

Chapter 4

Lithogeochemical investigation

4.1. Introduction

Previous regional lithogeochemical investigations of the rocks related to massive sulphide ore bodies in the eastern part of the Namaqua Province were done by Middleton (1976), Wagener et al. (1986), Geringer et al. (1987), Cilliers (1987), Schade et al. (1989), Theart et al. (1989), Geringer et al. (1990), Moore et al. (1990), Cornell et al. (1990a), Cornell et al. (1990b), Cornell et al. (1992), Humphreys (1993), Geringer et al. (1994) and Thomas et al. (1994a,b). These investigations demonstrated:

- the presence of a volcano-sedimentary succession;
- the deposit is of volcanic hosted massive sulphide (VHMS) type; and
- that the rocks underlying the massive sulphide ore body at the Copperton mine experienced hydrothermal alteration (Theart et al., 1989).

The objective of this chapter is to find evidence of similar hydrothermal alteration in the other deposits and to quantify the degree of alteration, so that it could be shown to be useful in regional lithogeochemical exploration.

During the formation of metalliferous VHMS deposits, hydrothermal fluids leach from, or add some chemical elements into the host rocks. Primary lithogeochemical dispersion haloes refer to that part of the enclosing rocks that were affected by this process. Some of these elements may be considered typomorphic of specific ore deposits and they are interpreted as a direct index or vector indicating the existence of a specific ore body. The

leached elements would have precipitated somewhere else, or were removed out of the system at the time of ore formation (Beus and Grigorian, 1977; Sanchez-Espana et al., 2000; Bonnet et al., 2005; Dawood et al., 2005). Systematic sampling of ore bodies and their enclosing rocks is therefore an essential requirement in establishing the characteristic lithogeochemical features that could be used in exploration for undiscovered ore bodies. The analytical data thus obtained is processed and used to determine the chemical characteristics of the geochemical haloes. With this objective in mind, the boreholes which intersect the hangingwall, ore zone and the footwall successions, were selected in the present study area i.e. boreholes AP2 and AP5 from the Areachap Cu-Zn deposit, and boreholes KN11 and KN12 from the Kantienpan Cu-Zn deposit.

The following lithogeochemical parameters and methods were adopted and expanded to be used for identifying and characterizing the alteration haloes in the footwall and hangingwall lithologies that developed in the precursor rocks at the time of sulphide mineralisation:

- 1) variations in the relative abundance of major element concentrations throughout the rock successions;
- 2) microprobe analyses of silicates and spinels to confirm the identity of some minerals and investigate the chemical variation in rock forming minerals near the ore zone;
- 3) norm calculations mainly as a method to identify peraluminous rocks in the rock successions;
- 4) alteration index (AI) (Ishikawa, et al., 1976) and Chlorite-Carbonate-Pyrite Index (CCPI) (Large et al., 2001) to distinguish the alteration process affecting the ore zone in the precursors of high grade metamorphosed rocks, by means of the box plot (Large et al., 2001);

- 5) immobile and mobile elements to separate the least altered rocks from the altered rocks and compare them with each other utilizing the isocon approach (Grant, 1986). This method is also used to quantify the degree of alteration;
- 6) Pearce element ratio (PER) analysis to identify the effects of hydrothermal fluids and metamorphism on major elements in specific minerals near the ore zone (Whitbread and Moore, 2004).

4. 2. Sampling, sample preparation and analytical methods

With regard to the litho-geochemical investigation, a total of 160 rock samples which include 73 samples from Areachap (27 samples from borehole AP2 and 46 samples from borehole AP5) and 87 samples from Kantienpan (49 samples from borehole KN11 and 38 samples from borehole KN12) were collected from available core of diamond-drilled holes (Appendix A, Fig. A.1 to A.4). The sample selection was based on the lithological variation observed in the successions intersected. In addition, five samples were taken from the scarce outcrops on the farm, Kantienpan (Appendix A, Fig. A.5).

Each sample was cut by diamond saw into two halves. One half was used for thin or polished thin sections, and for chemical analyses and the other half was kept for future use and quality control. In total 185 thin sections were made of which 172 polished for microprobe work. The petrographic investigation of these sections was done systematically. This study also served as a basis for microprobe analyses after selected mineral grains were marked. Coordinates of the spots, where analyses were required, were recorded and later used during the microprobe analysis of the mineral grains (Appendix B, Tables B.1 to B.7).

An ARL 9400XP+Wavelength dispersive X-ray Fluorescence Spectrometer (XRF) was used for the determination of whole rock major and trace elements at the Geology Department Laboratory, University of Pretoria. The sample material was crushed in a jaw crusher and milled to a grain size of less than 63 micron. Powder pellets for trace elements analysis and fused beads for major elements analysis were made from the

powder (Appendix C, Tables C.2 to C.7).

4.3. Major element variation near the ore zone

The variation of major element concentrations may be used as an index of compositional changes caused by alteration at the time of ore formation (Whitbread and Moore, 2004).

The diagram, which shows these variations, may be used to detect the presence of alteration pipes and the nature of the unaltered footwall lithologies.

The objective 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. It should be noted that in the case of the two study areas discussed below, the silicate rocks and associated ores, were metamorphosed and intensely deformed, and that no primary “way up” indicators survived these events.

For this purpose, two boreholes were selected, one from the Areachap mine (AP5) and the other from the Kantienpan mine (KN11). The variations of major element compositions are used in the paragraphs below to locate the alteration zones and to define their geochemical characteristics.

4.3.1. Interpretation of major elements variations adjacent to the ore zone in borehole AP5 (Areachap)

In AP5, the ore is hosted by biotite-gneiss or biotite-hornblende-gneisses (lithological zone AR6 in Fig. 4.1). The gneissic rocks structurally overlying the ore zone, is interpreted to represent the primary footwall in this particular case as explained below. These gneisses contain cordierite, sillimanite, garnet and biotite. The gneissic rocks structurally below the ore zone, which is interpreted to be the primary hangingwall in this particular case, contain more hornblende and biotite.

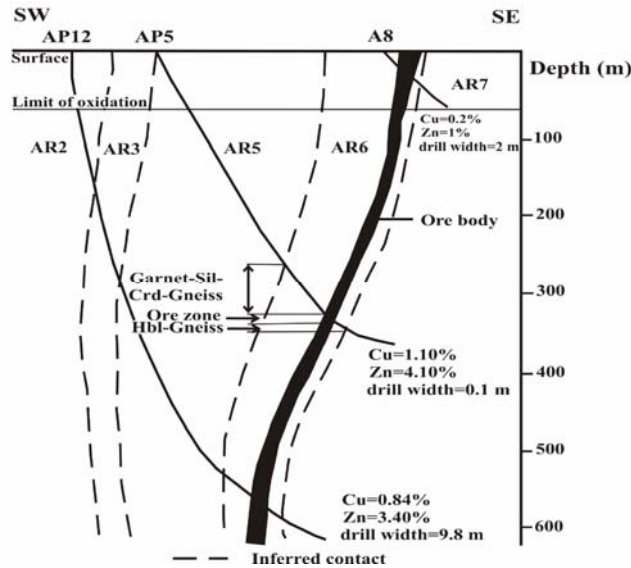


Figure 4.1: A cross-section of lithology at Areachap mine including the borehole AP5 (adopted from Voet and King, 1986) (Sil: sillimanite; Crd: cordierite and Hbl: hornblende)

The variations in CaO, Na₂O, K₂O and MgO (wt. %, all element concentrations are expressed as weight percent) in the lithological successions adjacent to the sulphide mineralisation are shown in Figures 4.2 to 4.5. The lowest CaO (0.01-1 %) and Na₂O (0.2-1.5 %) contents in AP5 occur in samples depicted above the ore zone in Figures 4.2 and 4.3. Intervals with low CaO and Na₂O are generally considered to represent a footwall alteration zone or an alteration pipe that characterizes VHMS deposits (Lydon, 1998b), therefore the interval described above probably represents the altered zone in the original footwall rocks of the deposit.

K₂O contents (1-2.6 %) in AP5 are generally higher between samples AP5/21 and AP5/37 and decreases from AP5/37 (0.75-1.25 %) towards AP5/45 (Fig. 4.4).

The MgO contents (2.5-7 %) are on average higher between samples AP5/21 and AP5/37 when compared to samples from AP5/37 to AP5/45 (0.9-1.2 % MgO) in borehole AP5 (Fig. 4.5).

Intervals with high MgO and K₂O are also generally considered to be characteristic of the footwall alteration zone of VHMS deposits (Lydon, 1998b), this therefore supports the interpretation that the above intervals (between AP5/21 and AP5/37)

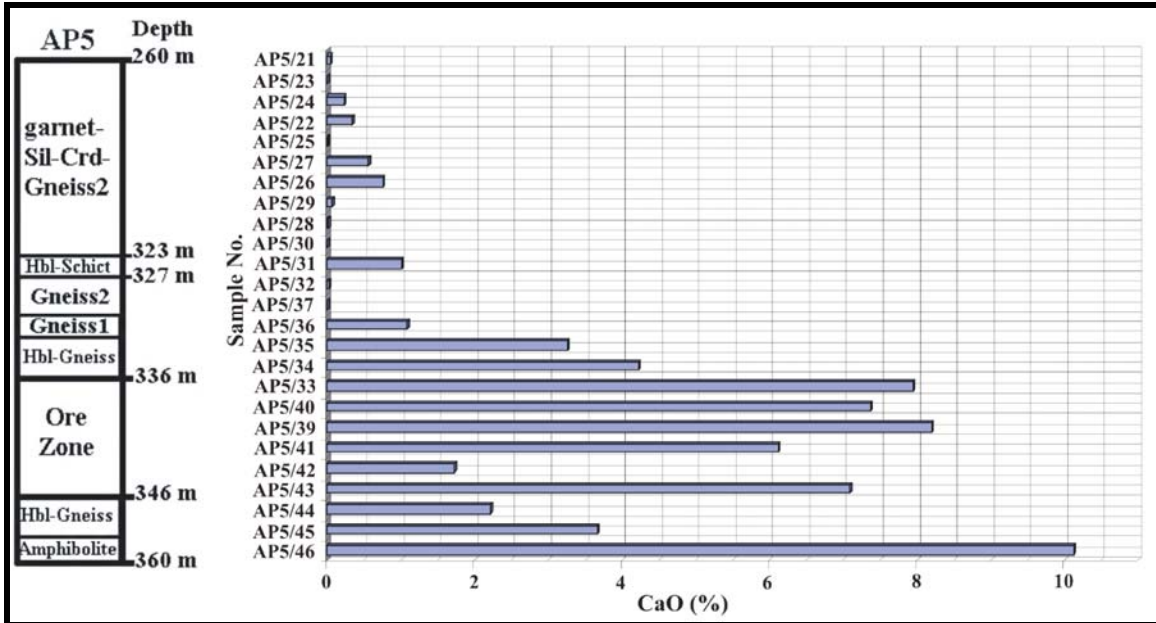


Figure 4.2: Variation of CaO through the lithological successions adjacent to the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

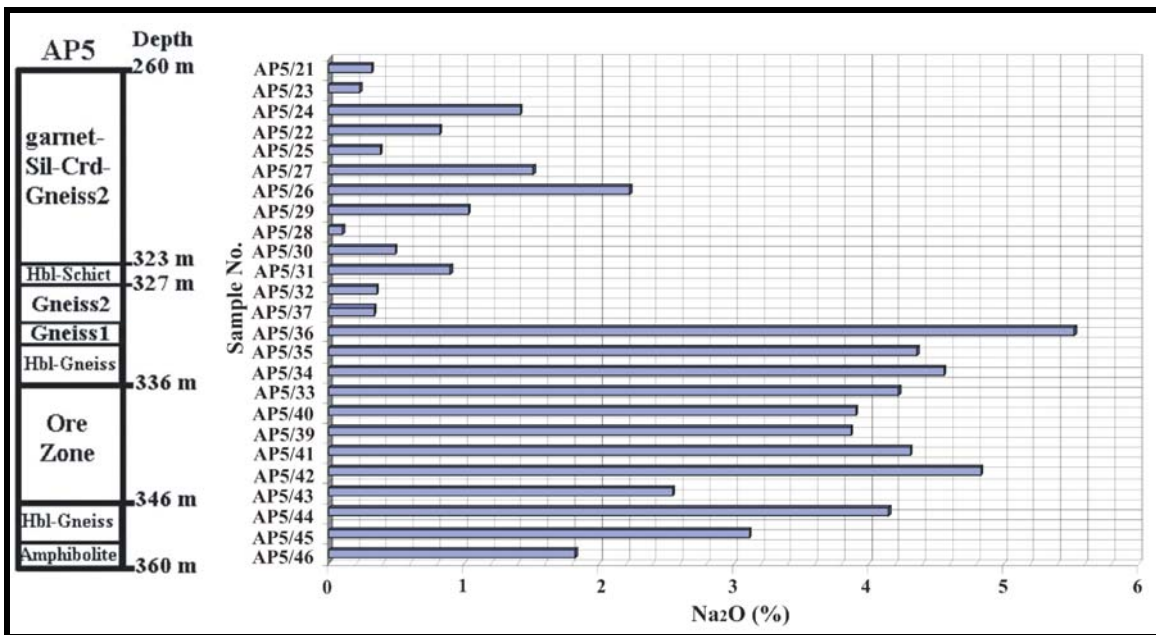


Figure 4.3: Variation of Na₂O through the lithological successions hosting the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

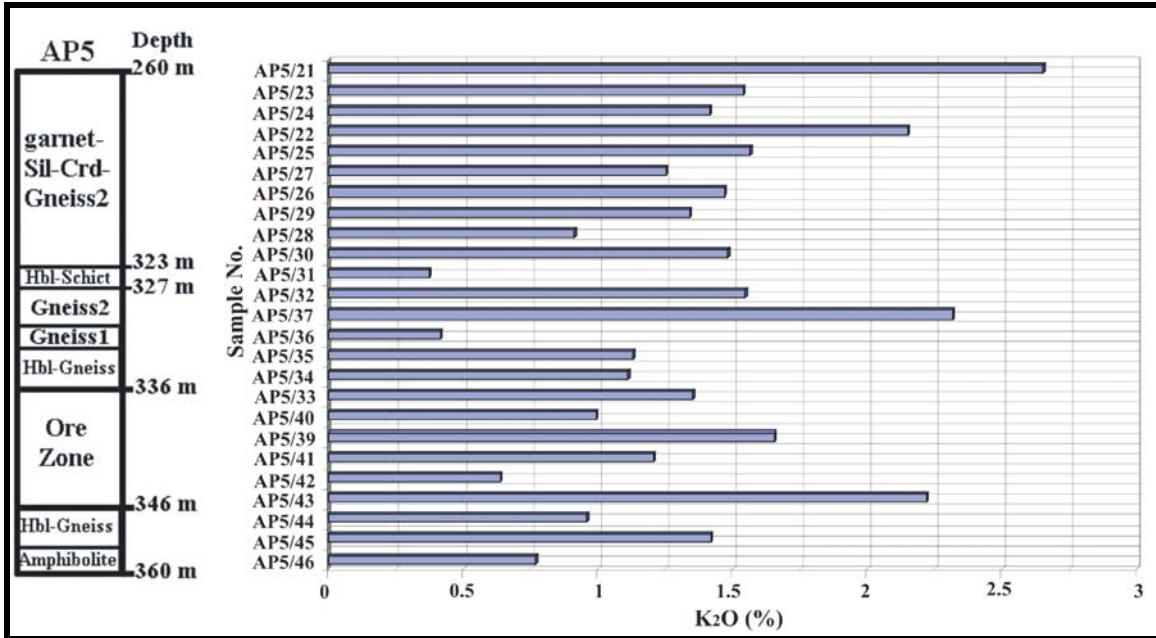


Figure 4.4: Variation of K₂O through the lithological successions adjacent to the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

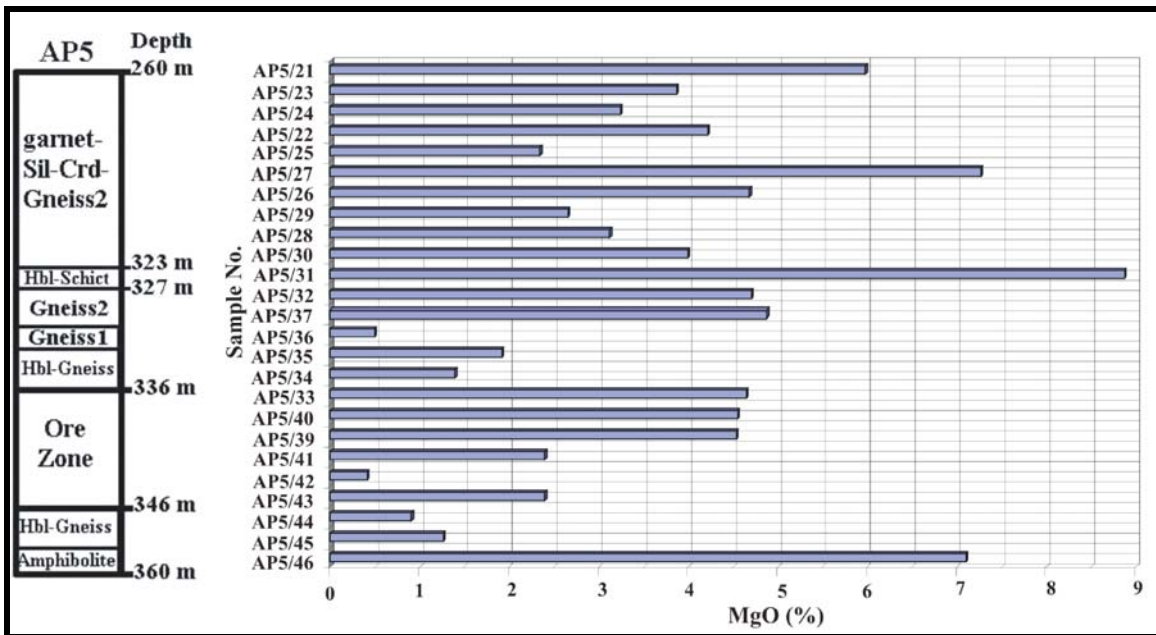


Figure 4.5: Variation of MgO through the lithological successions hosting the ore zone, at the Areachap deposit (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

probably represents the footwall alteration zone. This interpretation requires that the ore body must have been structurally turned over in acquiring its present habit.

4.3.2. Interpretation of major elements variation near the ore zone in borehole KN11 (Kantienpan)

In KN11, the ore is overlain by biotite-gneiss or biotite-hornblende-gneiss (unit number 5 in Fig. 4.6). 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 variations in CaO, Na₂O, K₂O and MgO (%) in the lithological successions hosting the sulphide mineralisation are shown in Figures 4.7 to 4.10. In KN11, the interval with the lowest CaO (0.01 %) and Na₂O (0.1-0.25 %) contents occur between the samples KN11/38 and KN11/43, which are located at the bottom of the ore zone. Based on the depletion of CaO and Na₂O, it is assumed that this interval represents the alteration pipe. This is also seen as evidence that the ore body has not been structurally over turned. This will be further demonstrated in subsequent sections.

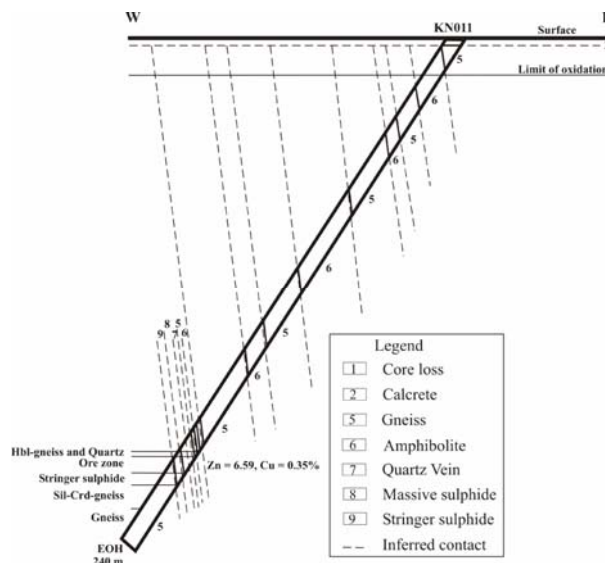


Figure 4.6: Cross-section of borehole KN11 in the Kantienpan area (Sil: sillimanite, Crd: cordierite and Hbl: hornblende).

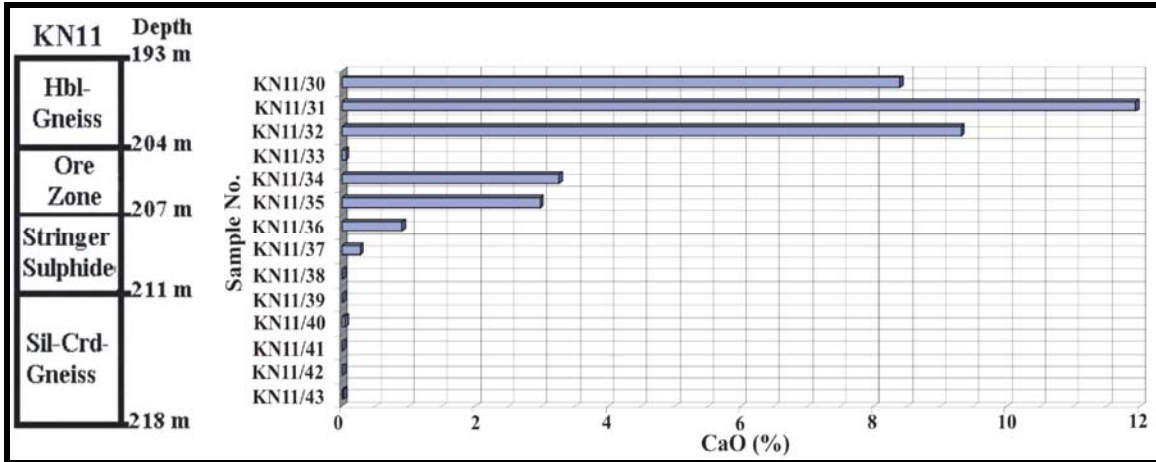


Figure 4.7: Variation of CaO through the lithological successions adjacent to the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

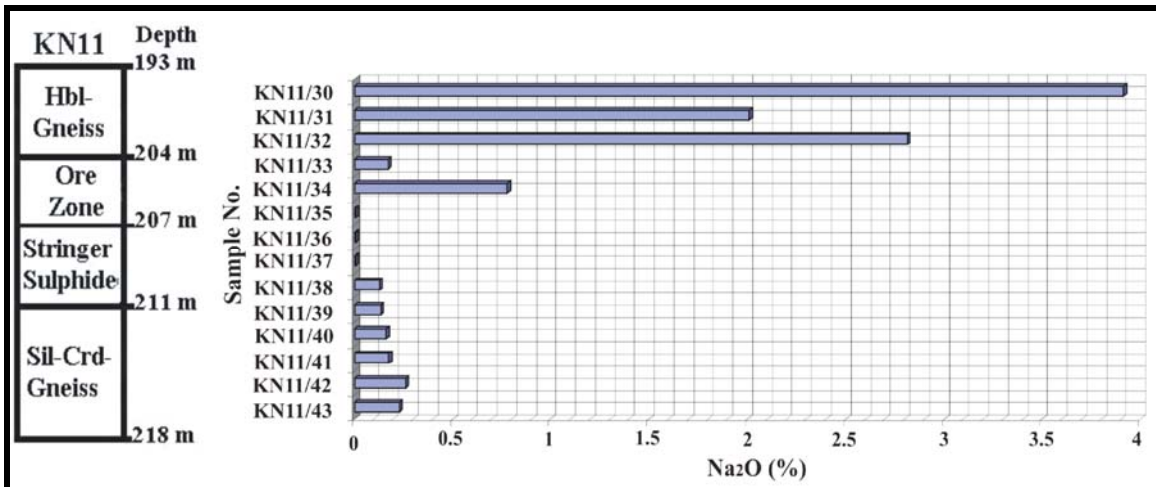


Figure 4.8: Variation of Na₂O through the lithological successions hosting the ore zone (Hbl: Hornblende; Crd: cordierite; Sill: sillimanite).

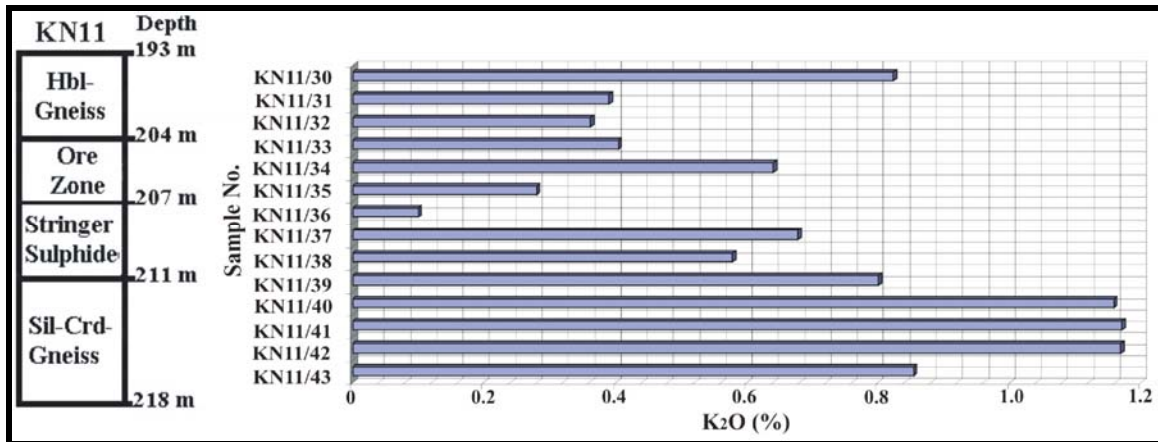


Figure 4.9: Variation of K₂O through the lithological successions adjacent to the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

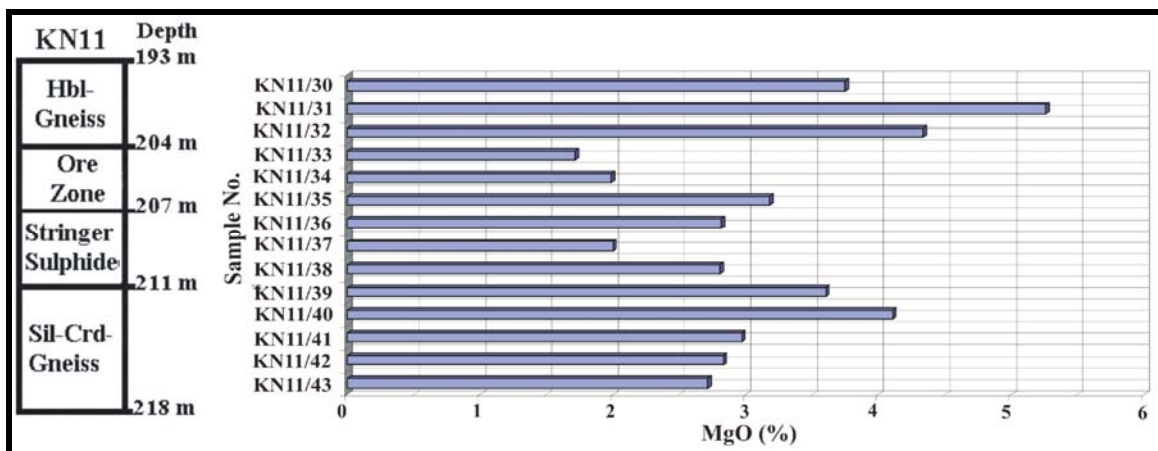


Figure 4.10: Variation of MgO through the lithological successions hosting the ore zone (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite).

In borehole KN11, K₂O 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 KN11/30 (Fig. 4.9). Unlike in the case with Na and Ca (i.e. low contents), the high K₂O 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 to samples from KN11/38 to KN11/30 (3.5-5.2 % MgO) in this borehole (Fig. 4.10). Samples KN11/30 to KN11/32 are biotite-hornblende-gneisses, which explain the high MgO contents in these samples.

4.4. Mineral chemistry near the ore zone

This section is intended to identify changes in the chemical composition of the rock forming minerals. These changes might be related to primary halo development and the minerals may supply additional evidence of the preservation of primary alteration features. For this purpose, the Na/Ca ratio in plagioclase, $Mg / (Mg + Fe + Ca)$ ratio in pyroxene, $Mg / (Mg + Fe)$ ratio in cordierite, the composition of garnet, the Mg / Fe ratio in biotite, and the composition of spinel are considered below. The $Mg / (Mg + Fe)$ ratio of retrograde chlorite is also considered. Microprobe analysis was done on selected samples from the rock successions adjacent to the ore body. A CAMECA EPMA- SX 100 electron microprobe was used to analyse the minerals i.e., feldspars, pyroxenes, cordierite, garnets, biotite and chlorite (Appendix B, Tables B.1 to B.7).

Table B.8 (Appendix B) represents the chemical composition of plagioclase from Areachap (AP5) and Kantienpan (KN11). The variation of Na ($100 * Na / (Ca + Na + K)$) and Ca values ($100 * Ca / (Ca + Na + K)$) in plagioclase in the vicinity of the ore zone is shown in Figure 4.11 for KN11. The Na values have the lowest value in rocks collected from both sides of the ore zone (An_{40} to An_{77}), reflecting that plagioclases are more Ca-rich close to the ore zone (samples KN11/32, KN11/40 and KN11/44). Plagioclases are more Na-rich further away from the ore zone (An_{19} to An_{33} , samples KN11/27 and KN11/28) in this intersection. A similar tendency has been noted in two samples from AP5 (An_4 to An_{19} , sample AP5/22 in Table B.8).

The chemical composition of the Kantienpan pyroxenes are shown in Figure 4.12. The samples that are adjacent to the ore zone in the footwall alteration zone (KN11/39, KN11/40 and KN11/44) have the highest Mg^* ratio ($100 * \text{cationic ratio of } Mg / (Mg + Fe + Ca)$). This value decreases in the stringer zone (KN11/38) and in the hangingwall (KN11/20) away from the ore zone. It is therefore suggested that the Mg^* ratios of pyroxenes reflects the compositional differences between the footwall and hangingwall lithologies.

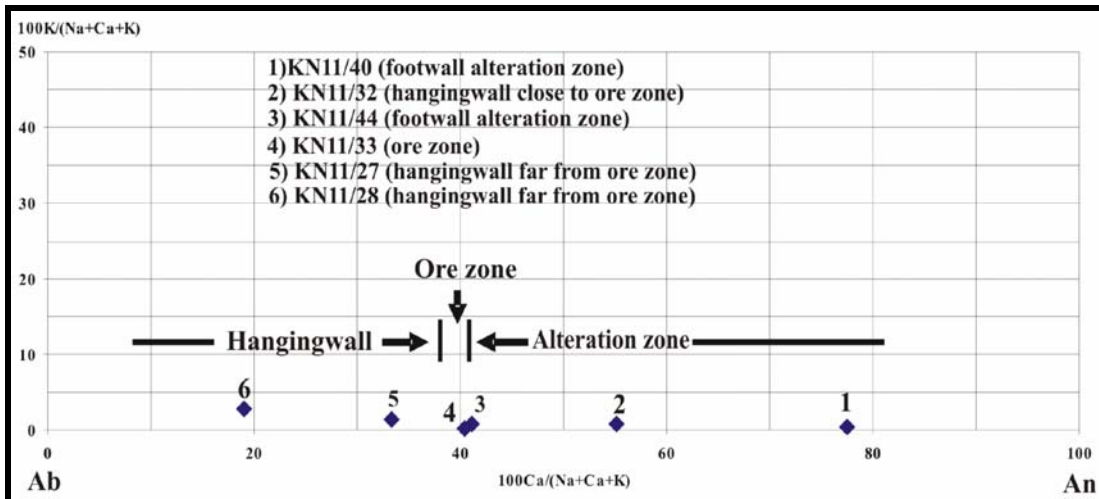


Figure 4.11: Variation of Na and Ca in plagioclase, Kantiapan (KN11) (Ab: albite and An: anorthite).

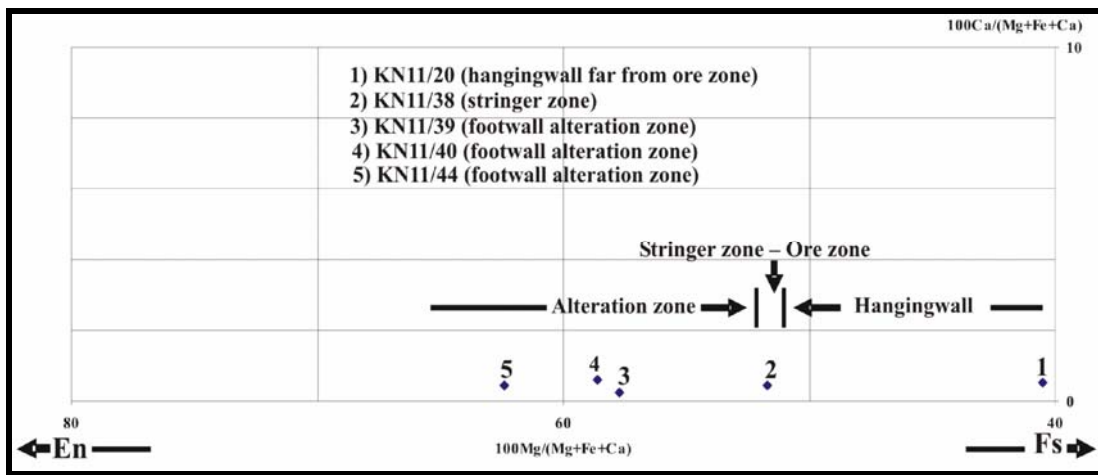


Figure 4.12: Variation of Mg, Fe and Ca in the pyroxene, Kantiapan (KN11), (En: enstatite and Fs: ferrosilite).

The variation in the magnesium number ($Mg\# = 100 \cdot Mg / (Mg + Fe)$) of cordierite adjacent to the ore zone (for KN11) is shown in Figure 4.13. The $Mg\#$ of cordierite in both footwall and hangingwall are generally high (>66.2), but cordierites from the hangingwall have slightly higher $Mg\#$ numbers (>82.5), compared to those from the footwall (66.2-73.1). The $Mg\#$ number of cordierite from the ore zone (89.4) is the highest, when compared to the hangingwall and footwall alteration zones.

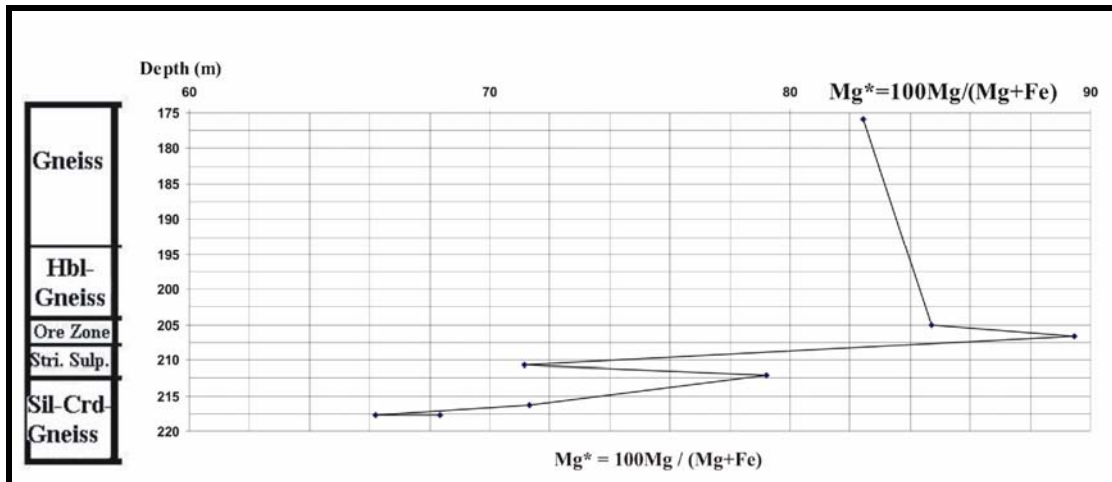


Figure 4.13: Variation of the Mg number in cordierite, Kantienpan, (KN11), (Hbl: Hornblende; Stri. Sulp.: stringer sulphide; Sil: sillimanite; Crd: cordierite).

In the footwall alteration zone in the Areachap deposit (Appendix B, Table B.10, samples AP5/23, AP5/25, AP5/29 and AP5/32), the Mg number of cordierite changes from 42.19 to 77.67 and is lower than the maximum value (89.44) in the ore zone of KN11.

The chemical composition of garnet is given in Table B.11 (Appendix B). Variation in the composition of garnet in the footwall alteration zone and the ore zone at Areachap is shown in Figure 4.14. The almandine and pyrope components in garnet grains from the footwall alteration zone (samples AP5/22, AP5/23, AP5/25 and AP5/28) are high, whereas the spessartine and grossular components are low. The garnets in the ore zone (samples AP5/42 and AP5/43) have high Ca contents but low Mg contents.

The chemical composition of mica in the host rocks of the Areachap and Kantienpan ore body are shown in Figure 4.15. The Mg-rich variety, phlogopite, (samples AP5/22 to AP5/32 and KN11/37 to KN11/44) is more common adjacent to the ore zone in the footwall alteration zones in both boreholes. In sample AP5/35, the biotite is more Fe-rich and may be referred to as annite. This sample reflects the composition of mica in samples immediately below the ore zone that probably escaped the alteration processes, because its precursors were probably a distance away from the primary feeder zone. Theart (1985) reported that the Mg / (Mg + Fe) ratio of biotite decreases both vertically away from the ore zone at the Prieska Cu-Zn mine in the footwall succession, as well as laterally in the

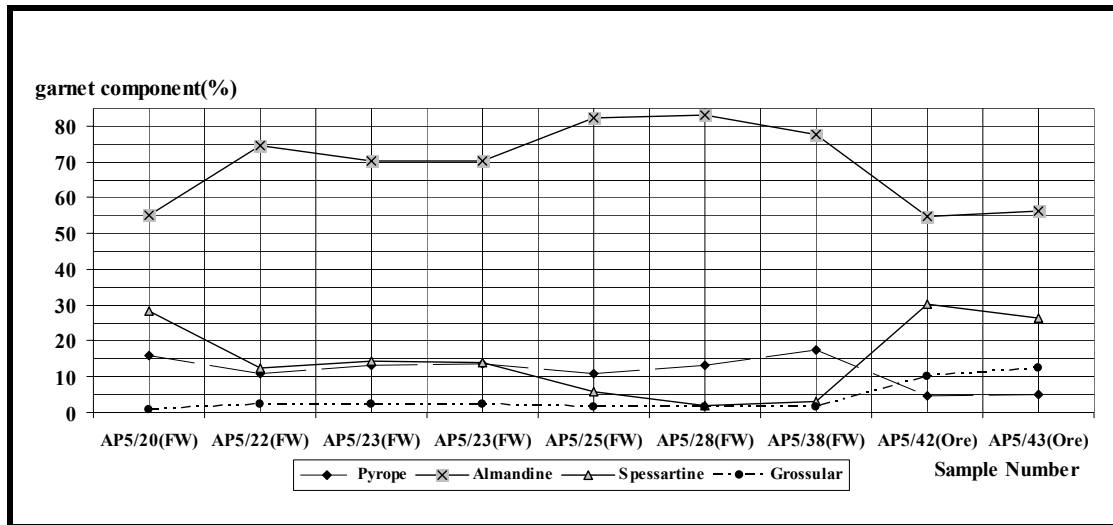


Figure 4.14: Chemical components of garnet in the alteration and ore zones, Areachap (AP5), (FW: footwall).

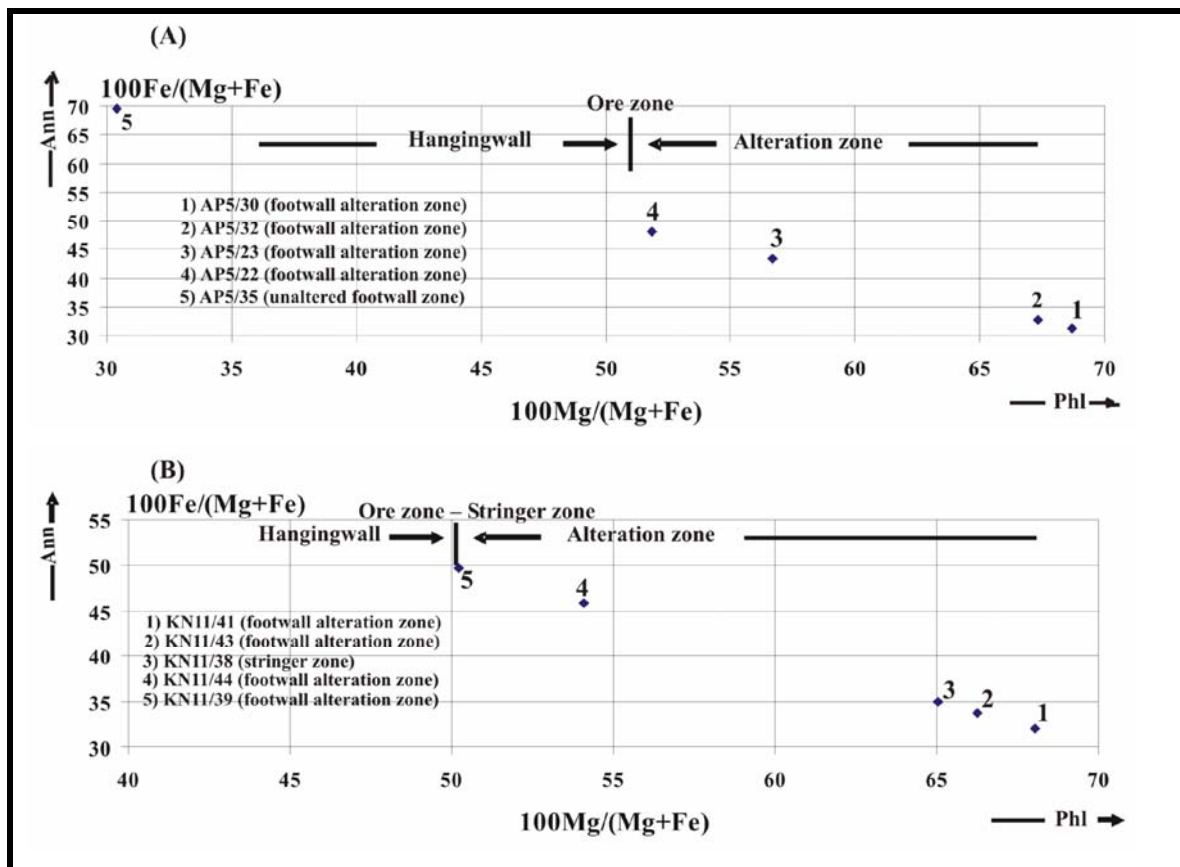


Figure 4.15: Variation of Mg and Fe in mica at Areachap (A) and Kantienpan (B), (Ann: Annite and Phl: phlogopite).

biotite schist on strike with the mineralization.

The chemical composition of spinel close to the ore zone at Kantienpan is given in Table 4.2. The high Al₂O₃ content of these rocks confirms the peraluminous characteristic of the footwall alteration zone and ore zone. These spinels may therefore be regarded as metamorphic indicator minerals of the hydrothermal alteration that affected the precursor rocks. Spinel has a high Zn content in the ore zone and in the footwall alteration zone in KN11 (samples KN11/34, KN11/42 and KN11/43) suggesting that the spinel is of the gahnite type.

Table 4.2: Chemical composition of spinel grains from Kantienpan.

	Spinel Analyses					Based on 32(O)					
	KN11_34B [P5_Spin (Ore)]	KN11_42 [P1_Spin (FW)]	KN11_43 [P4_Spin (FW)]	KN12_32 [P2_Gah (Ore)]	KN12_35A [P3_Spin (Ore)]		KN11_34B [P5_Spin (Ore)]	KN11_42 [P1_Spin (FW)]	KN11_43 [P4_Spin (FW)]	KN12_32 [P2_Gah (Ore)]	KN12_35A [P3_Spin (Ore)]
	Gahnite	Gahnite	Gahnite	Gahnite	Zincianspinel		Gahnite	Gahnite	Gahnite	Gahnite	Zincianspinel
SiO ₂	0.03	0.21	0.23	0.42	0.01	Si	0.01	0.05	0.05	0.10	0.00
Al ₂ O ₃	59.02	56.12	56.31	56.39	59.94	Al	15.86	15.76	15.71	15.67	15.76
Cr ₂ O ₃	0.01	0.01	0.01	0.01	0.00	Cr	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.00	0.01	0.01	0.00	0.02	Ti	0.00	0.00	0.00	0.00	0.00
FeO	5.39	13.71	12.04	9.50	16.60	Fe ⁺²	1.03	2.73	2.38	1.87	3.10
MgO	6.26	2.30	2.47	4.28	8.56	Mg	2.13	0.82	0.87	1.50	2.85
MnO	0.46	0.23	0.23	0.22	0.39	Mn	0.09	0.05	0.05	0.04	0.07
ZnO	29.39	26.43	28.69	27.94	14.10	Zn	4.95	4.65	5.01	4.87	2.32
CaO	0.00	0.00	0.00	0.00	0.00	Ca	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.01	0.00	0.00	0.01	Note: FW: footwall; Spin: Spinel; Gah: Gahnite and [Lab number].					
Na ₂ O	0.66	0.63	0.69	0.63	0.31						
F	0.00	0.06	0.00	0.02	0.00						
Total	101.27	99.73	100.68	99.41	99.94						

Note: KN11_34B [P5_Spin (Ore)] means borehole KN11_ sample No 34B [analysis point No_ in spinel (from the ore zone)].

Sample KN12/35A contains spinel with the highest Fe content and its Mg content is higher than that of Zn, but both Mg and Zn have lower molecular proportions than Fe. These spinels may be described as zincianspinel.

4.4.1. The retrograde chlorite

The chlorite minerals observed at both localities is a product of retrograde metamorphism. The chemical composition of chlorite adjacent to the ore deposit is given in Table 4.3. Chlorites of the ore zone are characterised by the highest Mg# (Mg# = Mg/ (Mg + Fe), 0.93 in sample KN11/36) in KN11 when compared to the footwall (0.59 in sample KN11/41). The highest Mg# in AP5 (0.45 in sample

AP5/40) is also considered for the sample in the ore zone, and it has lower values in the hangingwall (samples AP5/44 and AP5/45). Based on the low Mg# value of chlorite in the hangingwall lithologies of AP5 (0.35 and 0.44 in samples AP5/44 and AP5/45) these chlorites are classified as chamosite.

Table 4.3: The chemical composition of chlorite grains near the ore zone from Areachap and Kantienpan.

	Chlorite Analyses						Based on 28(O)						
	AP5_40 [P3_Bio (Ore Zone)]	AP5_42 [P3_Bio (Ore Zone)]	AP5_44 [P2_Chlorite (HW)]	AP5_45 [P4_Bio (HW)]	KN11_36 [P2_alt(chlorite or pin) (Stringer Zone)]	KN11_41 [P4_Amp (FW)]		AP5_40 [P3_Bio (Ore Zone)]	AP5_42 [P3_Bio (Ore Zone)]	AP5_44 [P2_Chlorite (HW)]	AP5_45 [P4_Bio (HW)]	KN11_36 [P2_alt(chlorite or pin) (Stringer Zone)]	KN11_41 [P4_Amp (FW)]
	Fe-Mg Chlorite	Fe- Chlorite	Fe- Chlorite	Fe-Mg chlorite	Mg- Chlorite	Mg-Fe chlorite		Fe-Mg Chlorite	Fe- Chlorite	Fe- chlorite	Fe-Mg chlorite	Mg- Chlorite	Mg-Fe chlorite
SiO ₂	29.07	27	26.21	26.55	30.22	25.43	Si	6.18	6.03	5.75	5.76	5.86	5.29
Al ₂ O ₃	16.9	17.01	18.46	18.23	12.57	23.09	Al	1.82	1.97	2.25	2.24	2.14	2.71
TiO ₂	0.39	0.79	0.04	0.17	0.00	0.03	Al	2.41	2.51	2.52	2.42	0.74	2.96
FeO	27.94	34.06	33.31	28.71	4.94	21.01	Ti	0.06	0.13	0.01	0.03	0.00	0.00
MgO	12.57	6.68	9.48	12.41	38.05	16.71	Fe ⁺²	4.96	6.36	6.10	5.20	0.80	3.66
MnO	0.42	0.88	0.68	1.05	0.76	0.31	Mg	3.98	2.23	3.10	4.01	11.00	5.19
CaO	0.04	0.14	0.02	0.09	0.13	0.01	Mn	0.08	0.17	0.13	0.19	0.12	0.05
K ₂ O	0.89	1.04	0.02	0.08	0.08	0.02	Ca	0.01	0.03	0.00	0.02	0.03	0.00
Na ₂ O	0.05	0.04	0.01	0.01	0.02	0.01	K	0.24	0.30	0.01	0.02	0.02	0.01
F	0.13	0.00	0.05	0.05	0.00	0.12	Na	0.02	0.02	0.00	0.00	0.01	0.00
Total	88.48	87.72	88.31	87.45	86.82	86.81	Mg#	0.45	0.26	0.34	0.44	0.93	0.59

Note: Mg# = Mg/(Mg+Fe); Bio: Biotite; Chl: Chlorite; Pin: Pinite; alt: altered; Amp: Amphibole; FW: footwall, HW: hangingwall and AP5_44 [P2_Chlorite (HW)] means borehole AP5_ sample No. 44 [analysis point No. in chlorite (from the hangingwall)].

It may be concluded that, notwithstanding the retrograde nature of the chlorite, the system behaved relatively closed during the retrograde stages of its evolution as the chlorite reflects the precursor bulk rock composition. It also indicates the addition of water, without major destruction of sulphide minerals.

4.5. Identification of Peraluminous rocks close to the ore zone using normative calculations

Normative calculations could be used to estimate the proportions of “standard or normative minerals” based on the chemical composition of the rock. The calculations assume that the crystallized assemblages could form from a magma of the same composition as the composition of the rock under ideal equilibrium conditions. An example is the Cross, Iddings, Pirsson and Washington (C.I.P.W.) method which is used here to determine the percentages of normative minerals. It should be noted that this method was developed for igneous rocks, but that the presence and abundance of

normative minerals may provide a holistic method to consider major element behaviour even in non-igneous rock types, given that it is not used to imply an igneous origin.

Normative corundum (Al_2O_3) is one of the diagnostic standard minerals because it gives a direct indication of the peraluminous character of rocks. The Minpet software was used to calculate the normative minerals of each sample based on the chemical composition of the rock as determined by XRF (Table 4.4). Those samples with exceptionally high percentages of normative corundum (≥ 9 wt. %) are listed in Table 4.4. Ten samples from AP5 and one from KN11 have exceptionally high percentages of normative corundum.

The peraluminous ratio ($\text{Al}_2\text{O}_3 / (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$) may also be used to define the peraluminous character of samples in the rock succession. The peraluminous ratio is listed for samples adjacent to the ore zone in boreholes AP5 and KN11 in Table 4.4.

The cumulative frequency versus probability behaviour of the peraluminous ratios in all of the samples (Fig. 4.15) identifies an anomalous sub-population. This principal is utilized in the Prob Plot software (Sinclair, 1976) 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 (Sinclair, 1976). It is suggesting that there are three sub-populations in the peraluminous value data set depicted in Figure 4.15. 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 4.5. Based on the threshold value of the peraluminous ratio for the third sub-population (≥ 4), 19 samples (AP5/21 to AP5/27, AP5/29 to AP5/37, KN11/33 and KN11/38 to KN11/43) were identified as anomalous (Table 4.4).

Table 4.4: Peraluminous ratio, normative corundum value and minerals present in AP5 and KN11

Sample No.	Depth (m)	Per. ¹ Ratio	N.C. ² Value	Minerals present	Sample No.	Depth (m)	Per. ¹ Ratio	Minerals present
AP5/21	270	4	≥9%	Bt,Qtz,Pl(alt),Crd, sil, Grt	KN11/30	195.35	1	Pl, Hbl, Bt, Qtz
AP5/23	278	6	≥9%	Qtz, Bt, Sil, Crd (alt), Grt	KN11/31	196.85	1	Pl, Hbl, Cpx, Bt, Qtz
AP5/24	281	4	<9	Qtz, Bt, Sil, Crd (alt)	KN11/32	198.80	1	Pl, Hbl, Qtz
AP5/22	283	4	<9	Bt, Qtz, Grt, Pl	KN11/33*	205.00	6	Qtz, Crd, Sil, Bt
AP5/25	298	6	≥9%	Qtz, Bt, Sil, Crd, Grt	KN11/34*	206.57	3	Qtz, Crd, opaque min., Grt, Bt
AP5/27	306	4	≥9%	Hbl, Bt, Qtz, Crd	KN11/35*	206.95	1	opaque min., Qtz, Crd (alt.)
AP5/26	312	3	≥9%	Pl, Qtz, Ms	KN11/36*	208.25	1	opaque min., Qtz, Crd (alt.)
AP5/29	317	4	<9	Qtz, Bt, Pl, Crd (alt), Sil	KN11/37*	209.20	1	opaque min., Qtz, Crd (alt.)
AP5/28	318.8	15	14	Qtz, Bt, Crd, Sil, Grt	KN11/38*	210.66	12	Qtz, Crd, Bt
AP5/30	318.9	6	≥9%	Qtz, Bt	KN11/39	212.16	10	Qtz, Crd, Bt, Opx
AP5/31	322.7	6	≥9%	Hbl, Pl (alt), epidote	KN11/40	216.23	7	Qtz, Opx, Bt, Crd
AP5/32	326.8	6	≥9%	Bt, Qtz, Crd (alt)	KN11/41	217.73	8	Qtz, Crd, Sil, Bt
AP5/37	328.4	5	≥9%	Qtz, Bt, Crd (alt), Sil	KN11/42	217.80	7	Qtz, Bt, Hercynite, Crd, Sil
AP5/36	331.3	2	<9	Pl, Qtz, Chl	KN11/43	218.19	7	Qtz, Crd, Sil
AP5/35	334.2	1	<9	Pl, Qtz, Chl, Bt	1. Per.: Peraluminous 2. N.C.: Normative corundum - 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 - AP5/33*, KN11/35*: Samples in the ore zone			
AP5/34	335.7	1	<9	Pl, Hbl, Qtz, Bt				
AP5/33*	337	1	<9	Hbl, Pl, Chl, opaque min				
AP5/40*	338	1	<9	Hbl, Qtz, Pl, Bt, opaque min				
AP5/39*	339	1	<9	Hbl, Kfs, Pl, Qtz, Chl, opaque min				
AP5/41*	341	1	<9	Pl, Hbl, Qtz, opaque min				
AP5/42*	344	2	<9	Pl, Qtz, Bt, Grt, opaque min				
AP5/43*	345	1	<9	Pl, Qtz, Bt, Grt, Hbl, opaque min				
AP5/44	349	2	<9	Hbl, Qtz, Pl				
AP5/45	354.8	2	<9	Pl, Qtz, Bt, Chl, Hbl				
AP5/46	360.1	1	<9	Hbl, Pl, Qtz				

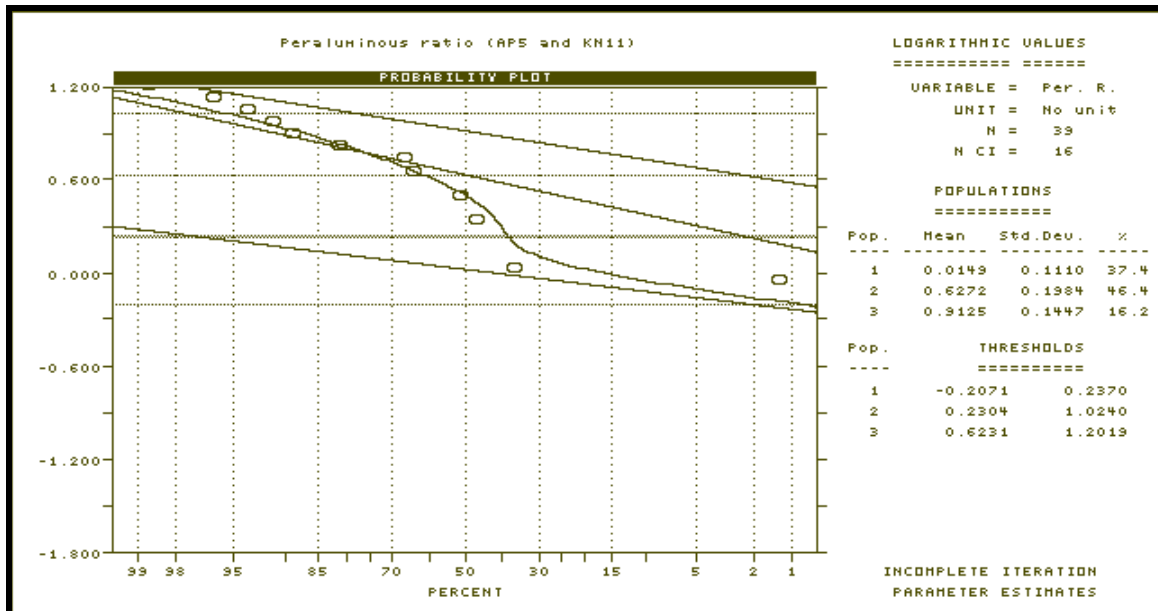


Figure 4.15: The probability plot of peraluminous ratio based on AP5 and KN11 data set

Table 4.5: The number of population, percentage, and threshold value for peraluminous ratio

Variable	No. of popul.	Means (M)	Stan. Dev. (SD)	%	Threshold values
Peraluminous Ratio	1	1	-0.80 1.34	37.4	0.6 1.7
	2	4	-2.68 6.69	46.4	1.7 10.6
	3	8	-5.86 11.41	16.2	4.2 15.9

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

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.

The variation of peraluminous ratio is plotted versus depth near the Areachap ore zone in borehole AP5 in Figure 4.16. As could be expected those samples with high peraluminous ratios (>3, between 270 to 330 meter depth) are situated above the ore zone in this borehole reflecting the inverted sequence. This depth interval may be described as the footwall alteration zone (Krishnakant Singh, et al., 2006). Those samples with low peraluminous values (<2) may be assumed to be located in the original hangingwall of the ore deposit.

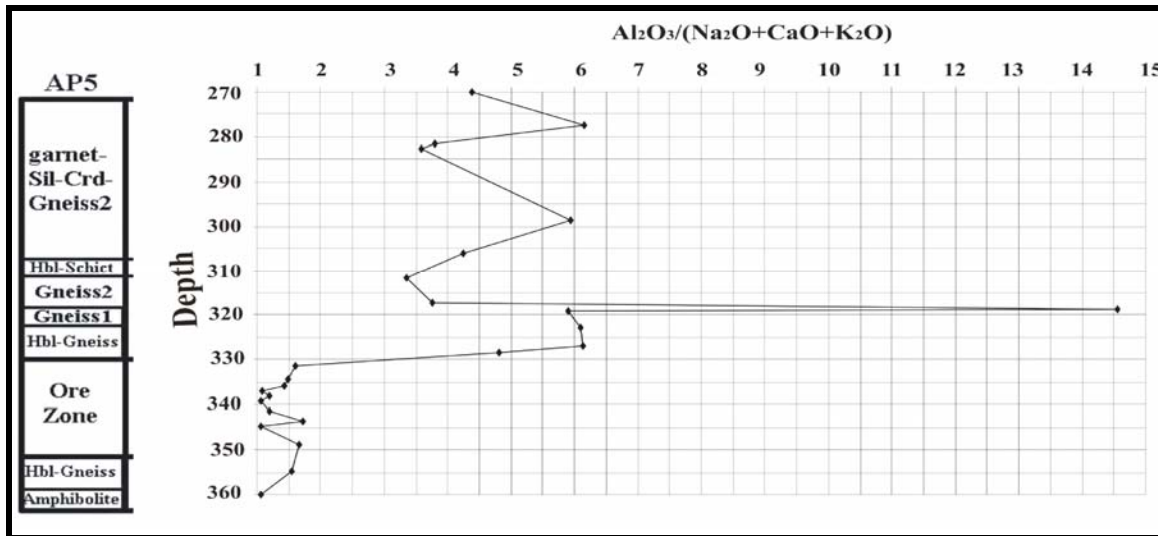


Figure 4.16: The variation of peraluminous ratio near the ore zone in borehole AP5 (Gneiss1: normal quartzo feldspathic gneiss; Gneiss2: peraluminous rocks; Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)

In Figure 4.17, 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.

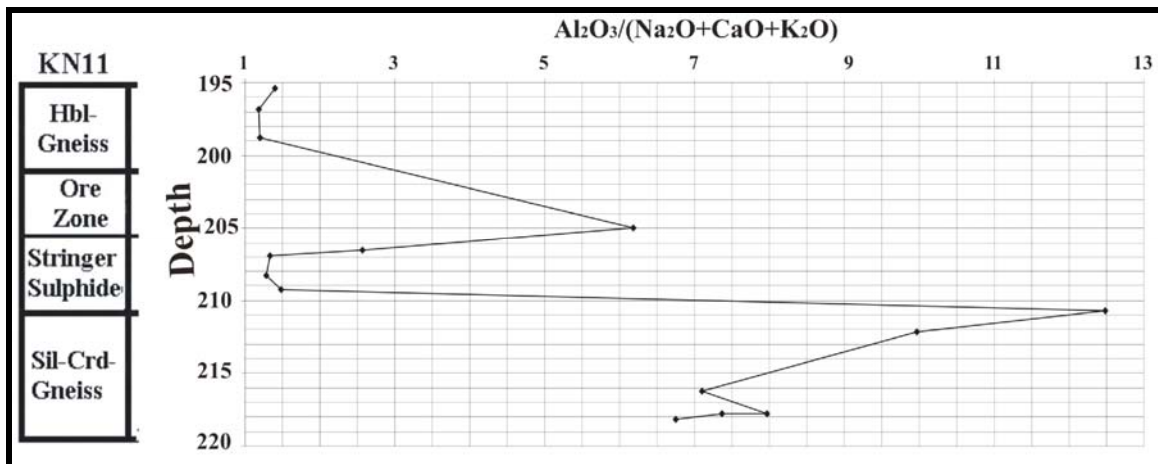


Figure 4.17: The variation of peraluminous ratio near the ore zone in borehole KN11 (Hbl: Hornblende; Crd: cordierite; Sil: sillimanite)

4.6. Quantification of the degree of alteration in the precursor rocks

In this section it would be attempted to quantify the degree of alteration in the precursor system, as seen in variation of the chemical composition of samples collected from the alteration zones identified above by using the isocon method, as proposed by Grant (1986).

Comparison between the rocks in the alteration zone and a similar rock that was not affected by the alteration event (known as a source rock or least altered precursor rock) is used to identify elements that remained in the rock during the alteration process (immobile) and those that were depleted from the rocks (mobile). Further more, these changes could be quantified using the isocon method.

In the isocon method, the percentage of gain and loss is calculated based on the slope of the isocon line. The isocon line is a line, which is extrapolated through the immobile elements and the origin-coordinate. Zr is an example of an element that has been found to behave immobile during hydrothermal alteration (Jenner, 1996). The distribution of this element is also not affected during metamorphism. For this reason Zr will be used here as an immobile element in the explanation given below. But, knowing that Zr could be expected to behave immobile, other elements plotting on or close to the isocon line could now also be identified that behaved relatively immobile during the specific alteration process.

The percentage of variation for each element or delta value is calculated as the residual value above or below the isocon line. The slope of the isocon line is calculated based on the immobile element (Zr) by the following formula:

$$\text{Slope of the isocon line} = (C^A / C^O)_{Zr}$$

C^A : the concentration of immobile element, Zr, in the altered rock, and

C^O : the concentration of immobile element, Zr, in the original or the least altered rock.

The Δ value of an immobile element, Zr, is calculated as follows and would be equal to zero based on the definition of immobile element in the isocon method (Grant, 1986):

$$\Delta (\text{value})_{\text{Zr}} = (C^{\text{A}} - C^{\text{O}})_{\text{Zr}} * (\text{Slope of the isocon line}) = \Delta C_{\text{Zr}} \quad (1)$$

Where ΔC_{Zr} = The change in concentration for an inspected element based on the Zr isocon line.

If there exists a direct relationship between the two samples where the one represents an altered variety of the other or the precursor prior to alteration, one may expect that the other elements that behaved immobile will plot on or close to the isocon line and will therefore display a small delta (Δ) value. As a corollary of this, one may also use this principal in identifying a suitable precursor composition.

The ΔC of each element based on the isocon line through Zr could now be calculated (formula 4 in chapter 3). The percentage of gain and loss is estimated based on formula (5) in chapter 3.

The isocon diagrams comparing the least altered biotite-gneiss, C_o , and altered biotite-gneiss, C_a , in the succession at Areachap is presented in Figure 3.1 and 4.18 to 4.20. The isocon line passed through the origin and immobile elements such as TiO_2 , Al_2O_3 , Zr, U, Th, Nb, Y, La, and Sc. The calculated Δ values for oxides and trace elements for borehole AP5 in the Areachap area are given in Table 4.6. These calculations were based on Zr as an immobile element, where AP5/35 (biotite-gneiss) is selected as the least altered sample. It should be noted that the alteration process affected the protoliths to a variable degree and to illustrate that, Table 4.6 lists both the minimum and maximum concentration changes. Based on these figures and this table, the rocks in the alteration zone are depleted in CaO and Na_2O , but enriched in K_2O , MgO and FeO. P_2O_5 , Cr, Y and Ce usually behave immobile during the weathering (Ohlander et al., 1996), but in the case of hydrothermal alteration Cr and Ce may be enriched or depleted. P_2O_5 and Y behave immobile, enriched or depleted during the alteration. The mineral forming or mineral destruction processes may be a reason for these behaviour, especially the formation of phosphate minerals. The alteration zone is generally enriched in S, Pb and

Ba. Gain and losses of Zn and Cu can be observed in different samples. This most probably reflect formation of sulphides in fractures and the leaching of these elements during the destruction of the primary rock forming minerals by the hydrothermal fluids.

Figure 4.21 shows an isocon diagram comparing an alternative original rock namely sample AP5/42 and altered sample AP5/25, both biotite-gneisses, in the Areachap succession. The calculated Δ values based on the Zr isocon line is given in Table 4.7. This confirms CaO and Na₂O depletion and K₂O and MgO enrichment in the alteration zone. In addition, Cr and Y are relatively enriched and P₂O₅ and Ce are depleted. In this sample Cu, Zn, Pb and S are depleted whereas Ba is enriched.

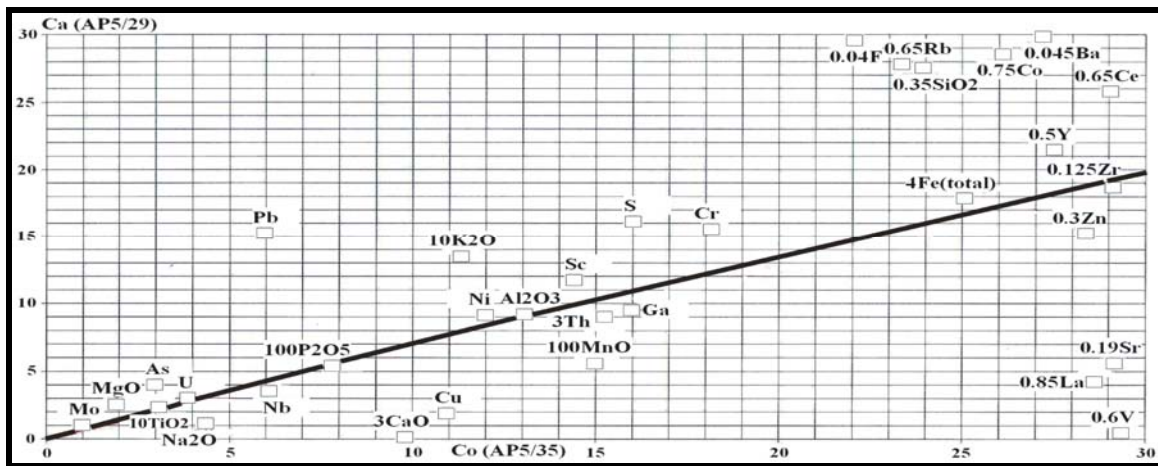


Figure 4.18: An isocon diagram of samples AP5/35, the least altered biotite-gneiss, and AP5/29, altered biotite-gneiss, from borehole AP5 in the Areachap area.

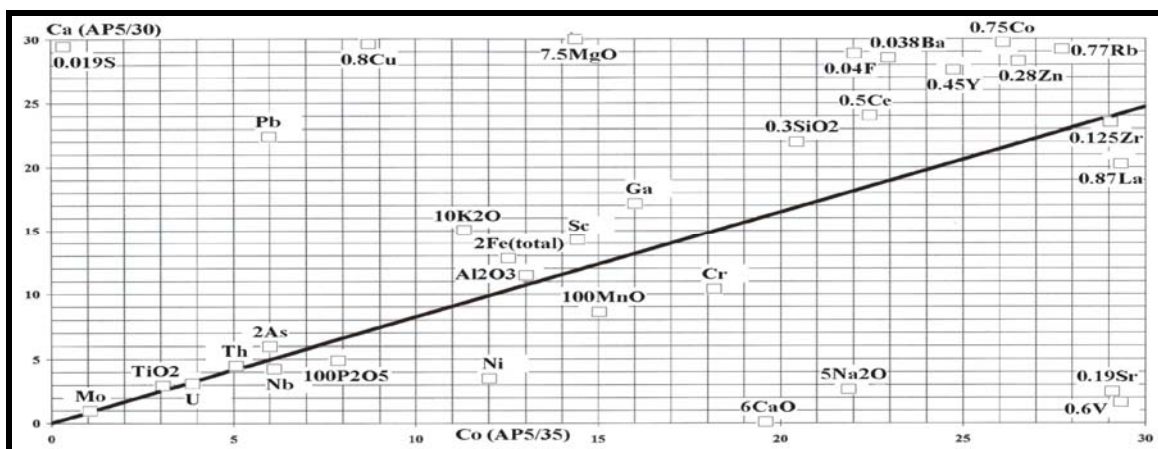


Figure 4.19: An isocon diagram of samples AP5/35, the least altered biotite-gneiss, and AP5/30, altered biotite-gneiss, from borehole AP5 in the Areachap area.

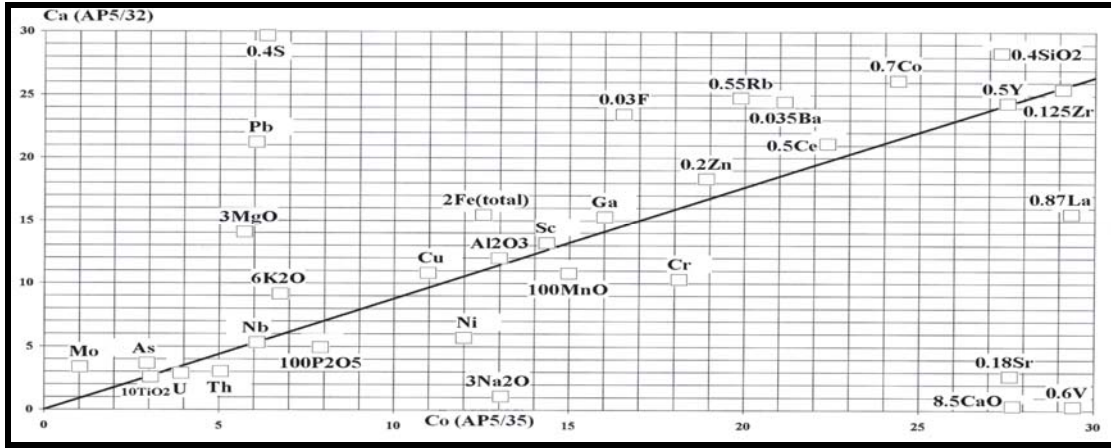


Figure 4.20: An isocon diagram for samples AP5/35 (the least altered biotite-gneiss) and AP5/32 (altered biotite-gneiss) from drill hole AP5 in the Areachap area.

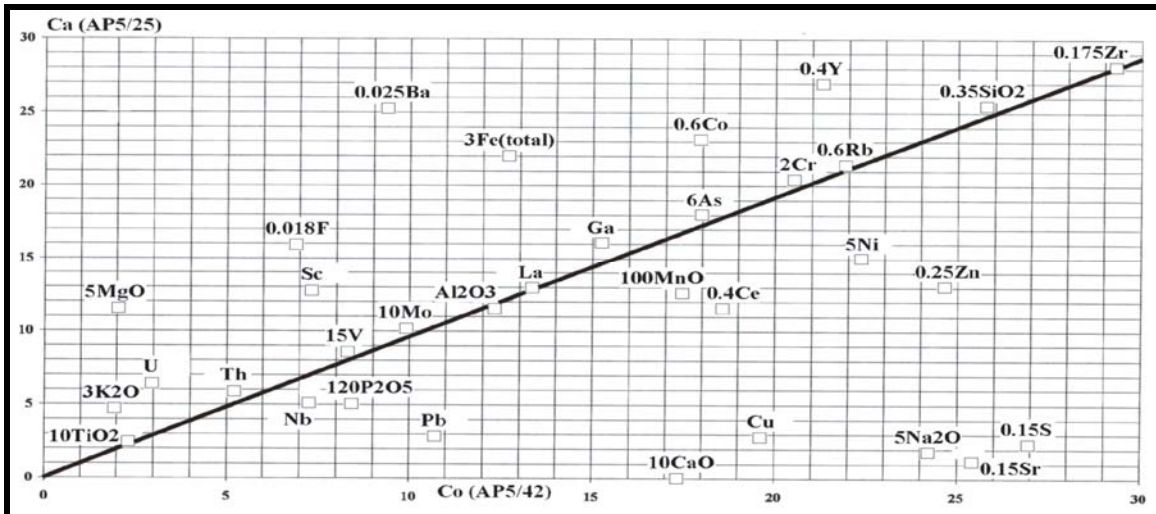


Figure 4.21: An isocon diagram for the least altered sample AP5/42 and altered sample AP5/25, altered biotite-gneiss, from borehole AP5 in the Areachap area.

Table 4.6: Percentage of gains and losses in borehole AP5 and Δ values for the Areachap samples. Sample AP5/35 is assumed to be the unaltered precursor for altered samples AP5/23, 29, 30, and 32 (Isocon line based on Zr).

Element	Min Δ Value	Max Δ Value	Composition AP5/35	% Gain or Loss	Gain/Loss
CaO	-2.82	-2.03	3.26	-62 to -87	Loss
Na ₂ O	-3.45	-1.78	4.36	-41 to -79	Loss
K ₂ O	0.56	0.61	1.13	50 to 54	Gain
MgO	1.42	3.03	1.92	74 to 158	Gain
FeO	0.44	8.28	6.28	7 to 132.2	Gain
SiO ₂	10.15	33.98	68.26	15 to 50	Gain
Al ₂ O ₃	-0.06	1.12	13.05	-0.5 to 9	Gain & Loss
TiO ₂	-0.03	0.04	0.31	-10 to 13	Gain & Loss
MnO	-0.05	-0.02	0.15	-13 to -33	Loss
P ₂ O ₅	-0.03	0.00	0.08	-38 to 0	Loss
Ga	-0.82	5.19	16	-5 to 32	Gain & Loss
Rb	0.69	19.59	36	2 to 54	Gain
Sr	-119.80	-69.13	153	-45 to -78	Loss
As	0.48	2.05	3	16 to 68	Gain
Ba	177.47	966.44	604	29 to 160	Gain
Cu	-5.06	128.28	11	-46 to 1173	Gain & Loss
Pb	-2.04	17.54	6	-34 to 292	Gain & Loss
S	5.67	27633.37	16	35 to 172709	Gain
Zn	-41.21	24.55	95	-44 to 26	Gain & Loss
Ce	-12.09	11.75	45	-27 to 26	Gain & Loss
Cr	-5.57	3.85	18	-31 to 21	Gain & Loss
Co	7.20	20.57	35	21 to 59	Gain
Ni	-7.08	1.19	12	-59 to 10	Gain & Loss
Sc	0.46	2.51	14	3 to 17	Gain
F	272.25	1152.13	551	49 to 209	Gain
Nb	-0.70	0.02	6	-11 to 1	Gain & Loss
La	-14.39	-3.98	34	-43 to -12	Loss
Th	-1.44	0.45	5	-28 to 9	Gain & Loss
V	-42.17	-31.08	49	-86 to -63	Loss
U	-0.38	0.50	4	-10 to 13	Gain & Loss
Y	0.78	16.93	55	1 to 31	Gain

The isocon diagram comparing the least altered biotite-gneiss, C_o, and altered biotite-gneiss, C_a, from the assumed alteration zone identified in borehole KN11, in the Kantienpan area, is shown in Figure 4.22. The calculated Δ values are given in Table 4.8. The least altered sample identified as precursor is sample KN11/44. CaO, Na₂O and K₂O are depleted, and MgO enriched in the alteration zone. Cr and Y are relatively enriched

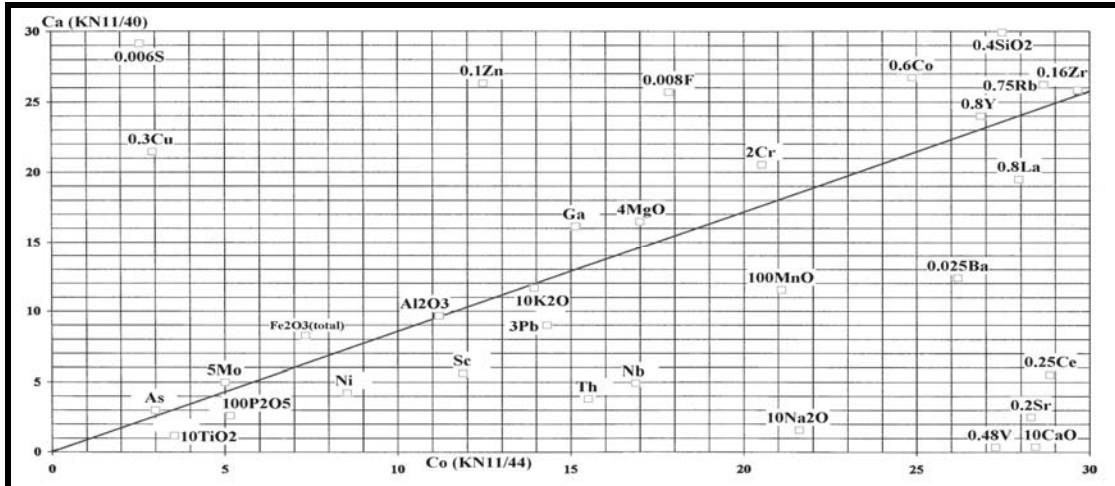


Figure 4.22: An isocon diagram for samples KN11/44 (the least altered biotite-gneiss) and KN11/40 (altered biotite-gneiss) from drill hole KN11 in the Kantienpan area.

and P₂O₅ and Ce are depleted during the alteration. Cu, Zn, and S are enriched, but Pb and Ba are depleted from the altered rocks.

Table 4.7: Percentage of gains and losses in borehole AP5 and Δ values for the Areachap sample. Sample AP5/42 is assumed to be the unaltered precursor for altered sample AP5/25 (Isocon line based on Zr).

Element	Δ Value	Composition AP5/42	% Gain or Loss	Gain/Loss
CaO	-1.65	1.73	-95	Loss
Na ₂ O	-4.26	4.83	-88	Loss
K ₂ O	0.95	0.64	148	Gain
MgO	1.94	0.41	473	Gain
FeO	3.25	4.23	78	Gain
SiO ₂	1.65	73.83	2.2	Gain
Al ₂ O ₃	-0.21	12.32	2	Gain
TiO ₂	0.03	0.23	13	Gain
MnO	-0.04	0.17	-24	Loss
P ₂ O ₅	-0.03	0.07	-43	Loss
Ga	1.57	15	10	Gain
Rb	0.47	37	1.3	Gain
Sr	-155.04	169	-92	Loss
As	0.12	3	4	Gain
Ba	647.35	376	172	Gain
Cu	-15.90	20	-81	Loss
Pb	-7.31	11	-68	Loss
S	-156.98	180	-87	Loss
Zn	-42.28	99	-43	Loss
Ce	-15.10	46	-33	Loss
Cr	0.40	10	3.9	Gain
Co	10.16	30	34	Gain
Ni	-1.30	5	-29	Loss
Sc	5.71	7	78	Gain
F	517.90	384	135	Gain
Nb	-1.86	7	-26	Loss
La	0.17	13	1	Gain
Th	0.99	5	19	Gain
V	0.02	~1	4	Gain
U	3.53	3	118	Gain
Y	16.43	53	31	Gain

Table 4.8: Percentages of gains and losses in borehole KN11 and Δ values for the Kantienpan samples. Sample KN11/44 is considered to be the unaltered precursor for altered sample KN11/40 (Isocon line based on Zr).

Element	Δ Value	Composition KN11/44	% Gain or Loss	Gain/Loss
CaO	-2.43	2.84	-85.6	Loss
Na ₂ O	-1.72	2.16	-79.6	Loss
K ₂ O	-0.05	1.39	-3.6	Loss
MgO	0.41	4.25	9.6	Gain
FeO	1.87	7.34	25.5	Gain
SiO ₂	15.47	68.55	22.6	Gain
Al ₂ O ₃	-0.07	11.19	-1	Loss
TiO ₂	-0.19	0.36	-53	Loss
MnO	-0.07	0.21	-33	Loss
P ₂ O ₅	-0.02	0.05	-40	Loss
Ga	2.99	15	20	Gain
Rb	1.71	38	5	Gain
Sr	-110.60	142	-78.1	Loss
As	0.39	3	13	Gain
Ba	-417.36	1048	-40	Loss
Cu	62.95	10	648	Gain
Pb	-1.15	5	-24	Loss
S	447.60	430	104	Gain
Zn	154.86	125	124	Gain
Ce	-78.24	116	-68	Loss
Cr	1.33	10	13	Gain
Co	8.52	42	21	Gain
Ni	-3.20	9	-38	Loss
Sc	-4.87	12	-41	Loss
F	1270.73	2228	57	Gain
Nb	-9.90	17	-59	Loss
La	-6.01	35	-17	Loss
Th	-10.02	16	-65	Loss
V	-48.67	57	-86	Loss
U	0.39	3	13	Gain
Y	0.79	34	2	Gain

It is possible to identify alteration zones in the original footwall lithologies of the massive sulphide ore bodies at Kantienpan and Areachap as Theart (1985) has done for the Prieska Cu-Zn deposit. The rocks least affected by the alteration process may be identified by utilization of major element comparison diagrams and iterative isocon calculations. These potential precursor rocks are used in identifying and quantifying the geochemical changes caused by the hydrothermal process related to the ore formation. In

general the alteration zones at Areachap and Kantienpan are enriched in Mg, Fe, S, Zn, Si, Co and F and depleted in Na, Ca, Sr, Ni, V and La. Ba is enriched in the footwall alteration zone at the Areachap and at the Prieska Cu-Zn deposits (Theart, 1989), but depleted at the Kantienpan deposit. Elements that behaved relatively immobile include Zr, Ti, P, Mn, Al, Y, and U. A notable feature is the enrichment in F at both of these deposits, but note that the F and S interpretations are based on semi-quantitative analyses. Theart (1989) reported a relatively enrichment of Mg, K, V, Sc, Ni, Ba, Cu and Zn and depletion of Si, Ca, Na and Sr in the alteration zone of the Prieska Cu-Zn deposit.

The Δ values may also be used as an indication of proximity to the ore zone.

Unfortunately the samples collected from these deposits for the current investigation are not suitable for demonstrating this aspect. Proximity indicators in theory should be useful in the footwall and hangingwall lithologies as well as for lithologies on strike of the deposit.

4.7. Development of alteration box plot for high-grade metamorphic rocks

In order to understand the collective mineral processes responsible for the whole rock composition, Large et al. (2001) proposed a box plot that attempts to illustrate the various mineral processes that affects the composition of rocks subjected to common geological processes and discriminate them from those related to hydrothermal alteration. Large et al. (2001) concentrated on the primary reactions and minerals that form at the time of ore formation. The challenge addressed here is to identify the high-grade metamorphic minerals, formed during isochemical metamorphism, that now represent the original mineral processes and to determine if retrograde minerals such as chlorite would preserve these features.

The successful identification of characteristic lithogeochemical characteristics and metamorphic mineral assemblages that could be related to primary ore forming processes could lead to the discovery of new ore bodies. Lithogeochemical investigations are usually based on chemical analyses and this data have limited meaning on its own (Large

et al., 2001). In the box plot the typical mineralogical reaction trends are shown by plotting AI against the CCPI (Large et al., 2001).

4.7.1. The location of rock forming minerals in the box plot

The location of the rock forming minerals in the box plot may help to demonstrate the dominant mineral processes. Mineral compositions determined by microprobe are used for this purpose. The AI and CCPI calculated for each mineral composition are plotted in the box plot.

Figures 4.23 and 4.24 show the positions based in mineral compositions determined by some of the samples from boreholes AP2, AP5, KN11 and KN12. The location of albite, calcite-epidote, chlorite, biotite, k-feldspar were determined in the box plot by Large et al. (2001). In order to use the box plot for the present study area, the high-grade metamorphic minerals (hornblende, clinopyroxene, gahnite, cordierite, orthopyroxene, garnet), and retrograde minerals (chlorite, pinite and muscovite) have to be also plotted in this diagram. The top of the box plot is characterized by the chlorite carbonate trend defined by Large et al. (2001) for unmetamorphosed sequences. Under the metamorphic conditions reflected in the rocks of the study area, the minerals with a high CCP index (trend 2 in Fig. 4.23) display the following alteration sequences:

- a) Augite to enstatite and clinoenstatite.
- b) Hornblende to gedrite.
- c) Grossular-rich garnet to almandine/pyrope-rich garnet.
- d) Fe rich cordierite to Mg rich cordierite.

The minerals showing a high alteration index defining the right side of the box plot shows the following sequence related to the primary alteration process (trend 1 in Fig. 4.24):

- a) Biotite (annite) to phlogopite.

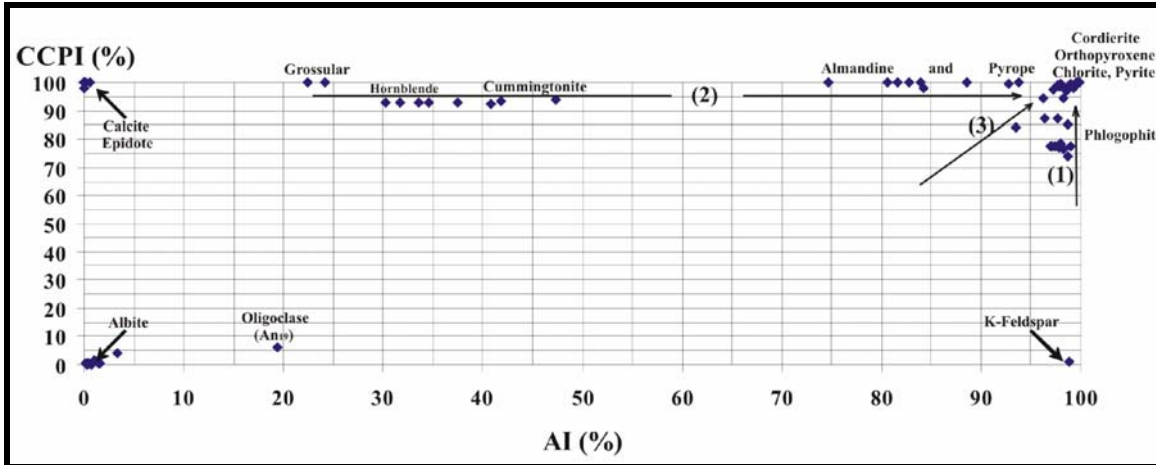


Figure 4.23: Box Plot of mineral compositions from Areachap (AP5 and AP2).

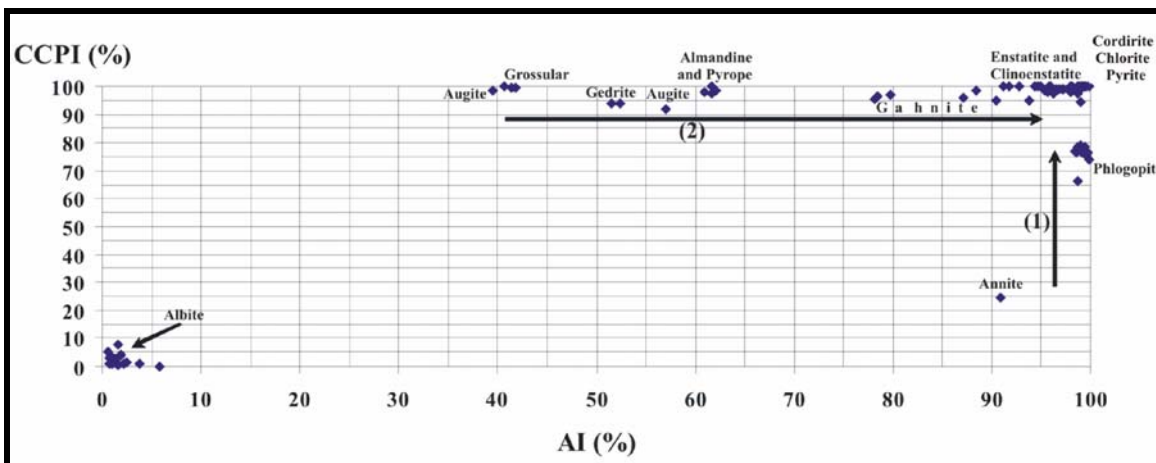


Figure 4.24: Box Plot of mineral compositions from Kantienpan (KN11 and KN12).

Cordierite, pinite and chlorite analysed in these rocks are located in the same place at the right-top corner of the box plot. Orthopyroxene plots very close to these minerals. Two groups of garnets are present in these rocks, grossular with low AI value (Ca-rich and low in Mg), which plots to the left, and the almandine and pyrope with high AI values (low in Ca and Mg-rich), plotting to the right (Fig. 4.23 and 4.24). Amphiboles of this trend include, hornblende with lower AI values (high Ca content), and cummingtonite and gedrite with higher AI values (high Mg contents).

4.7.2. Whole rock analysis and box plot

The Kantienpan deposit consists of stratiform Zn-Cu bearing massive sulphide lenses hosted by quartzo feldspathic gneiss, biotite-gneiss, hornblende-gneiss and biotite-hornblende-gneiss (Rossouw, 2003). The AI and CCPI values were calculated based on the whole rock XRF analyses, of samples from two boreholes KN11 and KN12. The lithochemical data are plotted in Figure 4.25. The data can be grouped into two major fields in the diagram, which are related to the alteration zones (shown in Fig. 3.2):

Field 1: The least altered rocks fall within a area bounded by an AI= 15 to 65% and a CCPI= 15 to 85%,

Field 2: All the samples identified by means of other lithochemical considerations (such as by the presence of normative corundum), as having been affected by hydrothermal alteration, plot in a field bounded by AI values that exceed 67, and CCPI values greater than 60.

The samples of rocks that were originally affected by diagenetic alteration display AI values of less than 57% and plots below the epidote-K feldspar join.

Samples from KN11 are used to demonstrate the variation of AI and CCPI in the lithological successions adjacent to the sulphide mineralisation at Kantienpan (Fig. 4.26). The figure shows that the highest values of the AI and CCPI (CCPI>90 and AI>90) correspond to the previously identified altered footwall near the ore zone.

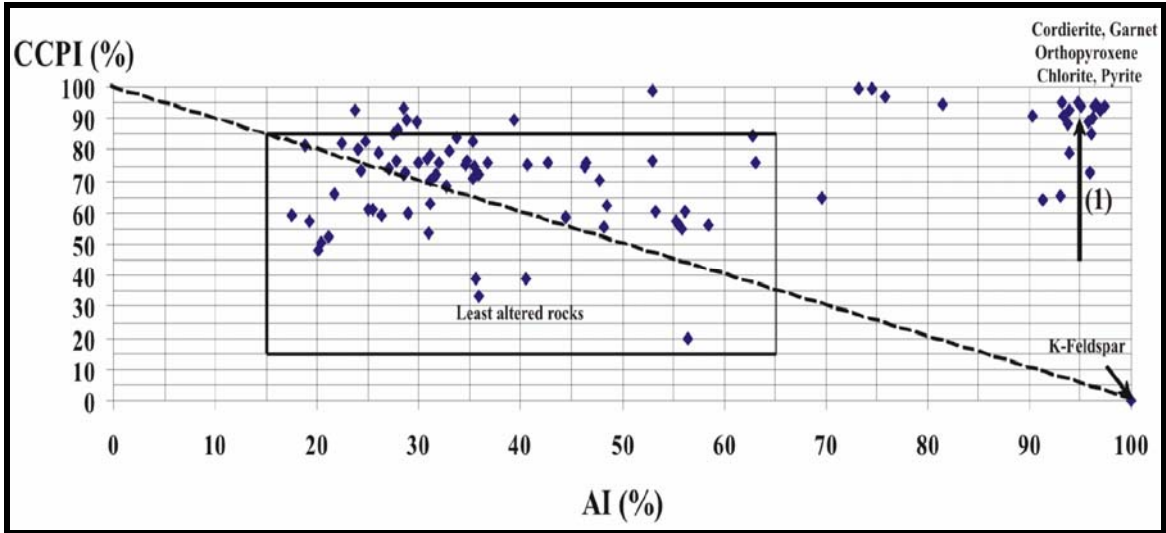


Figure 4.25: Box Plot of whole rock samples from Kantienpan (KN11, KN12 and surface outcrop).

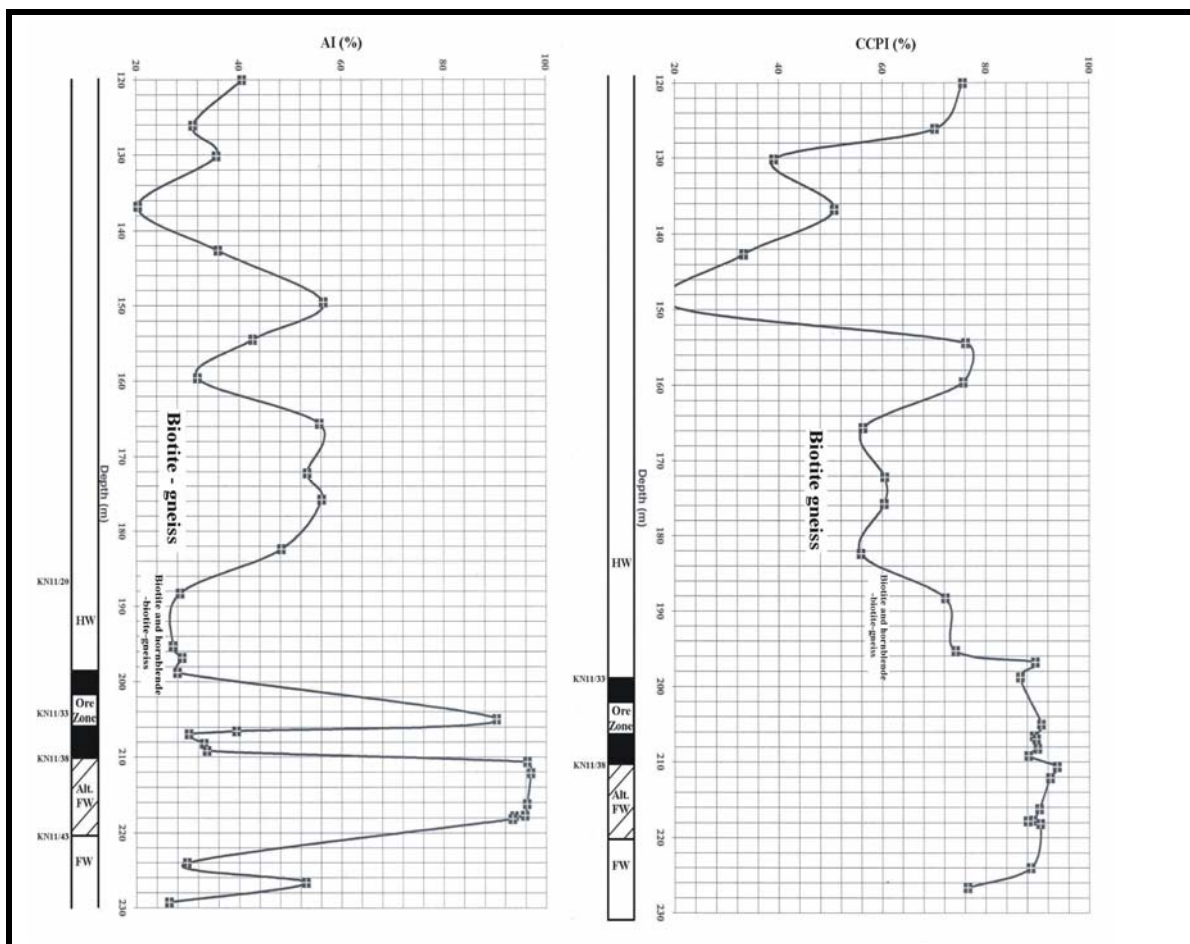


Figure 4.26: The variation of AI and CCPI values in samples from Kantienpan (KN11). Massive sulphide zone indicated in black and alteration zone hatched.

The ore body at the defunct Areachap Cu-Zn mine consists of discontinuous massive sulphide lenses. Locally, two layers of massive sulphide are intersected, separated by disseminated sulphides. Elsewhere only one massive and one disseminated layer were described (Vote and King, 1986). The total thickness of the mineralized zone ranges from 0.1 to 24.2 m.

The AI and CCPI calculated for the whole rock XRF analyses of samples from boreholes AP2 and AP5 and plotted in a box plot presented as Figure 4.27.

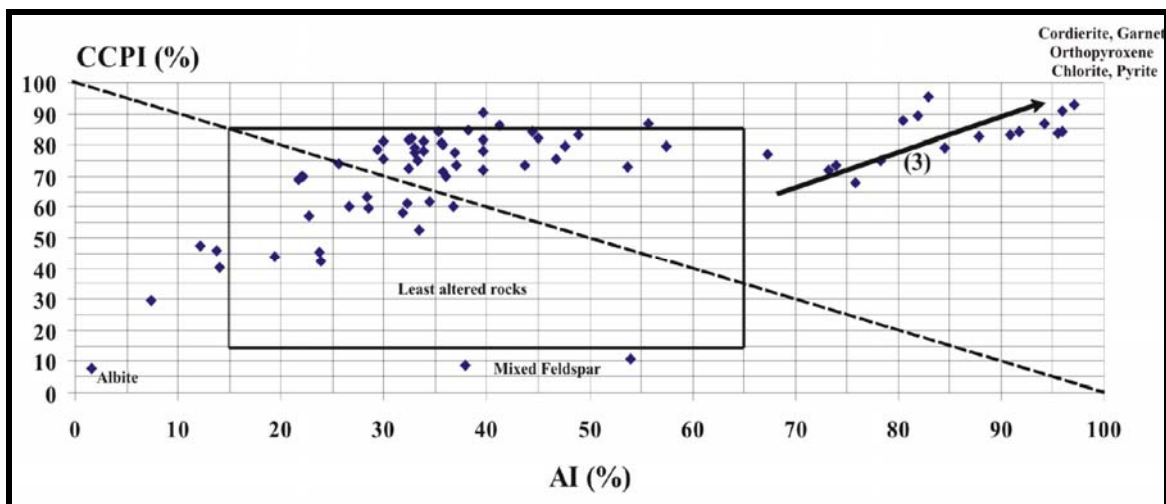


Figure 4.27: Box Plot of whole rock samples from Areachap (AP2 and AP5).

The data can be ascribed to three major fields in the diagram, which are related to the alteration zones described above (and in Figure 3.2 and 3.3), namely:

Field 1: The least altered rocks fall within the area bounded by an AI=15 to 65% and a CCPI= 15 to 85%,

Field 2: Samples assumed to have been affected by hydrothermal alteration have AI values in excess of 70 and the CCPI values greater than 70 (trend 3).

Field 3: Samples plotting outside the least altered field of Large et al. (2001). It is interesting to note that these samples are from rocks that could have had chemical sedimentary precursors, enriched in quartz, carbonate and sulphate minerals

(calcite, dolomite, barite and anhydrite) directly related to the sulphide ore zone, but since they are not believed to have formed during the primary alteration process itself, they will not be further considered here.

In order to demonstrate the variation of AI and CCPI in the lithological successions hosting sulphide mineralisation at Areachap, the variation with depth in borehole AP5 is demonstrated in Figure 4.28. This borehole intersects the footwall, ore zone and hangingwall successions. The figure shows that the highest values of AI and CCPI (AI>70 and CCPI>75) correspond to the previously identified footwall alteration zone.

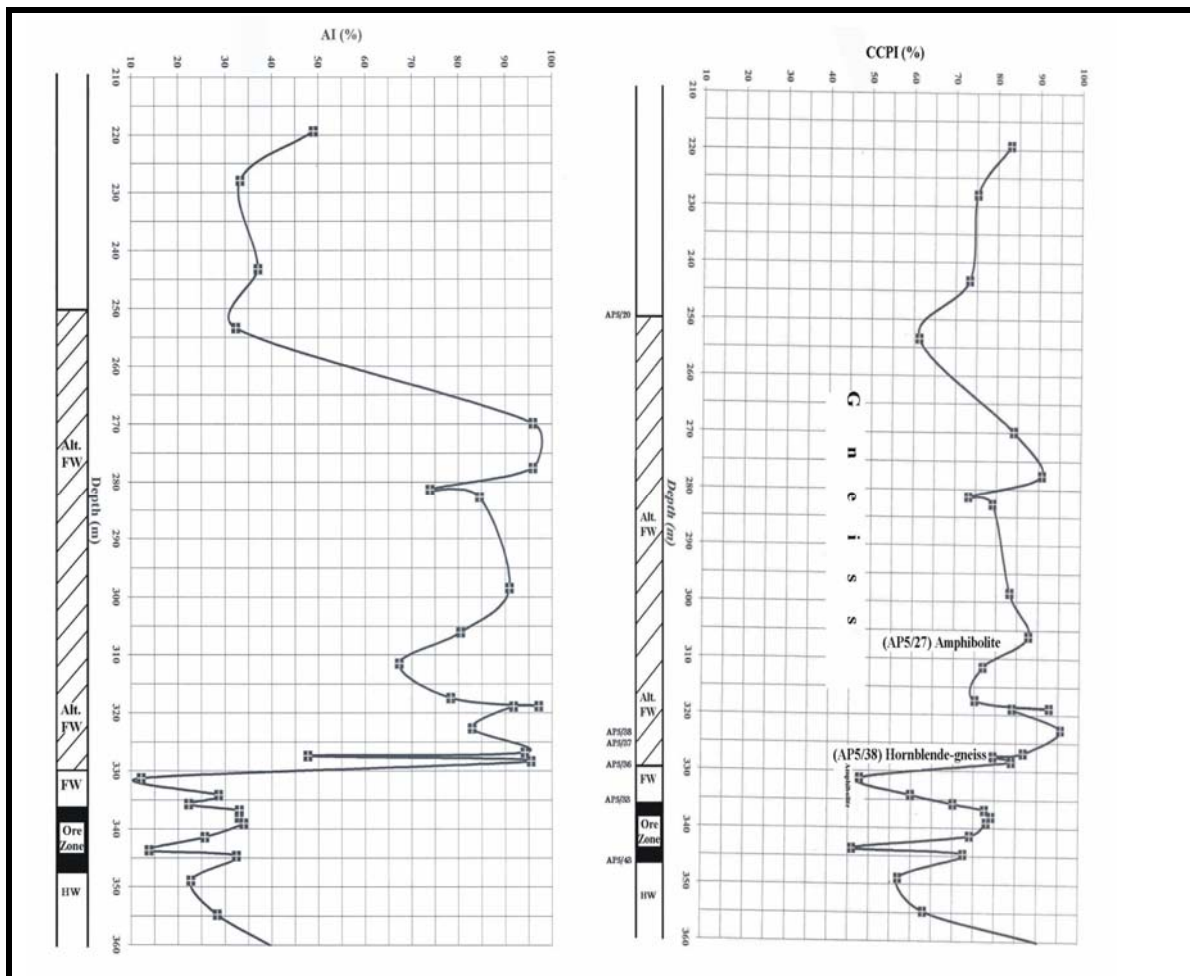


Figure 4.28: Inverted sequence seen in drill hole AP5 (Areachap) showing the variation in the AI and CCPI values. Massive sulphide zone indicated in black and alteration zone hatched.

4.7.3. Combination of isocon results and the box plot

As the source rock composition of the altered samples in the alteration zones has been independently determined using the isocon method, it can now be compared with the results of the box plot. For this purpose, the positions of the least altered and altered samples are highlighted in the box plot.

The results of isocon analyses are summarized in Table 4.9. The locations of source rock (KN11/44 and KN11/28) and altered products (KN11/40, 39 and 33) at Kantienpan are marked in the box plot (Fig. 4.29). In Figure 4.30 the source rock (AP5/35 and AP5/42) and altered products (AP5/23, 25, 29, 30 and 32) at Areachap are shown. Based on these two figures, it may be concluded that the results of the two methods confirm one another.

Table 4.9: The least altered and altered samples based on the isocon Analysis.

Borehole NO	Source rock (least altered)	Altered Equivalent for source rock ⁽¹⁾
AP5	AP5/35	AP5/29, 30, 32 [and 23]
AP5	AP5/42	AP5/25
KN11	KN11/44	KN11/40 [and 39]
KN11	[KN11/28 and 46]	[KN11/33]

(1): From footwall of the ore body

[]: Might be source rock or altered equivalent

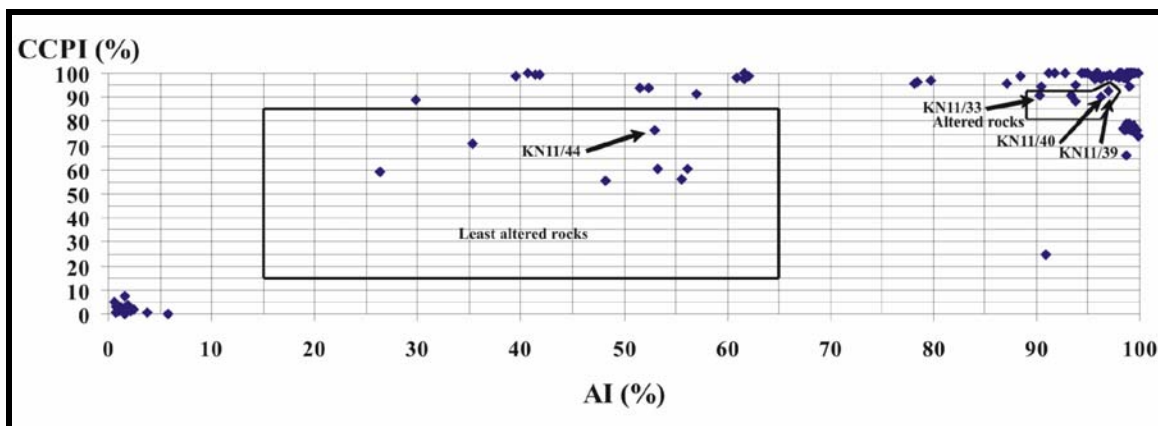


Figure 4.29: Box plot with isocon and microprobe results (Kantienpan area, KN1).

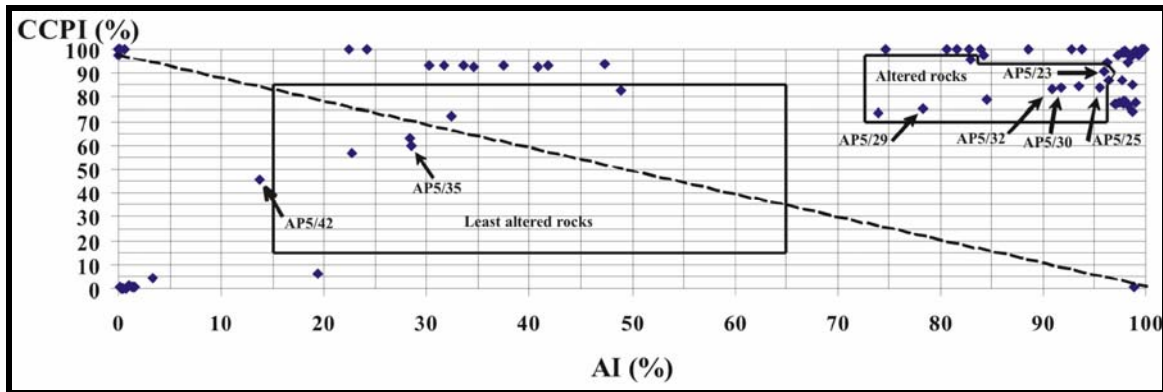


Figure 4.30: Box plot with the isocon and microprobe results (Areachap area, AP5).

Based on Figure 4.30, the least altered sample AP5/42 were more affected by the diagenetic alteration than sample AP5/35, which is close to the diametric line that is separating the hydrothermal alteration from diagenetic alteration.

Original complexities in the alteration zones are further shown by the variation in composition evident from the scatter of points in the box plot.

The value of the box plot lies in the fact that the composition of samples collected during regional lithogeochemical surveys of comparable rock types may be plotted to identify potential alteration zones.

4.8. Refinement of chemical structure in the upper right corner of the box plot

An alternative way to distinguish the mineralogical changes is to use the molar ratio or Pearce Element Ratio analysis (PER), based on the molecular proportion of major elements over the molecular proportion of an immobile element. A linear combination of major elements could remove the effect of some minerals and add the effects of others. These minerals might occur only in altered rocks where the new minerals formed as result of the alteration process. The method was introduced by Whitbread and Moore (2004).

In this research, the PER analysis is used to find out if it is possible to separate the mixed minerals at the upper right corner of the box plot (Fig. 4.23 and 4.24) and clarify this diagram. For this purpose, different molar ratios are calculated and the best ratio, which gives a better mineral separation, namely the molecular proportion ratio of Fe / Al versus Mn / Al, is plotted (Fig. 4.31 and 4.32).

Figure 4.31 is a log scale PER plot of the Kantienpan samples from KN11 and KN12. The figure shows that the Mn content of gahnite, cordierite and garnet in the ore zone is higher than in the footwall alteration zone. The Mn and Fe content of pyroxenes near the alteration pipe and ore zone is lower than those in pyroxenes that are further away from these zones. This trend was not observed in retrograde chlorite and chamosite an observation that may be ascribed to the redistribution and oxidation of Fe and Mn.

Similarly, Figure 4.32 is a log scale PER plot of the Areachap samples from boreholes AP2 and AP5. The Mn content of cordierite increases from the altered footwall towards the ore zone. The Mn content of garnets is higher in the ore zone than in the footwall alteration zone. Again, this trend was not observed in retrograde chlorite and chamosite.

This application of the PER analysis has clearly succeeded in resolving the upper right corner of the box plot and provided an added method that could be used as a proximity indicator for the identification of massive sulphide mineralization.

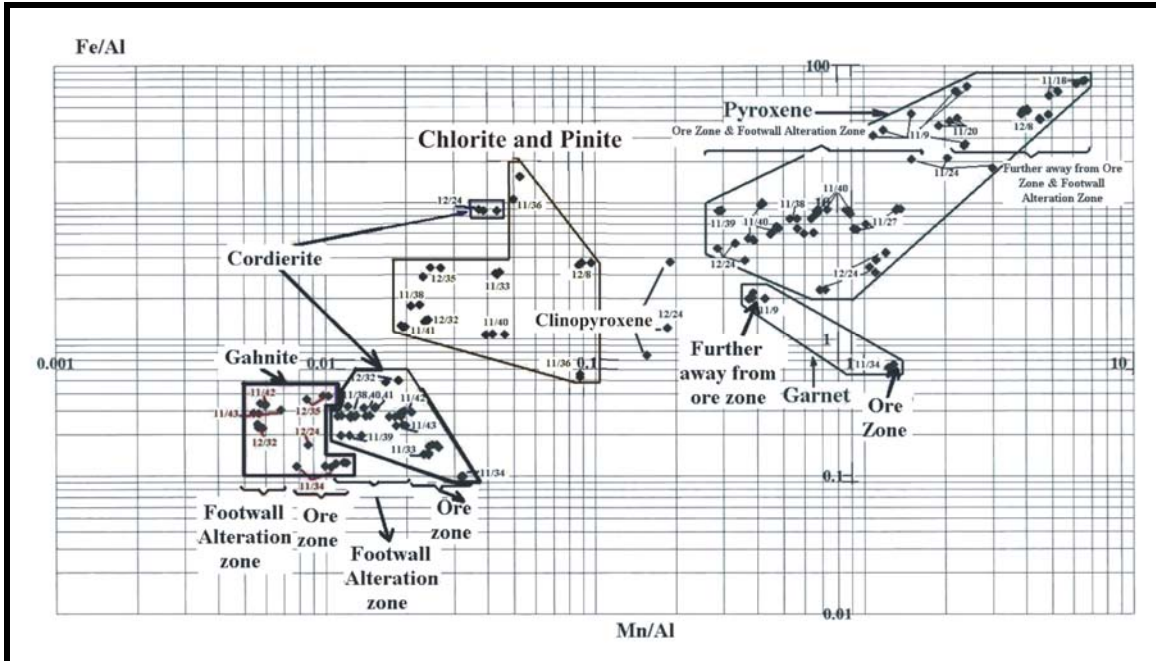


Figure 4.31: PER analysis for samples from drill holes KN11 and KN12, Kantiapan area. The Mn content of gahnite, cordierite and garnet from the ore zone is higher than in the identified footwall alteration zone. Pyroxene has lower Mn and Fe contents in the ore zone and altered footwall (11/43: borehole KN11/ sample number).

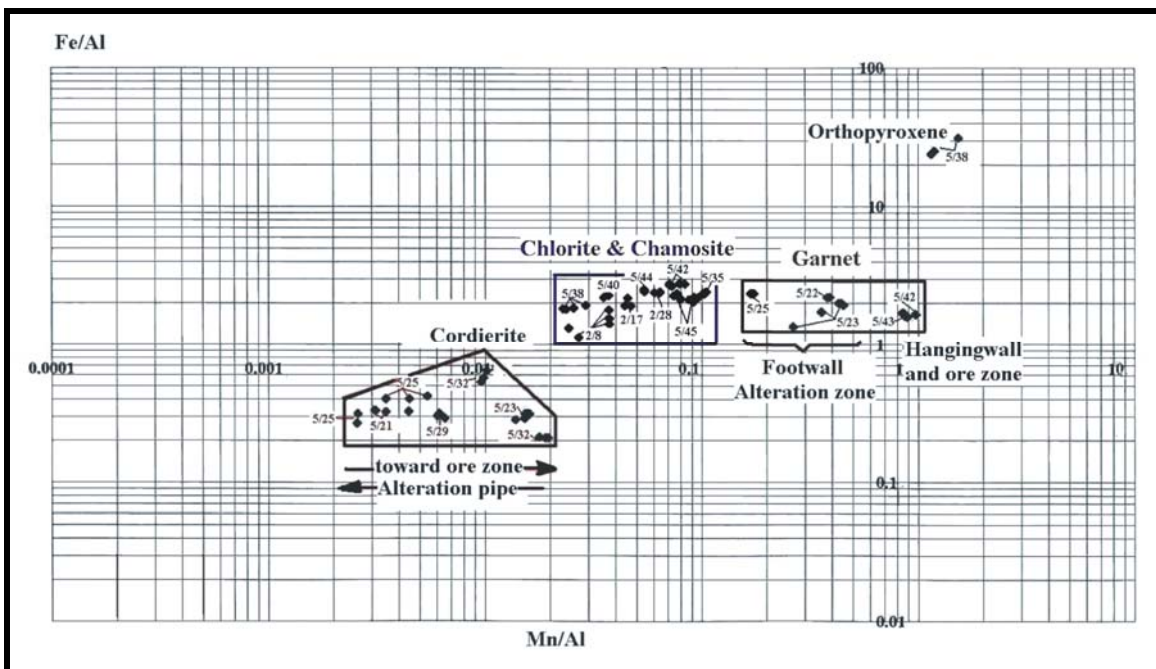


Figure 4.32: PER analysis of boreholes AP2 and AP5 in the Areachap area. The Mn content of Cordierite increases from the altered FW toward ore zone. The Mn content of garnets is higher in ore zone than in footwall alteration zone. No trend is evident in the composition of chlorite and chamosite (5/27: borehole AP5/ sample number).