

CHAPTER SIX: WHOLE-ROCK CHEMISTRY

6.1 Introduction

Thirty-two samples of gabbro/orthopyroxene, gabbro, hornfels and calcsilicate were analysed for whole rock major elements and lithophile trace elements using an ARL 9400XP+ wavelength dispersive XRF Spectrometer at the University of Pretoria. Twenty-seven of the samples were additionally analysed for platinum-group elements (PGE) by instrumental neutron activation analysis (INAA) at the University of Quebec at Chicoutimi, Canada. Analytical details are given in Appendix I and the analyses are tabulated in Appendix V.

6.2 Major Element Chemistry

Compositional ranges of major element oxides in the different Platreef layers are given in Table 6.1. The data are displayed as bivariate plots with MgO as the differentiation index in Fig. 6.1. Compositions of plagioclase, orthopyroxene, olivine and clinopyroxene determined by electron microprobe and B1 and B3 Bushveld parental magmas (Curl, 2001) were also plotted. This was done to determine whether the Platreef rocks are mixtures of the cumulus minerals and Bushveld trapped melt or whether there is an additional component present, possibly derived from the floor rocks.

When compared to the Merensky Reef in the Western Bushveld Complex (Barnes and Maier, 2002) it is clear that the Platreef on average has lower SiO_2 , Al_2O_3 and Na_2O (with the

exception of the Lower Platreef) but markedly higher CaO and K₂O contents (Table 6.1). This pattern cannot be explained by variation in plagioclase or orthopyroxene content, but instead indicates addition of external CaO and K₂O to the Platreef magma or rocks.

| wt. % | Lower Platreef | Middle Platreef | Upper Platreef | Pegmatoidal feldspathic pyroxenite of the Upper Platreef | Merensky Reef |
|--------------------------------|----------------|-----------------|----------------|--|---------------|
| SiO ₂ | 47.4-49.92 | 39.11-49.58 | 42.82-51.38 | 41.64-46.68 | 51.09 |
| MgO | 13.76-16.64 | 19.06-26.18 | 18.32-20.91 | 16.32-21.4 | 18.89 |
| Fe ₂ O ₃ | 10.07-13.82 | 8.25-21.53 | 10.73-14.41 | 13.18-18.99 | 9.15 |
| Al ₂ O ₃ | 8.35-13.87 | 4.28-9.64 | 6.52-7.29 | 6.51-16.77 | 10.60 |
| CaO | 6.04-12.21 | 4.17-13.24 | 6.34-13.1 | 3.21-4.57 | 6.20 |
| Na ₂ O | 0.01-1.04 | 0.01 | 0.01-0.13 | 0.01-0.52 | 0.75 |
| K ₂ O | 0.31-0.76 | 0.12-0.44 | 0.26-0.46 | 0.34-0.48 | 0.20 |
| Cr ₂ O ₃ | 0.09-0.32 | 0.01-0.2 | 0.04-0.39 | 0.06-0.29 | 1.08 |

Table 6.1: Ranges of whole rock compositions for Platreef rocks compared to those from the Merensky Reef (Barnes and Maier, 2002)

The concentrations of the other major elements are broadly comparable in the Platreef and the Merensky Reef. Amongst the three Platreef layers, the Lower Platreef has the lowest MgO and Fe₂O₃ contents, but the highest Al₂O₃ contents. The Lower Platreef has higher contents of modal plagioclase than the other two Platreef layers, possibly explaining the high Al₂O₃ contents.

It is notable that there is little correlation between MgO and Fe₂O₃ (Fig. 6.1a), (and MnO, not shown in figure 6.1) similar to that observed in the mafic-ultramafic rocks of the UCZ (Maier and Eales, 1997). It is possible that this is partly due to the presence of sulphides and/or Fe-oxides. This interpretation is supported by the fact that several samples plot outside the compositional field defined by plagioclase, orthopyroxene, clinopyroxene and olivine (figure 6.1a). In terms of Al₂O₃, CaO and TiO₂, little evidence for the addition of components from the country rocks is evident (figures 6.1b, c and d). In contrast, the SiO₂ versus MgO diagram (Fig. 6.1e) may indicate an important role for calcsilicate. The alternative possibility, i.e. that the low SiO₂ contents are a function of significant amounts of modal olivine, is not supported by the Al₂O₃, Fe₂O₃, CaO or TiO₂ vs MgO diagrams.

Selected major elements are plotted against depth in figure 6.2. The data show a broad increase in MgO with height, and decreases in TiO₂ and Al₂O₃, confirming the trend shown by mineral chemistry data that indicated a reverse differentiation trend in the Platreef with height.

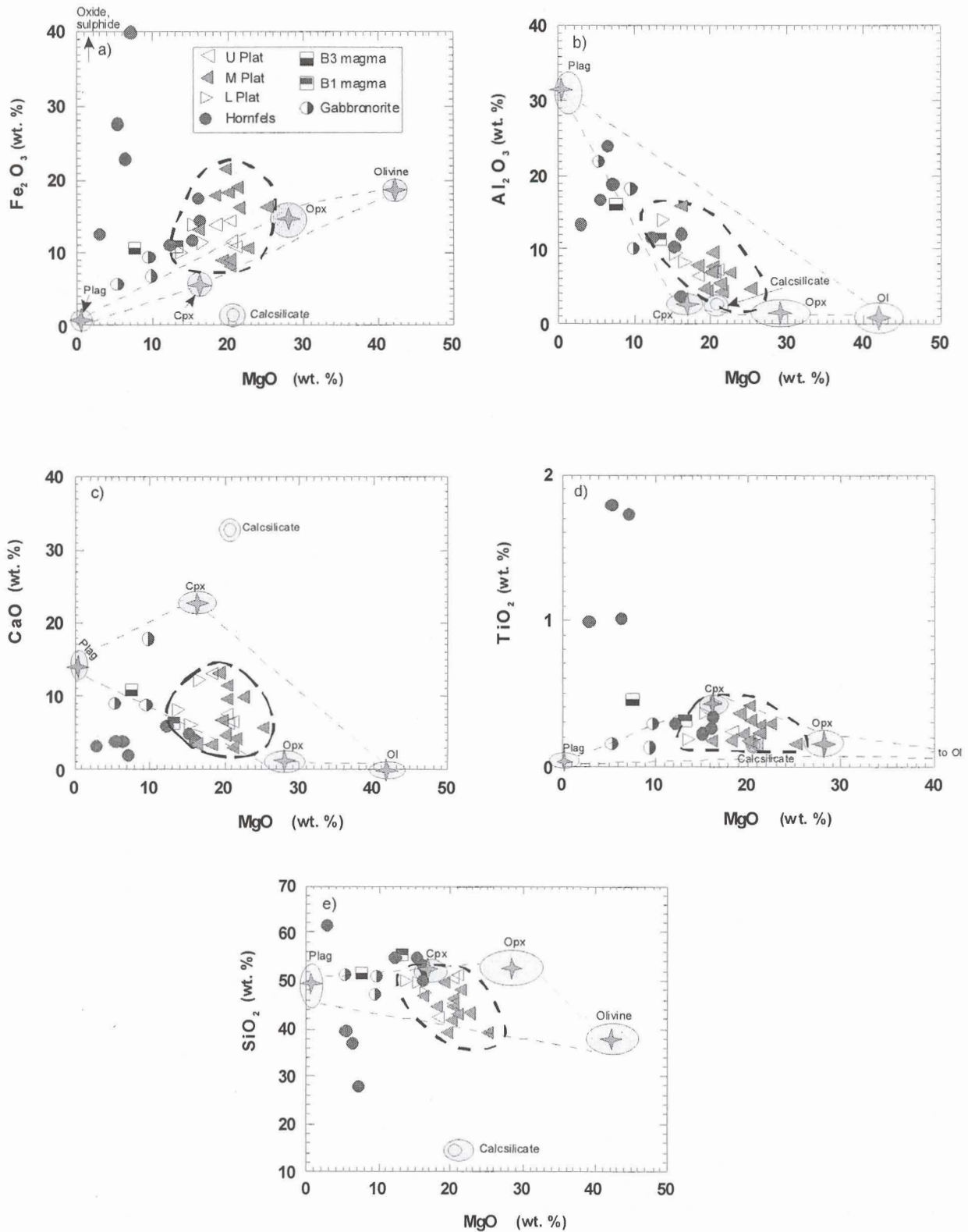


Fig. 6.1: a) Fe_2O_3 , b) Al_2O_3 , c) CaO, d) TiO_2 and d) SiO_2 versus MgO. Also plotted are B1 and B3 Bushveld parental magmas (Curl, 2001) and averaged microprobe mineral compositions for the Platreef. U Plat = upper Platreef, M Plat = middle Platreef, L Plat = lower Platreef. Stippled lines represent Platreef field.

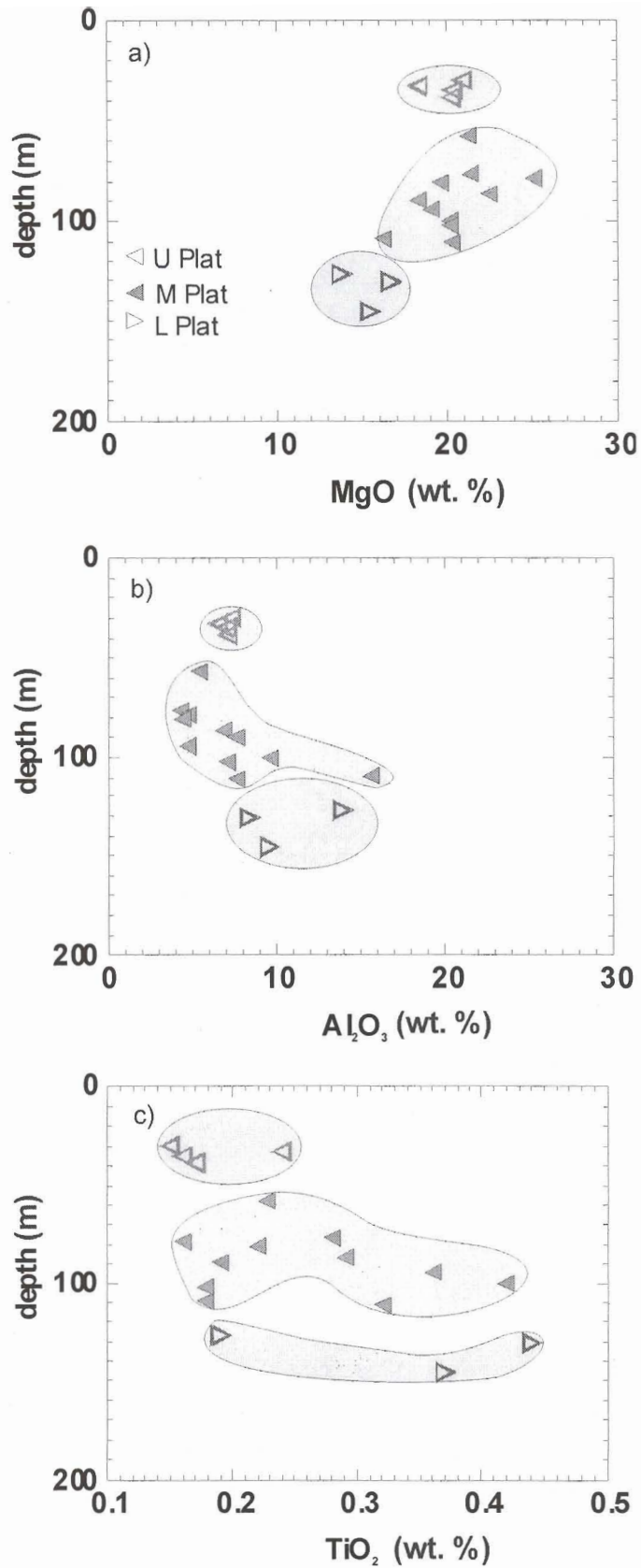


Fig. 6.2: Variation of a) MgO, b) Al₂O₃ and c) TiO₂ with depth. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef.



6.3 Trace Element Chemistry

Compositional ranges of the individual trace elements in the different Platreef layers are presented in Table 6.2 and plotted in Fig. 6.3.

| Element | Lower Platreef | Middle Platreef | Upper Platreef | Pegmatoidal feldspathic pyroxenite | Merensky Reef (UCZ pyroxenite) |
|---------|----------------|-----------------|----------------|------------------------------------|--------------------------------|
| Sr | 276-407 | 58-232 | 103-214 | 149-226 | 30-90 |
| Rb | 17-34 | 7-23 | 12-26 | 19-26 | 6-9 |
| Zr | 36-75 | 24-58 | 19-35 | 33-66 | 2-25 |
| Y | 13-19 | 7-22 | 6-13 | 8-11 | 0-15 |
| Nb | 3-4 | 2-5 | 2-3 | 2-5 | <2 |
| Zn | 81-86 | 62-125 | 81-109 | 115-143 | 60-160 |
| Cu | 46-3519 | 17-3510 | 131-2463 | 2132-8239 | 700-800 |
| Ni | 336-1988 | 58-14072 | 572-3451 | 2188-7285 | 2300-3100 |
| Co | 66-112 | 45-292 | 87-124 | 123-305 | 106-143 |
| Cr | 683-2408 | 57-1560 | 251-3029 | 427-2063 | 6979-7390 |
| V | 69-132 | 66-119 | 78-112 | 59-66 | 60-100 |
| Sc | 13-21 | 5-19 | 12-21 | 8-17 | 24-31 |
| Ga | 12-14 | 7-13 | 8-9 | 9-17 | |
| Pb | 11-36 | 3-37 | 6-46 | 10-27 | |
| Cl | 257-585 | 413-1224 | 35 | 356-878 | |
| F | 1411-3727 | 1303-7130 | 905-2531 | 1174-6037 | |
| S | 16-11821 | 16-47608 | 554-13739 | 8796-37522 | 4000-5100 |

Table 6.2: Trace element distribution in the different Platreef layers compared to that from the Merensky Reef (Barnes and Maier, 2002)

It is evident that relative to the Merensky Reef, the Platreef has high contents of Sr, Rb, Zr, Y, Nb, V as well as Cu and Ni but low contents of Cr, Sc and Zn. The elevated Sr contents cannot be explained by a relatively high modal abundance of plagioclase, as the Platreef has approximately the same plagioclase content as the Merensky Reef

(Fig. 6.4). Thus, the relatively elevated concentration of the incompatible trace elements and Sr points either to a relatively larger proportion of trapped melt, or an enhanced component of crust.

The first proposition cannot explain the observed trace element variation. Bushveld B1 magma has 10 ppm Y, 66 ppm Zr and 29 ppm Rb (Curl, 2001). The Platreef rocks would require between 20 and 100 % trapped melt to satisfy the mass balance which seems unrealistic. Further, Y/Zr ratios of Platreef rocks are markedly higher than those in B1 Bushveld magma (Fig. 6.4a). This implies that the Platreef rocks contain a significantly larger component of crust than the B1 magma.

Plots of Cu versus Zr and Cu versus Y (Fig. 6.4b and c, respectively) do not show correlations among these trace elements. Zr, Cu and Y are highly incompatible elements in the absence of sulphides and should progressively increase in concentration with differentiation to show a positive correlation among themselves. The lack of correlation between Zr and Y with Cu and the high supracrustal Cu/Zr and Cu/Y ratios (up to 128.4 Cu/Zr and 757 Cu/Y) point to the presence of exsolved sulphides.

This model is supported by the S contents of the rocks in cases. Sulphur contents of the Platreef rocks range from 0.0016 to 4.76 % indicating ca. 0.004 to 13.5 % sulphide. Many basaltic magmas and the Bushveld B1 magma have ca. 1000 ppm S (~0.25 % sulphide) (Barnes and Maier, 2002). In the case of S-undersaturation during crystallisation, the Platreef cumulate would be expected to contain about 0.025 %

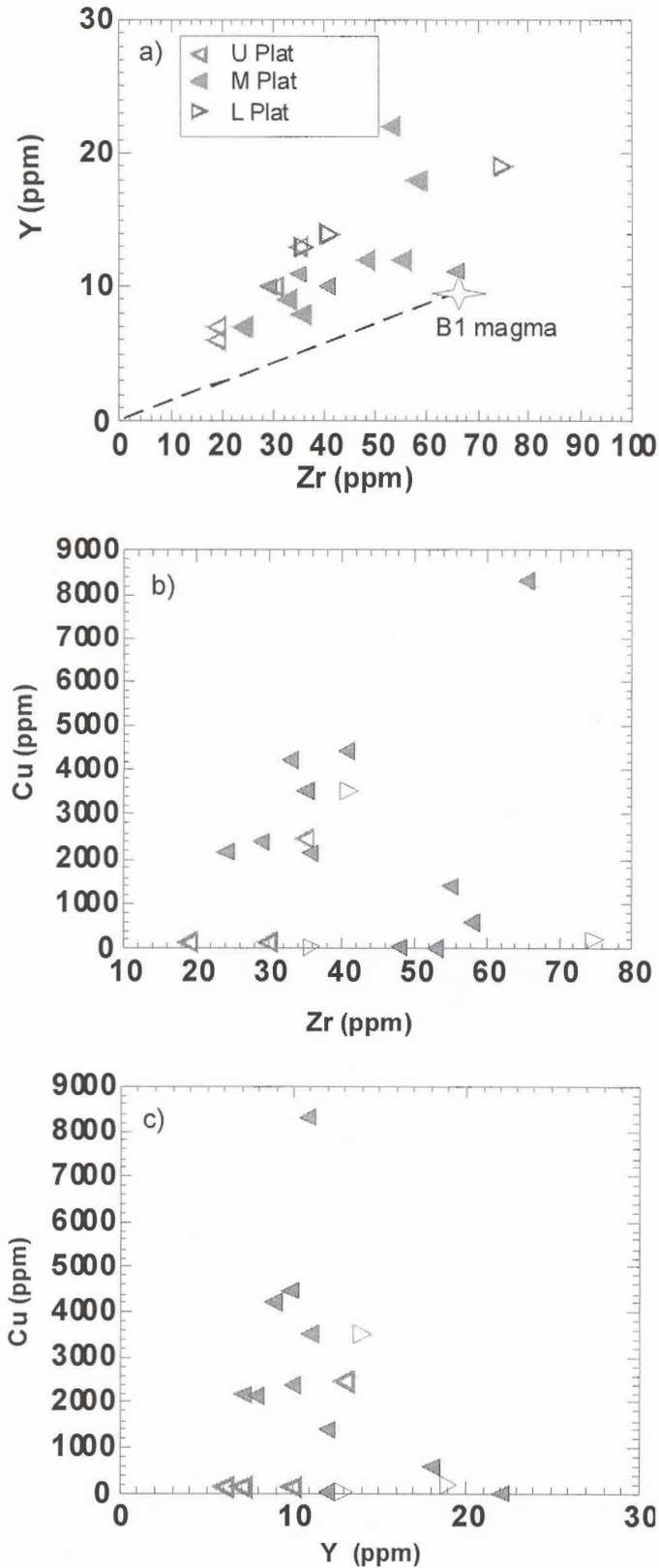


Fig. 6.3: Plot of a) Y versus Zr, b) Cu versus Zr and c) Cu versus Y. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef. Stippled line represents back projection of B1 Bushveld parental magma (Curl, 2001).

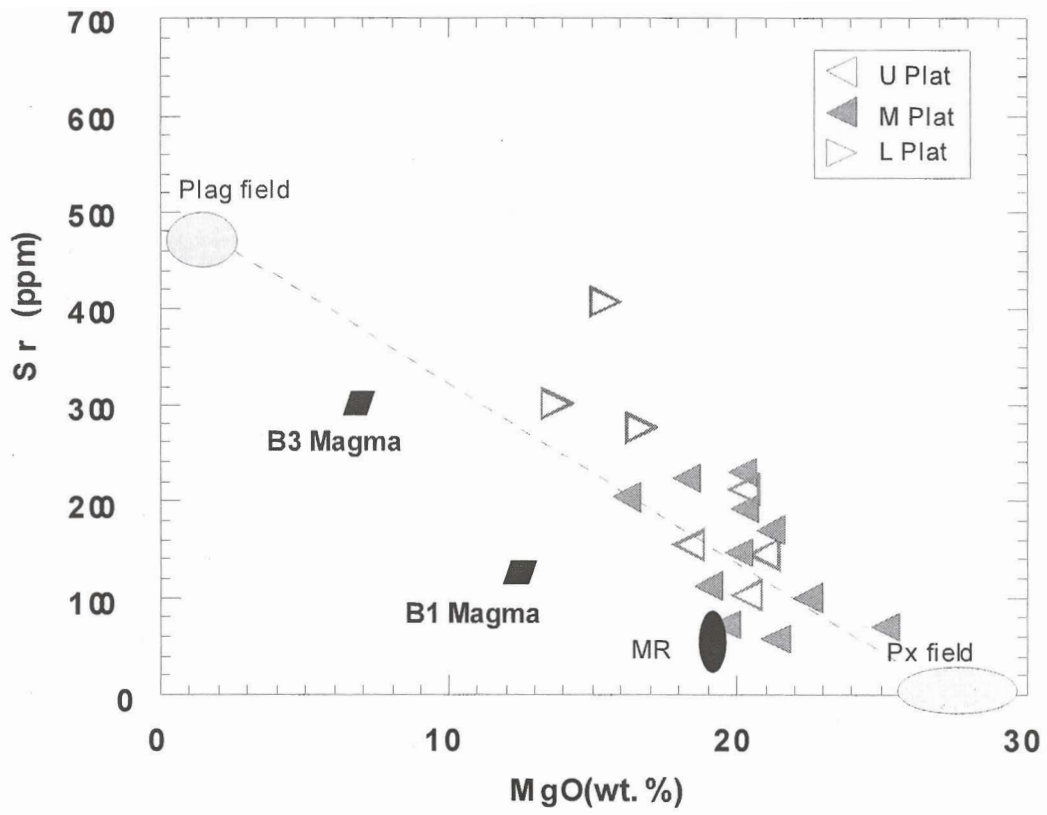


Fig. 6.4: Variation diagram of Sr versus MgO. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef, MR = Merensky Reef.

sulphide (100 ppm S), assuming 10 % trapped melt. If the magma was S-saturated, one could expect on the order of 1000 ppm S in the rocks. When S is plotted against height (Fig. 6.5d), it is clear that most of the rocks of the Platreef have S contents above 1000 ppm suggesting that the rocks contain a large amount of exsolved sulphides.

The bulk of the Ni content of the rocks is also controlled by sulphides. Ni concentrations range from 58 to 14072 ppm. The sample with the highest Ni concentration is from the Middle Platreef, where the average Ni concentration is 3650 ppm. Pegmatoidal feldspathic pyroxenite has the highest average Ni concentration of 5247 ppm. These Ni contents are far higher than those of pyroxenites and norites from the UG 2 - Merensky Reef interval of the western Bushveld Complex (Maier and Eales, 1997). The Lower and Upper Platreefs have average Ni concentrations of 1542 and 916 ppm, respectively, indicating much lower sulphide contents and/or lower metal tenors of the sulphides.

Cr shows a general increase in concentration towards the top of the Platreef, suggesting that the upper Platreef layers are relatively more primitive, as was suggested by the mineral chemistry data (Figure 5.3a).

When trace element data are plotted versus height, it is evident that the concentrations of the incompatible elements Y and Zr decrease with height (Figs. 6.5e and f respectively). This could suggest that the lowermost rocks (i.e. the Lower

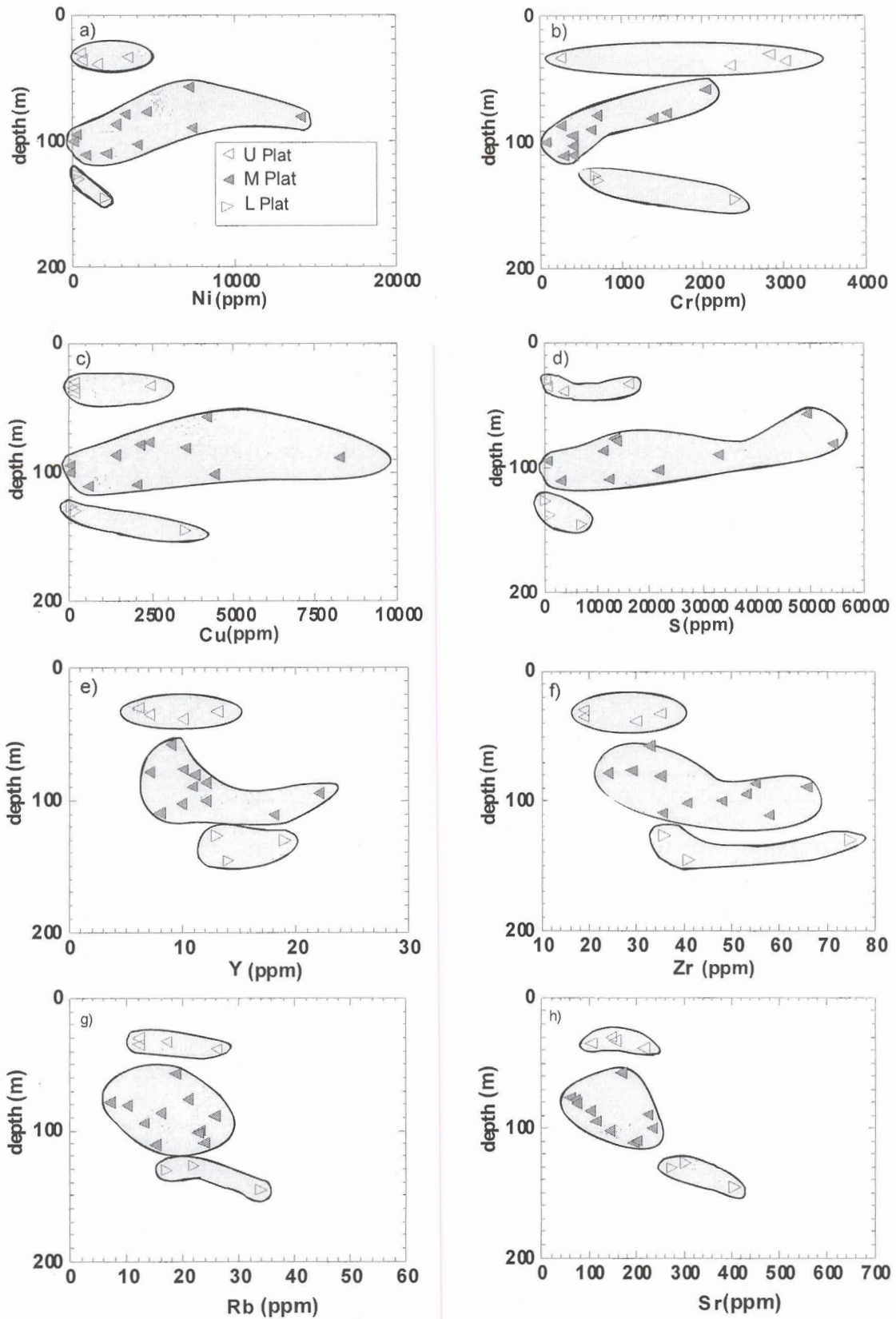


Fig. 6.5: Trace element variation with depth for the Platreef lithologies. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef.

Platreef) have assimilated more crust or that they contain a larger proportion of trapped melt.

6.4 Platinum-group elements

The noble metal concentrations are normalised to primitive mantle and plotted in order of decreasing melting temperature in Fig 6.6. Noble metal concentrations of the Merensky Reef, B1 and B3-type Bushveld parental magmas are shown for comparison. Ni is included in the plots to the left of Os, and Cu (as well as Au) to the right of Pd due to their broadly similar behaviour to Os and Pd, respectively, during fractionation. In general, the three Platreef layers on farm Townlands show a broadly similar noble metal pattern, with variation only seen in the metal contents. They are all PGE enriched when compared to the B1 and B3 parental magmas of the Bushveld Complex. The Middle Platreef and the associated pegmatoidal feldspathic pyroxenite, have the highest PGE contents followed by the Upper Platreef, with the Lower Platreef having the lowest PGE contents. The PGE content of the Middle Platreef is economic while those of the Lower Platreef and Upper Platreef are presently uneconomic and close to 'background'. The patterns are characterised by a broadly flat pattern from Ni to Ir, a progressive increase from Ir to Pd followed by a decrease from Pd to Cu. This is in marked contrast to the Merensky Reef pattern which shows an arch-shaped mantle-normalised pattern, reflecting a strong enrichment of all PGE relative to Ni and Cu. The lack of a strong PGE enrichment over Ni and Cu in most of the Platreef, may suggest that the sulphides segregated at a relatively low R factor (ratio of silicate melt to sulphide melt).

The metals are plotted versus stratigraphic height in Fig. 6.7. It is evident that the three platiniferous layers have different PGE concentrations. The Middle Platreef has

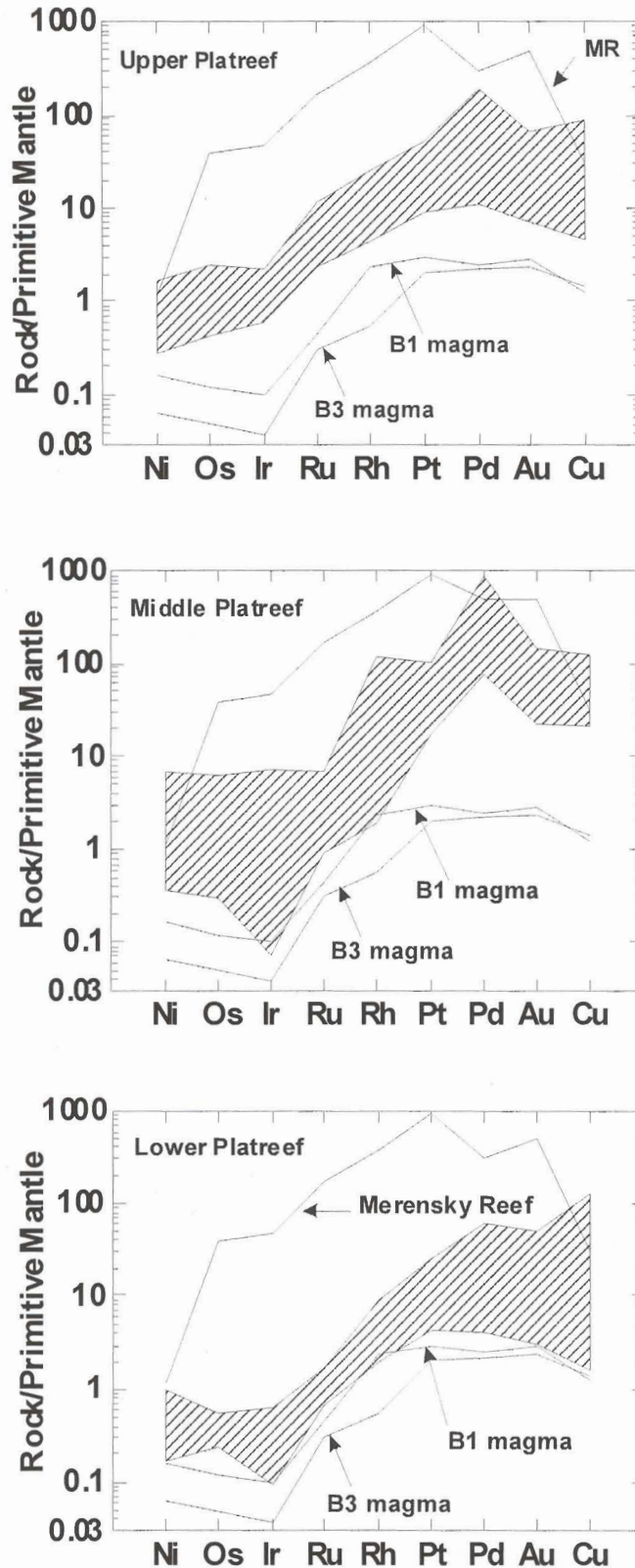


Fig. 6.6: Mantle-normalised PGE spider diagrams for rocks from the Platreef on the farm Townlands. Included are PGE concentrations for the B1 and B3 Bushveld parental magmas (Curl, 2001) and the Merensky Reef (Barnes and Maier, 2002). (Normalisation factors are from Barnes and Maier 1999).

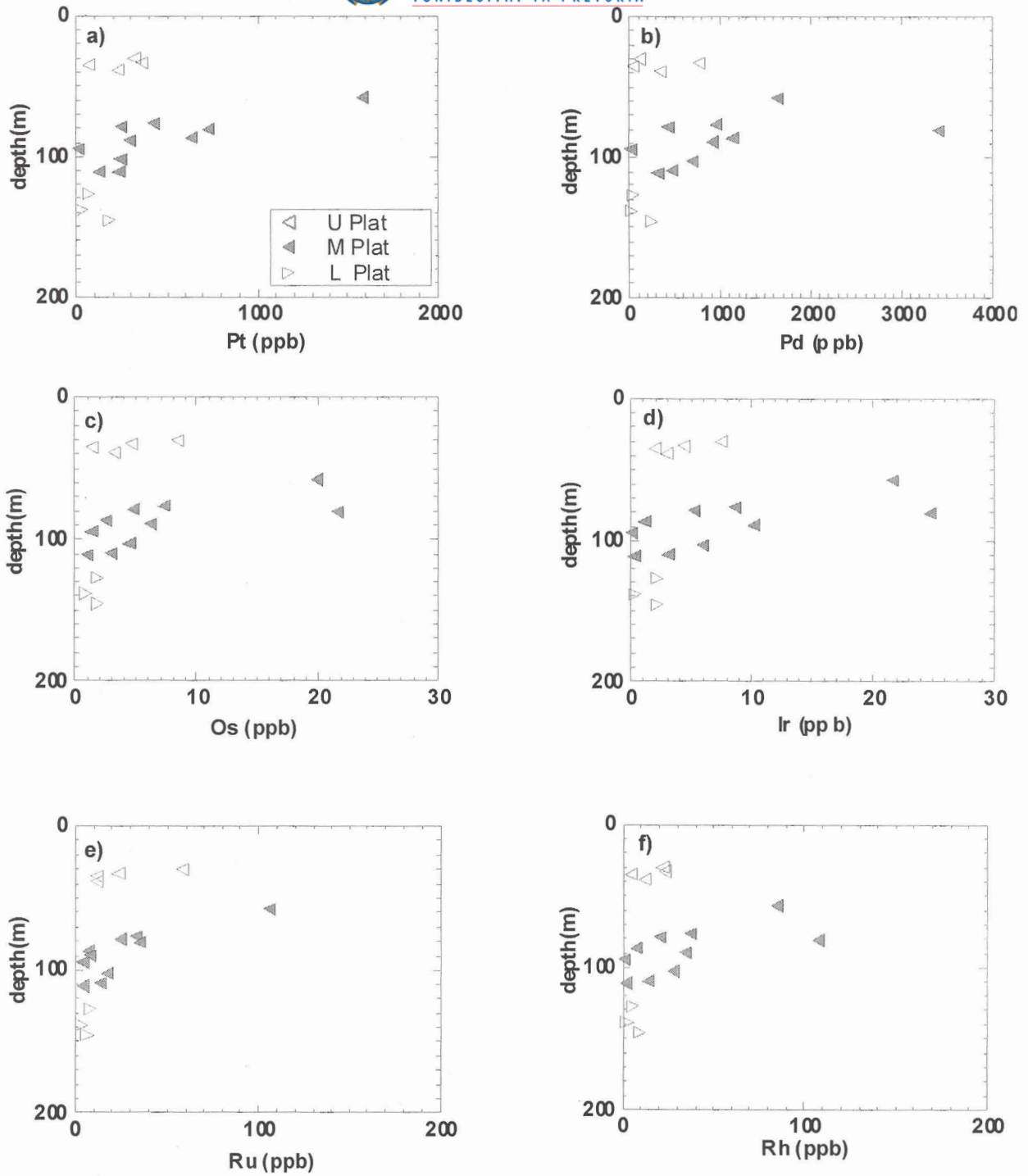


Fig. 6.7: Concentration of PGE plotted versus stratigraphic height. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef. MR = Merensky Reef.

the highest PGE concentrations, with the Lower Platreef having the lowest PGE concentrations. Pd/Ir and Pt/Pd ratios are plotted versus height in Fig. 6.8. It is evident that in each platiniferous layer, there is a trend of decreasing Pd/Ir ratio with height (Fig. 6.8a). The fact that Pd/Ir ratios change with height may suggest that Pd and Ir have different D values with respect to sulphide melt. Most authors found that PGE have broadly similar D values with respect to sulphide melt although the experimental data are understandably scattered (Barnes and Maier, 1999) and some authors (e.g. Bezmen et al., 1994) found considerable difference between D values. The change of the ratio may also suggest that other phases besides sulphides exerts some control on the PGE contents in the rocks (e.g. silicates, oxides, PGM or hydrothermal fluids). No clear trends are observed in the plot of Pt/Pd versus height (Fig. 6.8b).

To assess the nature of the phases controlling the PGE, the PGE are plotted against each other in Fig. 6.9. Pt shows a fairly good positive correlation with Pd and Ir, and Pd shows a good correlation with Ir, suggesting the PGE are essentially controlled by the same phase. The few outliers may be due to later remobilization of PGE. Pd and Pt (not shown) do not display a good correlation with Cu (Fig. 6.9f) suggesting remobilization of Cu, possibly due to hydrothermal processes.

Pt, Pd, Ir, Ru, Rh and Os show fairly good positive correlations with S (Fig. 6.10a-f, respectively). This suggests that sulphide was the primary metal collector. This is contrary to the situation at Sandsloot where Armitage et al. (2002) report that the PGE are mostly not hosted by sulphides, but by platinum-group minerals (PGM) that are enriched in low-temperature metals and semi-metals. They interpreted this to be a

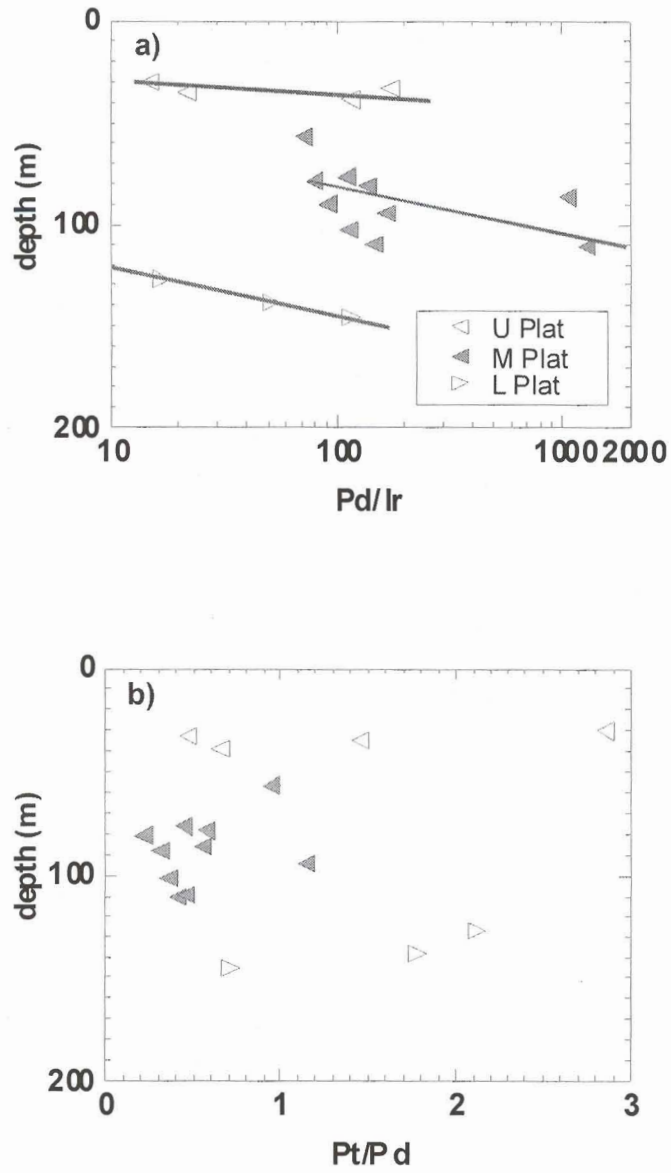


Fig. 6.8. Plots of a) Pd/Ir and b) Pd/Pd versus depth. Note that the Pd/Ir axis in 6.8(a) is in log-linear scale. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef. MR = Merensky Reef.

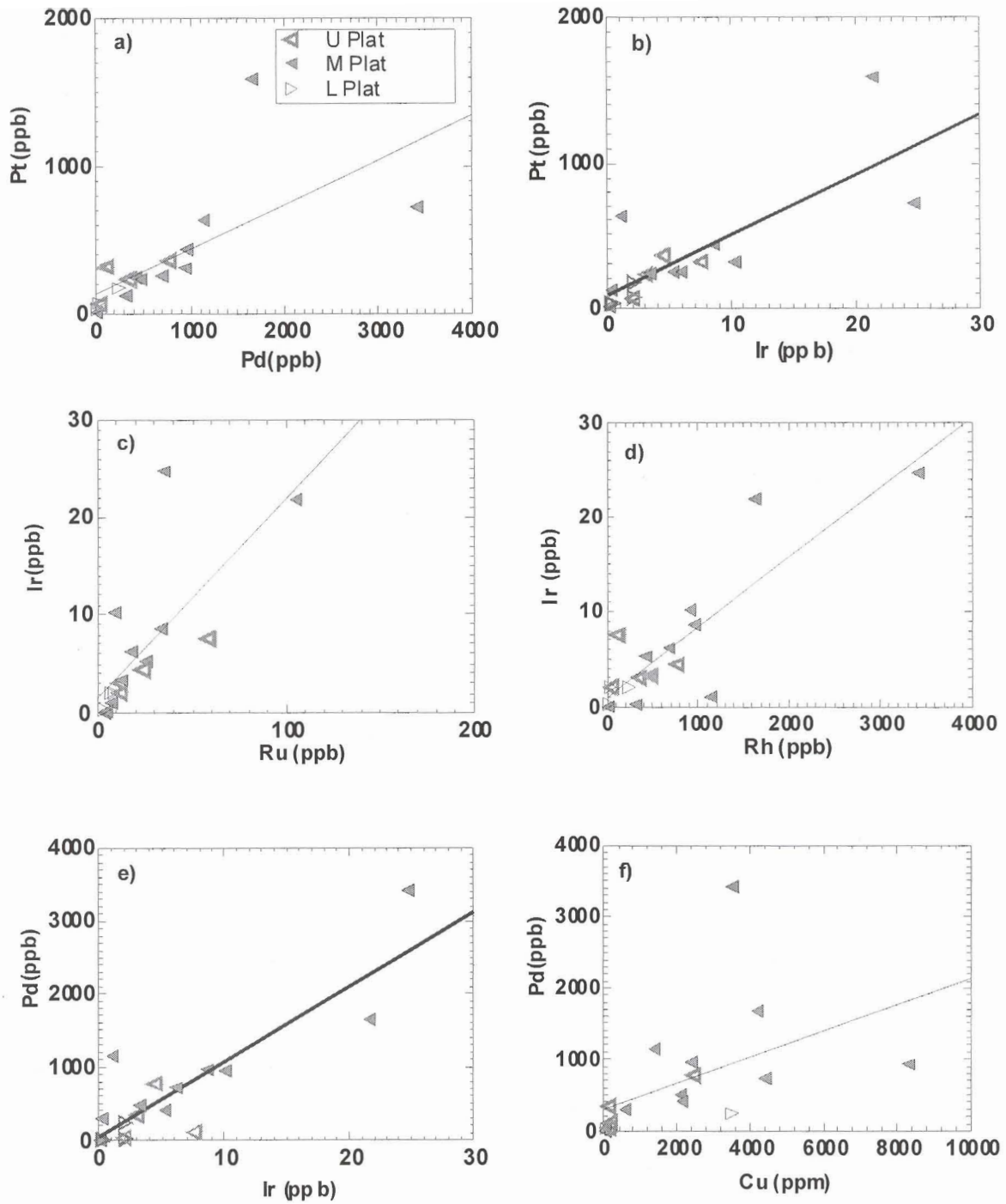


Fig. 6.9: PGE binary plots of the Platreef on the farm Townlands. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef. MR = Merensky Reef.

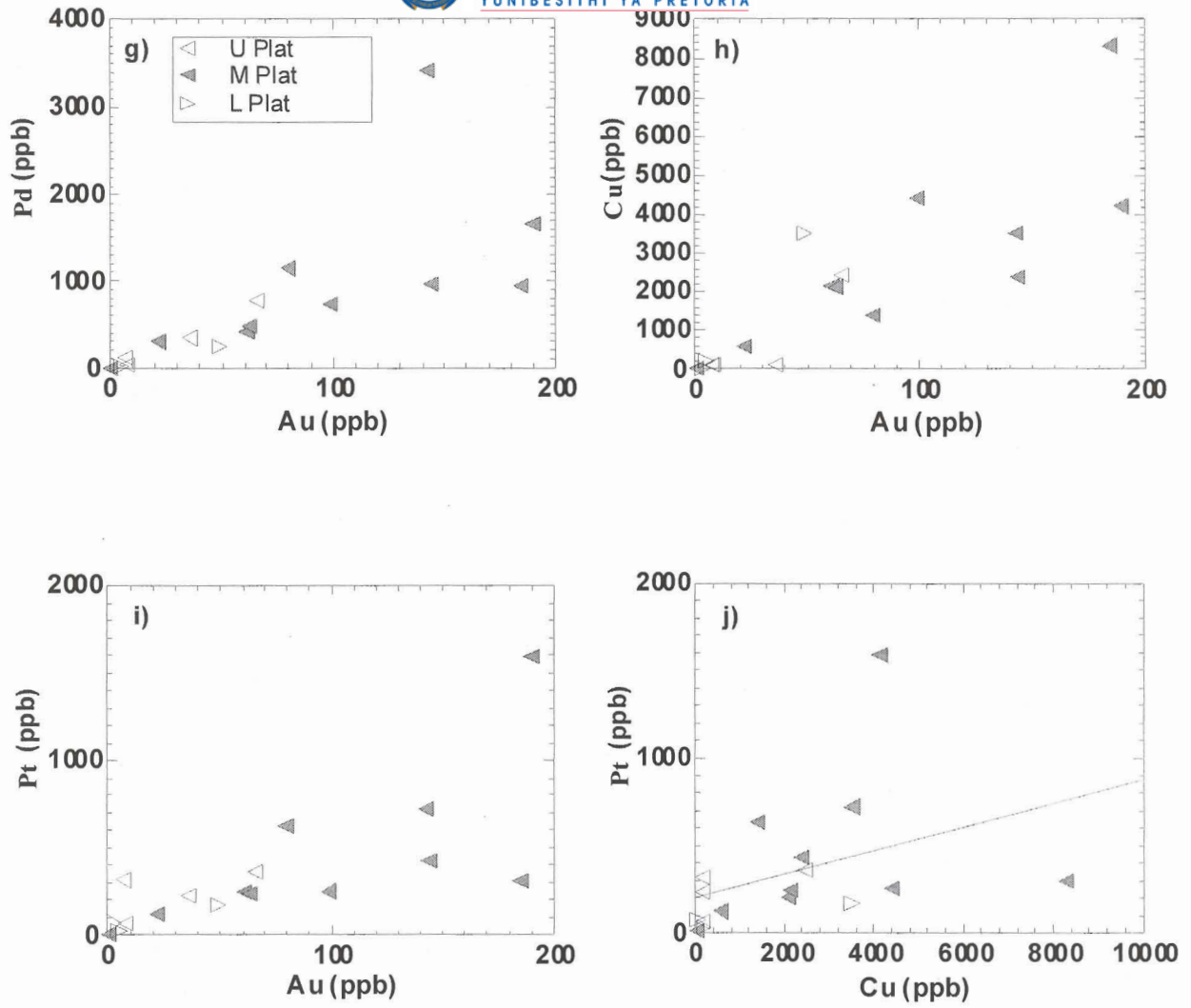


Fig. 6.9: (contd): PGE variation diagrams of the Platreef on the farm Townlands. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef. MR = Merensky Reef.

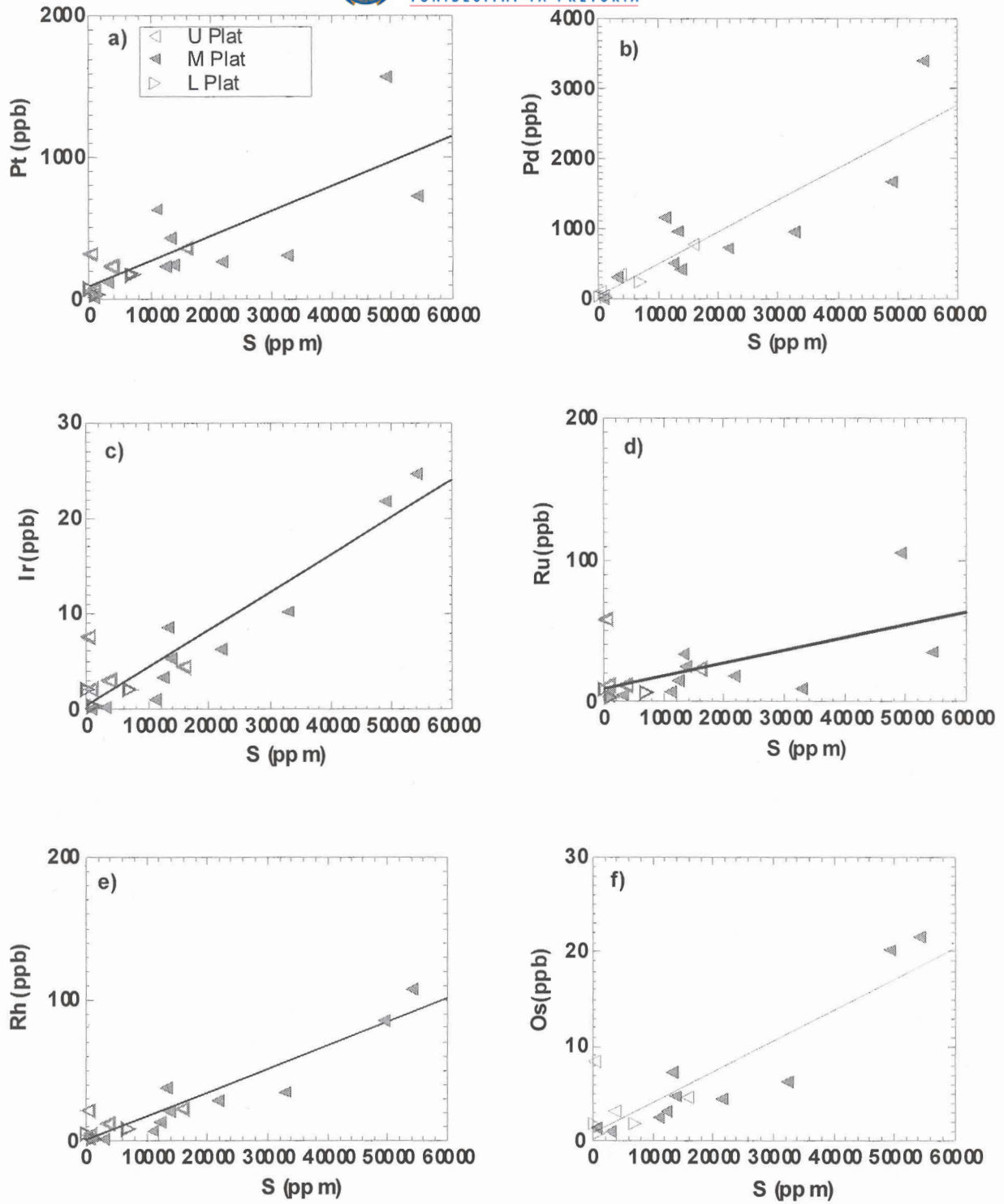


Fig. 6.10. Plots of PGE versus S with regression lines plotted. U Plat = Upper Platreef, M Plat = Middle Platreef and L Plat = Lower Platreef. MR = Merensky Reef.



Platreef rocks, ii) ^{18}O depletion in calcsilicate rocks within and just above the Platreef, which may have occurred during interaction with fluids, iii) the occurrence of sulphide mineralisation in the parapyroxenite suggesting the sulphides were at least in part, transported by fluids.