were applied in to evaluate results, which would be successful and commercially viable in a general exploration programme, using regolith samples. The results of the two methods above were then compared to another patented partial extraction method (mobile metal ion, MMI) on a data set previously reported on by Rossouw (2003). At Kantienpan, where the sand cover is very shallow to absent, dispersion appears to be more related to the secondary redistributions of gossaniferous clasts, than to dispersion of mobile metal ions on the surface of sand particles. The XRF method shows a wider dispersion halo here than methods based on partial extraction. Whereas, at Areachap, where a relatively thick sand (approximately one metre) covers the calcrete layer, partial extraction (based on a NH₄EDTA solution extraction) results in a larger, recognizable, dispersion halo than that detected by XRF. The MMI results show a larger span for Zn, followed by NH₄EDTA and finally

XRF. For Cu, the NH₄EDTA method exhibits the largest span followed by XRF and then MMI.

The anomalous Cu, Zn and Pb contents extracted by partial extraction methods from the wind blown sand deposits indicate that these elements were derived from the ore minerals related to the massive sulphide deposits. However, Mn and Fe contents analysed by XRF also show high values that could not be only related to derivation from massive sulphide ores. Some of the high concentrations of these elements in the sand cover is ascribed to the weathering of other iron-rich rock forming minerals.

CONTENTS

	Page
Chapter 1: Introduction	1
1.1. Purpose of the investigation	1
1.2. Locality of the study area	1
1.3. The method of investigation.....	3
1.4. Acknowledgements.....	3
 Chapter 2: Geology of the Upington Terrane, Eastern Namaqua Province.....	 5
2.1. Introduction	5
2.2. Tectonic setting and regional geological succession	6
2.3. Regional metamorphism and tectonism	9
2.4. Regional data set	11
2.5. Local geology	12
2.5.1 Lithological succession at Areachap mine	12
2.5.2. Metamorphism in Areachap Mine	16
2.5.3. The sulphide minerals in defunct Areachap mine	16
2.5.4. Lithological succession of the Kantienpan deposit	17
2.6. Geomorphological evolution	19
2.7. Calcrete environments	22
2.7.1. Definition of calcrete	22
2.7.2. Calcrete classification	23
2.7.3. Mineralogy of calcretes	24
2.7.4. Mechanism of carbonate accumulation	25
2.7.5. Calcrete in the study area	26
 Chapter 3: Literature review of VHMS deposits and related lithogeochemical alteration	
3.1. Introduction	29
3.2. Classification and geological setting of VHMS deposits	29
3.3. Classification of metamorphosed massive sulphide deposits of the Namaqua Province	 31
3.4. Hydrothermal Models for Formation of VHMS deposits	32
3.4.1. Convection cell model	32
3.4.2. Stratal aquifer model	32
3.4.3. Magmatic hydrothermal model	33
3.5. Mineral zonation in the alteration pipe and ore zone	33
3.5.1. Mineral variation in the ore zone	33
3.5.2. Wall rock alteration	35
3.5.3. Metamorphism of VHMS deposits and their alteration zones	37

3.6. Quantification of chemical changes in altered rocks	37
3.6.1. The isocon method	37
3.6.2. The alteration index and the Chlorite-Carbonate-Pyrite index	40
3.6.3. The mineralogical variation index (Pearce Element Ratio (PER) analysis)	43
Chapter 4: Lithogeochemical investigation	45
4.1. Introduction	45
4.2. Sampling, Sample preparation and analytical methods	47
4.3. Major element variation near the ore zone	48
4.3.1. Interpretation of major elements variation adjacent to the ore zone in borehole AP5 (Areachap)	48
4.3.2. Interpretation of major elements variation near the ore zone in borehole KN11 (Kantienpan)	52
4.4. Mineral chemistry near the ore zone	55
4.4.1. The retrograde chlorite	59
4.5. Identification of Peraluminous rocks close to the ore zone using normative calculations	60
4.6. Quantification of the degree of alteration in the precursor rocks	65
4.7. Development of alteration box plot for high-grade metamorphic rocks	73
4.7.1. The location of rock forming minerals in the box plot	74
4.7.2. Whole rock analysis and box plot	76
4.7.3. Combination of isocon results and the box plot	80
4.8. Refinement of chemical structure in the upper right corner of the box plot	81
Chapter 5: Lithogeochemistry as an exploration tool	84
5.1. Introduction	84
5.2. Lithogeochemical interpretation of borehole information	85
5.3. Economic element vectors of mineralization	86
5.4. Peraluminous, gneiss, and amphibolite factors	87
5.4.1. Peraluminous factors	87
5.4.2. Gneiss factors	89
5.4.3. Amphibolite factors	91
5.5. Application of factors to the regional data set	92
5.6. Prioritization of the anomalous samples in the regional data set	104
Chapter 6: Regolith geochemistry	117
6.1. Introduction.....	117
6.2. The concept of mobile metal ions and selective extraction techniques	118
6.2.1. Mobile Metal Ions (MMI) concept	119
6.2.2. Selective extraction techniques	121
6.3. Sampling programme	123
6.4. Selection of the most appropriate extraction reagent	124
6.5. Calculation of the threshold value for the anomalous population	124
6.5.1. The threshold value for NH ₄ EDTA extraction	126
6.5.2. The threshold value for Ca(H ₂ PO ₄) ₂ extraction	129
6.5.3. The threshold value for MMI-A analyses results	133
6.5.4. The threshold value for total analyses (XRF method)	134
6.6. Discrimination of concealed ore zones in the surface samples	140

6.6.1. Comparison of partial extraction techniques with total analysis method ...	140
6.6.2. Discrimination of the secondary dispersion haloes in other traverses	156
6.6.3. Discrimination of the secondary dispersion haloes (MMI results, Kantienganpan)	166
6.6.4. The comparison of NH ₄ EDTA, MMI and XRF methods	169
6.7. Dispersion of the elements of the interest in the calcrete environment	170
6.7.1. Kantienganpan calcrete samples	171
6.7.2. Areachap calcrete samples	174
6.7.3. Comparison of calcretes close to the ore zone and further away	179
 Chapter 7: Discussion and conclusion	 182
7.1. Lithochemical characteristics of the hydrothermal alteration zones in VHMS deposits and vectors for further exploration	182
7.2. The Suitability a regolith geochemical survey of non-residual sand deposit cover for detecting concealed mineralization	186
7.3. Signature of the mineralization in the calcrete regolith	187
7.4. An integrated approach to geochemical exploration of arid areas	188
 References	 191
 Appendix A: Cross sections and extra figure	 209
Extra Figures	219
 Appendix B: Microprobe Analysis	 220
 Appendix C: Sample preparation and whole rock analysis	 232
C.1. Sample preparation for XRF Analysis	232
C.1.1. Calibration	233
C.3. XRF analytical precision and accuracy	233
C.4. Results of XRF analyses	233
 Appendix D: Analytical methods and results of regolith analyses	 261
D.1. Regolith samples	261
D.1.1. NH ₄ NO ₃ extraction	262
D.1.2. NH ₄ OAC extraction	264
D.1.3. NH ₄ EDTA extraction	266
D.1.4. Ca (H ₂ PO ₄) ₂ extraction	270
D.1.5. XRF total analyses	273
D.1.6. Regolith data set of the Kantienganpan traverses	275
D.1.7. Regolith data set of the Areachap traverses	279
D.2. Calcrete samples	282
 Appendix E: XRD analyses results	 300
 Appendix F: Confidential agreement with Kumba Resources Limit.....	 306

List of Figures

	Page
Figure 1.1: Location map	2
Figure 2.1: The location of Namaqua-Natal Province (After Moen, 1999) and the study area	6
Figure 2.2: Geological map of the Areachap Group in the eastern part of Namaqua Sub-province	8
Figure 2.3: A cross-section of lithology at Areachap mine including the borehole AP5	14
Figure 2.4: Geological map of the Areachap area (after Voet and King, 1986)	14
Figure 2.5: Geology map of the Kantienpan area (after Rossouw, 2003) (TDEM: Time domain electro-magnetic conductor)	18
Figure 2.6: Cross-section of borehole KN11 (after Rossouw, 2003)	18
Figure 2.7: The genetic calcrete classification (after Carlisle, 1980)	23
Figure 3.1: An isocon diagram for sample AP5/35 (least altered biotite-gneiss) and AP5/23 (altered biotite-gneiss) from drill hole AP5 in the Areachap area	40
Figure 3.2: Field for hydrothermal alteration described in the text (modified after Large et al., 2001)	41
Figure 3.3: Field for diagenetic alteration described in the text (after Large et al., 2001)	42
Figure 3.4: K/Ti versus Al/Ti PER diagram of Elura Zn-Pb-Ag deposit (adopted from Whitbread and Moore, 2004)	44
Figure 4.1: A cross-section of lithology at Areachap mine including the borehole AP5 (adopted from Voet and King, 1986) (Sil: sillimanite; Crd: cordierite and Hbl: hornblende)	49
Figure 4.2: Variation of CaO through the lithological successions adjacent to the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	50

Figure 4.3: Variation of Na ₂ O through the lithological successions hosting the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	50
Figure 4.4: Variation of K ₂ O through the lithological successions adjacent to the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	51
Figure 4.5: Variation of MgO through the lithological successions hosting the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	51
Figure 4.6: Cross-section of borehole KN11 in the Kantienpan area (Sil: sillimanite, Crd: cordierite and Hbl: hornblende)	52
Figure 4.7: Variation of CaO through the lithological successions adjacent to the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	53
Figure 4.8: Variation of Na ₂ O through the lithological successions hosting the ore zone (Hbl: Hornblende; Crd: cordierite; Sill: sillimanite)	53
Figure 4.9: Variation of K ₂ O through the lithological successions adjacent to the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	54
Figure 4.10: Variation of MgO through the lithological successions hosting the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	54
Figure 4.11: Variation of Na and Ca in plagioclase, Kantienpan (KN11) (Ab: albite and An: anorthite)	56
Figure 4.12: Variation of Mg, Fe and Ca in the pyroxene, Kantienpan (KN11), (En: enstatite and Fs: ferrosilite)	56
Figure 4.13: Variation of the Mg number in cordierite, Kantienpan, (KN11), (Hbl: Hornblende; Stri. Sulp.: stringer sulphide; Sil: sillimanite; Crd: cordierite)	57
Figure 4.14: Chemical components of garnet in the alteration and ore zones, Areachap (AP5), (FW: footwall)	58
Figure 4.15: Variation of Mg and Fe in mica at Areachap (A) and Kantienpan (B), (Ann: Annite and Phl: phlogopite)	58

Figure 4.15: The probability plot of peraluminous ratio based on AP5 and KN11 data set	63
Figure 4.16: The variation of peraluminous ratio near the ore zone in borehole AP5 (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	64
Figure 4.17: The variation of peraluminous ratio near the ore zone in borehole KN11 (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)	64
Figure 4.18: An isocon diagram between samples AP5/35, the least altered biotite-gneiss, and AP5/29, altered biotite-gneiss, from borehole AP5 in the Areachap area	67
Figure 4.19: An isocon diagram between samples AP5/35, the least altered biotite-gneiss, and AP5/30, altered biotite-gneiss, from borehole AP5 in the Areachap area	67
Figure 4.20: An isocon diagram for samples AP5/35 (the least altered biotite-gneiss) and AP5/32 (altered biotite-gneiss) from drill hole AP5 in the Areachap area	68
Figure 4.21: An isocon diagram between the least altered sample AP5/42 and altered sample AP5/25, altered biotite-gneiss, from borehole AP5 in the Areachap area	68
Figure 4.22: An isocon diagram for samples KN11/44 (the least altered biotite-gneiss) and KN11/40 (altered biotite-gneiss) from drill hole KN11 in the Kantienpan area	70
Figure 4.23: Box Plot of mineral compositions from Areachap (AP5 and AP2)	75
Figure 4.24: Box Plot of mineral compositions from Kantienpan (KN11 and KN12)	75
Figure 4.25: Box Plot of whole rock samples from Kantienpan (KN11, KN12 and surface outcrop)	77
Figure 4.26: The variation of AI and CCPI values in samples from Kantienpan (KN11). Massive sulphide zone indicated in black and alteration zone hatched	77
Figure 4.27: Box Plot of whole rock samples from Areachap (AP2 and AP5)	78

Figure 4.28: Inverted sequence see in drill hole AP5 (Areachap) showing the variation in the AI and CCPI values. Massive sulphide zone indicated in black and alteration zone hatched	79
Figure 4.29: Box plot with isocon and microprobe results (Kantienpan area, KN1) ..	80
Figure 4.30: Box plot with the isocon and microprobe results (Areachap area, AP5)	81
Figure 4.31: PER analysis for samples from drill holes KN11 and KN12, Kantienpan area. The Mn content of gahnite, cordierite and garnet from the ore zone is higher than in the identified footwall alteration zone. Pyroxene has lower Mn and Fe contents in the ore zone and altered footwall (11/43: borehole KN11/ sample number)	83
Figure 4.32: PER analysis of boreholes AP2 and AP5 in the Areachap area. The Mn content of Cordierite increases from the altered FW toward ore zone. The Mn content of garnets is higher in ore zone than in footwall alteration zone. No trend is evident in the composition of chlorite and chamosite (5/27: borehole AP5/ sample number)	83
Figure 5.1: The tree diagram of the peraluminous rocks	88
Figure 5.2: The tree diagram of the gneissic rocks	90
Figure 5.3: The tree diagram of the amphibolite rocks	91
Figure 5.4: The peraluminous factor (FPer) versus alteration factor (FAR), regional data set [189: Kantienpan (Boks); 92*: north west of Upington (UpUp); 426: south of Upington (BeUp)]	96
Figure 5.5: The pelitic factor (FPR) versus alteration factor (FAR), regional data set [189: south of Kantienpan (Boks); 903: south of Upington (BeUp)]	96
Figure 5.6: The peraluminous factor (FPer) versus amphibolite factor (FOrtho-Amp1) for the regional data set [189:south of Kantienpan (Boks); 903:south of Upington (BeUp); 196/: north west of Bokspuit (Kant)]	98
Figure 5.7: The para-amphibolite factor (Fpara-amp3) versus ortho-amphibolite factor (Fortho-amp1), regional amphibolite and peraluminous data set [196/: north west of Bokspuits (Kant); diamond filled: peraluminous and square filled: amphibolite]	99

Figure 5.8: The para-amphibolite factor (Fpara-amp3) versus general amphibolite factor (Famp2) for the regional amphibolite data set	99
Figure 5.9: Biotite-hornblende-gneiss factor (FHbl-Gn) versus peraluminous factor (FPer), combined data set of biotite-hornblende-gneiss and peraluminous samples, regional data set [diamond filled: peraluminous and square filled: biotite-hornblende-gneiss samples]	100
Figure 5.10: The leucogneiss factor (FLeu-Gn) versus peraluminous factor (FPer), mixed of peraluminous and leuco-gneissic samples, regional data set [diamond filled: peraluminous and square filled: leucogneiss samples]	102
Figure 5.11: The probability plot of whole regional data set for the alteration factor (FAR)	105
Figure 5.12: The probability plot of anomalous values of the last stage for the alteration factor (FAR), regional data set	106
Figure 5.13: Box plot of the final results for the regional data set	109
Figure 5.14: The probability plot of Zn contents based on the data in Table 5.9, regional data set	110
Figure 5.15: The probability plot of Cu contents based on the data in Table 5.9, regional data set	110
Figure 5.16: The probability plot of Ni contents based on the data in Table 5.9, regional data set	110
Figure 5.17: Geology of the northern part of the Areachap Group, eastern Namaqua Province	114
Figure 5.18: The alteration factor versus sample number in-prioritised Traverses, rank one	115
Figure 5.19: The alteration factor versus sample number in-prioritised traverses, rank two	115
Figure 6.1: Schematic model of convection cell in connection with mobile metal ions in the secondary environment (after Mann et al., 1997)	119
Figure 6.2: Regolith traverses and geology map of the Kantienpan area (after Rossouw, 2003)	125

Figure 6.3: Regolith traverses and geology map of the Areachap area (after Voet and King, 1986)	125
Figure 6.4: Probability plot of the log values for Cu (A), Zn (B), Pb (C), Mn (D) and Ba (E), whole Kantienpan regolith data set (ICP-MS method, n=52 samples)	128
Figure 6.5: Probability plot of the log values for Cu (A), Zn(B), Pb(C), Mn (D) and Fe (E), whole Areachap regolith data set (ICP-MS method, n=61 samples)	130
Figure 6.6: Probability plot of S, Kantienpan (Ca (H ₂ PO ₄) ₂ , shaking time of 120-minutes, ICP-MS method)	131
Figure 6.7: Probability plot of S, Areachap (Ca (H ₂ PO ₄) ₂ , shaking time 120-minutes, ICP-MS method)	132
Figure 6.8: Probability plot of the normal and log values for Cu (A) and Zn (B) (MMI method, n=58 samples)	134
Figure 6.10: Probability plot of Zn based on the regolith traverse KP12 data, Kantienpan, XRF method	136
Figure 6.9: Probability plot of the normal and log values for Cu (A), Zn (B), Pb (C), MnO (D) and S (E), regolith traverse KP12, Kantienpan (XRF method, n=19 samples)	137
Figure 6.12: Probability plot of Zn, regolith traverse T2 (XRF method, n=25 samples)	138
Figure 6.11: Probability plot of the normal and log values for Cu (A), Zn (B), Pb (C), MnO (D), Fe ₂ O ₃ (E) and S (F), regolith traverse T2, Areachap (XRF method, n=21 samples)	139
Figure 6.13: Variation of Cu in regolith traverse KP12 based on ICP-MS (A, by using NH ₄ EDTA and 180-minutes shaking times) and XRF analyses (B)	141
Figure 6.14: Variation of Zn in regolith traverse KP12 based on ICP-MS (A, by using NH ₄ EDTA and 180-minutes shaking times) and XRF analyses (B)	142
Figure 6.15: Variation of Pb in regolith traverse KP12 based on ICP-MS (A, by using NH ₄ EDTA and 180-minutes shaking times) and XRF analyses (B)	143
Figure 6.16: Variation of Mn in regolith traverse KP12 based on ICP-MS (A, by using NH ₄ EDTA and 180-minutes shaking times) and XRF analyses (B)	144

Figure 6.17: Variation of S in regolith traverse KP12 based on ICP-MS (A, by using NH ₄ EDTA and 180-minutes shaking times) and XRF analyses (B)	145
Figure 6.18: Variation of Cu in the regolith traverse T2 based on ICP-MS (A) (NH ₄ EDTA, 180-minutes shaking times) and XRF (B) analysis	148
Figure 6.19: Variation of Zn in the regolith traverse T2 based on ICP-MS (A) (NH ₄ EDTA, 180-minutes shaking times) and XRF (B) analysis	149
Figure 6.20: Variation of Pb in the regolith traverse T2 based on ICP-MS (A) (NH ₄ EDTA, 180-minutes shaking times) and XRF (B) analysis	150
Figure 6.21: Variation of Mn in the regolith traverse T2 based on ICP-MS (A) (NH ₄ EDTA, 180-minutes shaking times) and XRF (B) analysis	151
Figure 6.22: Variation of Fe in the regolith traverse T2 based on ICP-MS (A) (NH ₄ EDTA, 180-minutes shaking times) and XRF (B) analysis	152
Figure 6.23: Variation of S in the regolith traverse T2 based on ICP-MS (A) (NH ₄ EDTA, 180-minutes shaking times) and XRF (B) analysis	153
Figure 6.24: Variation of Cu (A) and Zn (B) in the regolith traverse KP5 (Kantienpan) based on ICP-MS analysis (using NH ₄ EDTA and 180-minutes shaking times)	157
Figure 6.25: Variation of Mn in the regolith traverse KP5 (Kantienpan) based on ICP-MS analysis (using NH ₄ EDTA and 180-minutes shaking times)	158
Figure 6.26: Variation of Cu (A) and Zn (B) in the regolith traverse KP8 based on ICP-MS analysis (using NH ₄ EDTA solutions and 180-minutes shaking times)	159
Figure 6.27: Variation of Mn in the regolith traverse KP8 based on ICP-MS analysis (using NH ₄ EDTA solutions and 180-minutes shaking times)	160
Figure 6.28: Variation of Cu (A) and Zn (B) in the regolith traverse T1 based on ICP-MS analysis (NH ₄ EDTA, 180-minutes shaking times)	161
Figure 6.29: Variation of Pb (A) and Mn (B) in the regolith traverse T1 based on ICP-MS analysis (NH ₄ EDTA, 180-minutes shaking times)	162
Figure 6.30: Variation of Cu (A) and Zn (B) in the regolith traverse T3 based on ICP-MS analysis (NH ₄ EDTA, 180-minutes shaking times)	164
Figure 6.31: Variation of Pb (A) and Mn (B) in the regolith traverse T3 based on ICP-MS analysis (NH ₄ EDTA, 180-minutes shaking times)	165

Figure 6.32: Variation of Cu (A) and Zn (B) in the regolith traverse 7800NW, MMI method (Sil: sillimanite; Crd: cordierite and Hbl: hornblende)	167
Figure 6.33: Variation of Cu (A) and Zn (B) in the regolith traverse 7700NW, MMI method	168
Figure 6.34: The calcrete layer in an old excavation at Areachap. Calcrete profile Calc1 (A), Calc2 (B) and a gossan rock with malachite and calcrete-filled veinlets at the bottom of calcrete layer (C)	175
Figure 6.35: Major oxides variation versus depth in the Areachap (visually cleaned samples referred to as Calc1)	176
Figure 6.36: Variation of Cu, Zn, Pb and S versus depth in the calcrete layer, Areachap (visually cleaned samples referred to as Calc1).....	177
Figure 6.37: Major oxides variation versus depth (visually cleaned samples referred to as Calc2) in Areachap	178
Figure 6.38: Variation of Cu, Zn, Pb and S versus depth in the calcrete layer, Areachap (visually cleaned samples referred to as Calc2).....	179
Figure 6.39: Variation of trace elements (A and B) and major components (C) of calcrete samples close to ore deposit and further away from the mineralized zone	180
Figure A.1: Cross section includes borehole AP2 and sample locations	210
Figure A.2: Cross section includes borehole AP5 and sample locations	211
Figure A.3: Cross section includes borehole KN12 and sample locations	212
Figure A.4: Cross section of KN11 and location of samples	217
Figure A.5: Geology map of the Kantienpan area (after Rossouw, 2003) and locations of rock samples (TDEM: Time domain electro-magnetic conductor) ...	219
Figure A.6: Box plot of final results of regional data set (Figure 5.18)	219
Figure D.1: Optimization of the shaking times and concentrations for Zn (A and C), Cu (B and D) and Pb (E and F) within and outside of the halo, NH ₄ EDTA method	269
Figure D.2: Optimization of the shaking times and concentrations of S for sample from inside of the halo, Ca (H ₂ PO ₄) ₂ method	272
Figure D.3: Flow chart of the separation of magnetic and non-magnetic parts of calcrete samples [(in bracket): sample number for XRF analysis]	283
Figure E.1: XRD result for original sample KPR12/4	301

Figure E.2: XRD result for sample Non-Mag 1	301
Figure E.3: XRD result for sample Non-Mag 2	302
Figure E.4: XRD result for sample Non-Mag 3	302
Figure E.5: XRD result for sample Mag 1	303
Figure E.6: XRD result for sample Mag 2.....	303
Figure E.7: XRD result for sample Mag 3.....	304
Figure E.8: XRD result for sample Mag 4.....	304
Figure E.9: XRD result for sample Mag 5.....	305

List of Tables

	Page
Table 2.1: Regional succession of Copperton Formation	7
Table 2.2: Regional succession of Jannelsepan Formation in Upington area	8
Table 2.3: Regional succession of Bokspits Formation in Van Wykspan area	9
Table 2.4: Summary of geomorphic events	20
Table 2.5: Classification of calcrete based on the weather conditions (after Khadkikar et al., 2000)	25
Table 2.6: Different Formations of the Kalahari Group. Data summarised from Malherbe (1984)	27
Table 4.2: Chemical composition of spinel grains from Kantienpan	59
Table 4.3: The chemical composition of chlorite grains near the ore zone from Areachap and Kantienpan	60
Table 4.4: Peraluminous ratio, normative corundum value and minerals present in AP5 and KN11	62
Table 4.5: The number of population, percentage, and threshold value for peraluminous ratio	63
Table 4.6: Percentage of gains and losses in borehole AP5 and Δ values for Areachap samples. Sample AP5/35 is assumed to be the malted precursor for altered samples AP5/23, 29, 30, and 32 (Isocon line based on Zr)	69
Table 4.7: Percentage of gains and losses in borehole AP5 and Δ values for Areachap sample. Sample AP5/42 is assumed to be the malted precursor for altered sample AP5/25 (Isocon line based on Zr)	71
Table 4.8: Percentages of gains and losses in borehole KN11 and Δ values for Kantienpan samples. Sample KN11/44 is considered to be the malted precursor for altered sample KN11/40 (Isocon line based on Zr)	72
Table 4.9: The least altered and altered samples based on the isocon Analysis	80

Table 5.1: Sorted data set based on the peraluminous factor (FPer) for the regional data set	94
Table 5.2: Sorted data set based on the alteration factor (FAR) for the regional data set	95
Table 5.3: Sorted data set based on the pelitic factor (FPR) for the regional data set	95
Table 5.4: Sorted data set based on peraluminous factor and calculation of amphibolite factor for the regional data set	97
Table 5.5: Sorted the peraluminous factor (FPer) and calculation of biotite-hornblende-gneiss factor for the regional data set	101
Table 5.6: Sorted the peraluminous factor (FPer) and calculation of the leucogneiss for the regional data set	103
Table 5.7: The threshold value for each factor, regional data set (n= 2016 samples)	106
Table 5.8: The threshold value for peraluminous and alteration factors, regional data set (n= 975 samples)	107
Table 5.9: The sample numbers and localities for anomalous samples with selected chemical data	108
Table 5.10: The threshold value for Zn, Cu and Ni, regional data set (n= 57 samples)	111
Table 5.11: Ranking the anomalous values based on MgO & K ₂ O contents, peraluminous ratio, AI, CCPI, FAR and FPer	113
Table 6.1: Different extractants classified by acidity (sequential leaching process and/or selective leaches)	122
Table 6.2: Some other extractants for selective leaching	122
Table 6.3: Selective extraction methods for Cu, Zn, Pb, Cd and S in the soil	123
Table 6.4: Results of the normality test for the data from Kantienpan (ICP-MS method, n = 52)	127
Table 6.5: The threshold values of elements in the Kantienpan data set (ICP-MS method, n=52 samples)	127

Table 6.6: The results of the normality test for the data set from Kantienpan (ICP-MS method, n = 52)	129
Table 6.7: The threshold values for whole Areachap data set (NH ₄ EDTA method, n=61)	129
Table 6.8: The normality test of distribution of S in Kantienpan data set (ICP-MS method, n = 33 samples)	131
Table 6.9: S values for samples within and outside the halo and blank sample, Kantienpan and Areachap	131
Table 6.10: The threshold values of S for the Kantienpan data set (ICP-MS method, n=33 samples)	132
Table 6.11: The normality test for the distribution of S in the Areachap data set (ICP-MS method, n = 21 samples)	132
Table 6.12: The threshold values of S for the Areachap data set (ICP-MS method, n=21 samples)	133
Table 6.13: Results of the normality test (MMI method, n = 58 samples)	133
Table 6.14: The threshold values of Cu and Zn (MMI method, n=58 samples)	134
Table 6.15: Results of the normality test for regolith traverse of KP12 (XRF method, n = 19)	135
Table 6.16: Threshold values for regolith traverse KP12 (XRF method, n=19)	135
Table 6.17: The threshold value of Zn for regolith traverse KP12 (XRF analysis, n=19 samples)	136
Table 6.18: Results of the normality test for regolith traverse of T2 (XRF method, n = 25)	136
Table 6.19: Threshold values for regolith traverse T2 (XRF method, n=25)	138
Table 6.20: Threshold values for Zn, regolith traverse T2 (XRF method, n=25 samples)	138
Table 6.21: Anomaly to background ratio of different analytical methods for Cu, Zn, Pb, Mn and S	169

Table 6.22: The comparison of major and trace elements in original, magnetic and non-magnetic parts of calcrete sample KP12/4, Kantienpan (A: ampere)	172
Table 6.23: Mineralogical ratios of the more common minerals in magnetic and non-magnetic part of the calcrete	173
Table 6.24: The comparison of major oxides and trace elements of interest in visually cleaned parts of calcrete samples in the Kantienpan (A: ampere; *: semi-quantitative analyses)	174
Table 6.26: Chemical composition of visually cleaned calcretes near the ore zone (Calc1-3 and Calc2-3 at Areachap) and further away from the mineralized zone (Vcal2 and Vcal3)	180
Table A.1: Depth of samples in drill hole AP2, Areachap	210
Table A.2: Depth of samples in drill hole AP5, Areachap	211
Table A.3: Depth of samples in drill hole KN12, Kantienpan	212
Table A. 4: Lithological description of borehole KN12 (Rossouw, 2003)	213
Table A. 5: Lithological description of borehole KN7 (Rossouw, 2003)	214
Table A. 6: Lithological description of borehole KN3 (Rossouw, 2003)	215
Table A. 7: Lithological description of borehole KN2 (Rossouw, 2003)	216
Table A.8: Depth of samples in drill hole KN11, Areachap	217
Table A. 9: Lithological description of borehole KN11 (Rossouw, 2003)	218
Table B.1: Chemical composition of feldspar grains adjacent to the ore zone (Areachap and Kantienpan)	221
Table B.2: Chemical composition of pyroxene grains near the ore zone (Areachap and Kantienpan)	222
Table B.3: Chemical composition of cordierite grains close to the ore zone (Areachap and Kantienpan)	223
Table B.4: Chemical composition of garnet grains adjacent to the ore zone (Areachap)	224
Table B.5: Chemical composition of biotite grains near the ore zone (Areachap and Kantienpan)	224
Table B.6: Chemical composition of gahnite (spinel group) grains close the ore zone (Kantienpan)	225

Table B.7: Chemical composition of chlorite grains near the ore zone (Areachap and Kantienpan)	225
Table B.8: Chemical composition and unit formulae of plagioclase grains close to the ore zone (Areachap and Kantienpan)	226
Table B.9: Chemical composition and unit formulae of pyroxene grains close to the ore zone (Areachap and Kantienpan)	227
Table B.10: Chemical composition and unit formulae of cordierite grains near the ore zone (Areachap and Kantienpan)	229
Table B.11: Chemical composition and unit formulae of garnet grains near the ore zone (Areachap)	230
Table B.12: Chemical composition and unit formulae of biotite grains near the ore zone (Areachap and Kantienpan)	231
Table C.1: Standard deviation and detection limit of XRF analysis	234
Table C.2: XRF analytical results for samples from borehole AP5 (Areachap)	235
Table C.3: XRF analytical results for samples from borehole AP2 (Areachap)	241
Table C.4: XRF analytical results from surface (Kantienpan)	245
Table C.5: XRF analytical results for samples from borehole KN12 (Kantienpan)	247
Table C.6: XRF analytical results for samples from borehole KN11 (Kantienpan)	253
Table D.1: ICP-MS analytical results of wind blown sand samples (5 gram sample + 50 ml of 0.2 M NH ₄ NO ₃ solution, 30minute shacking times)	263
Table D.2: Results of statistical analysis on duplicate samples and the null hypothesis (0.2 M NH ₄ NO ₃ solution, 30 min shacking time, n=16)	264
Table D.3: ICP-MS analytical results of sand samples (2.5 gram sample + 45 ml of 1 M NH ₄ OAC solution, different shacking times)	265
Table D.4: Results of statistical analysis on duplicate samples and null hypothesis (1 M NH ₄ OAC solution, different shacking time, n=13)	266
Table D.5: ICP-MS analytical results of sand samples (2 gram sample + 50 ml of 0.02 M NH ₄ EDTA solution, different shacking times)	267
Table D.6: Results of statistical analysis on duplicate samples and null hypothesis (1 M NH ₄ EDTA solution, different shacking time, n=9)	268
Table D.7: ICP-MS analytical results of sand samples for sulphur (5 grams sample + 50 ml of 0.02 M Ca (H ₂ PO ₄) ₂ solution, 120-minute shacking times)	271
Table D.8: Results of statistical analysis on duplicate samples and null hypothesis (0.02 M Ca (H ₂ PO ₄) ₂ solution, different shacking times, n=12)	271

Table D.9: ICP-MS analytical results of sand samples for S for different shaking times (5 gram sample + 50 ml of 0.02 M Ca (H ₂ PO ₄) ₂ solution)	272
Table D.10: XRF analytical results of regolith sampling traverse KP12 for the <75 μ size fraction	273
Table D.11: XRF analytical results of regolith sampling traverse T2 for the <75 μ finest size fraction	274
Table D.12: ICP-MS results of regolith sampling traverse KP12 (0.02 M Ca (H ₂ PO ₄) ₂ solutions for S, shaking time: 120-minutes, and 0.02 M NH ₄ EDTA solutions for the rest of the elements shaking time 180-minutes)	275
Table D.13: ICP-MS results of regolith sampling traverse KP5 (0.02 M NH ₄ EDTA solutions for Cu, Zn, Pb, Ba, Mn and Fe, shaking time: 180-minutes) ..	276
Table D.14: ICP-MS results of regolith traverse KP8 (0.02 M NH ₄ EDTA solutions for Cu, Zn, Pb, Ba, Mn and Fe, shaking time: 180-minutes)	277
Table D.15: MMI results of regolith traverses 7700NW and 7800NW for Cu and Zn (Rossouw, 2003)	278
Table D.16: ICP-MS results of regolith sampling traverse T1 (0.02 M NH ₄ EDTA solutions for Cu, Zn, Pb, Ba, Mn and Fe, shaking time: 180-minutes; <75μ size fraction)	279
Table D.17: ICP-MS results of regolith sampling traverse T3 (0.02 M NH ₄ EDTA solutions for Cu, Zn, Pb, Ba, Mn and Fe, shaking time: 180-minutes; <75μ size fraction)	280
Table D.18: ICP-MS results of regolith sampling traverse T2 (0.02 M NH ₄ EDTA solutions for Cu, Zn, Pb, Ba, Mn and Fe, shaking time: 180-minutes; <75μ size fraction)	281
Table D.19: XRF results of the magnetic, non-magnetic and visually cleaned parts of the calcrete sample KPR12/4, Kantienpan (major elements: wt. %)	284
Table D.20: XRF results of calcrete samples and magnetic parts, Kantienpan (major elements: wt. %, A: ampere)	286
Table D.21: XRF results of calcrete samples and magnetic parts, Kantienpan (major elements: wt. %, A: ampere)	289
Table D.22: XRF results of calcrete samples and magnetic parts, Areachap (major elements: wt. %, A: ampere, Sample set Calc1)	291
Table D.23: XRF results of calcrete samples and magnetic parts, Areachap (major elements: wt. %, A: ampere, Sample set Calc2)	293

Table D.24: Chemical composition of calcretes near the ore zone (Calc1-3 and Calc2-3) and further away from ore zone (Vcal2 and Vcal3)	295
Table D.25: Chemical composition of magnetic parts of calcretes near the ore zone (Calc1-3) and further away from ore zone (Vcal2 and Vcal3) (A: ampere in)	297
Table D.26: Chemical composition of calcretes near and further away from ore zone analyzed by the XRF method (Vermaak, 1984)	299
TABLE E.1: Instrument and data collection parameters	300