



## CHAPTER TEN: SULPHUR-ISOTOPE GEOCHEMISTRY

The formation of magmatic Cu-Ni-(PGE) sulphide deposits is controlled by the interaction between the sulphide saturation state of mafic magmas and dynamic processes by which immiscible sulphide liquid can be concentrated into favorable locations (Ripley, 1999). In many sulphide-rich Cu-Ni deposits, addition to the magma of external S is considered important. Examples include Kambalda (Naldrett, 1989), Voisey's Bay (Li *et al.*, 2000), Noril'sk (Godlevsky and Grinenko, 1963; Gorbachev and Grienko, 1973; Naldrett *et al.*, 1996) and Pechenga (Green and Melezhik, 1999). A similar model has been proposed by Buchanan *et al.* (1981) for the Platreef on the farm Tweefontein and by Manyeruke (2003) at Townlands. Alternatively, assimilation of sulphide-poor siliceous or carbonaceous country rocks may also induce sulphide saturation (De Waal, 1977; Gain and Mostert, 1982; Naldrett *et al.*, 1986; Li and Naldrett, 1993). Sulfur isotope compositions may be used as tracers to detect the presence of external sulphur and thus can potentially constrain the ore forming process and may be used as a guide to ore. Mantle  $d^{34}\text{S}$  values are in the range  $\sim 0 \pm 3$  ‰ (Ripley, 1999), whereas sedimentary rocks may have strongly negative or positive values. Thus, if igneous rocks show substantial deviation from the mantle values, this may indicate assimilation of crustal sulphur (Ripley, 1999). It should, however, be noted that contamination with Archean sedimentary host rocks may be difficult to detect as these rocks generally have  $d^{34}\text{S}$  values in the range of mantle values (Ripley, 1999).



The available S isotopic database for the Platreef is shown in Table 7a and Fig. 10.1. Liebenberg (1968) reported sulphur isotopic values for the Northern limb of the Bushveld Complex on the farm Zwartfontein, with  $d^{34}\text{S}$  values of +0.7 and +1.9 ‰ for a calc-silicate and a pegmatoidal norite, respectively. Buchanan *et al.* (1981) carried out S-isotopic analyses on 9 samples (+6.3 to +9.2 ‰) of the Platreef on the farm Tweefontein, where the floor rocks consist of calc-silicate, banded ironstone and argillaceous sediments. This was followed by the work of Hulbert (1983) on Lower Zone pyroxenites and chromitites, Critical Zone pyroxenites, chromitites, anorthosites and Platreef-type rocks on Grasvally to the south of Mokopane.  $d^{34}\text{S}$  values of +0.96 to +7.54 ‰ were reported for the Platreef. Manyeruke (2003) provided S-isotopic data on 12 samples ( $d^{34}\text{S}$  values of +2.6 to +10.1 ‰) covering the Platreef and its floor rocks on the farm Townlands where the floor rocks consist of metasediments of the Silverton Formation of the Transvaal Supergroup. Sharman-Harris and Kinnaird (2004) published results of  $d^{34}\text{S}$  analyses on pyrrhotite and chalcopyrite on the farms Rietfontein, Turfspruit and Macalacaskop ( $d^{34}\text{S}$  of +4.5 to +5.6 ‰). Tuovila (in preparation) analysed sulphide-bearing pyroxenite sills several km below the basal contact of the Bushveld, on the farm Uitloop. These yielded  $d^{34}\text{S}$  values from +8 to +15 ‰. Holwell *et al.* (2005, 2007) reported magmatic signatures for S-isotopic analyses of the pyroxenites on the farm Overysel ( $d^{34}\text{S}$  +1.7 to +2.0 ‰) where the floor rocks consist of granite gneisses.

In the course of the present study, a total of 7 samples from the Platreef on Nonnenwerth were analysed at Indiana University, Bloomington, U.S.A. Analytical



Farm	$d^{34}\text{S}$ (‰ VCDT)	Reference
Grasvally	+0.96 to +7.54	Hulbert (1983)
Rooipoort	+2.0 to +5.0	Maier <i>et al.</i> (2007)
Townlands	+4.0 to +8.0	Manyeruke (2005)
Macalacaskop	+2.9	Sharman-Harris <i>et al.</i> (2005)
Uitloop	+8.0 to +15.0	Touvila (in preparation)
Turfspruit	+5.2	Sharman-Harris <i>et al.</i> (2005)
Rietfontein	+5.0	Sharman-Harris <i>et al.</i> (2005)
Tweefontein	+6.3 to +9.2	Buchanan <i>et al.</i> (1981)
Tweefontein Hill	+ 6.3 to 9.0	Scholtyssek (2005)
Sandsloot	0 to +2.6	Holwell <i>et al.</i> (2007)
Zwartfontein	+0.7 – 1.9	Liebenberg (1968); Holwell <i>et al.</i> (2007)
Overysel	+1.7 to +2.0	Holwell <i>et al.</i> (2005)

Table 7a: S-isotopic analyses of the Platreef along strike from south to north.

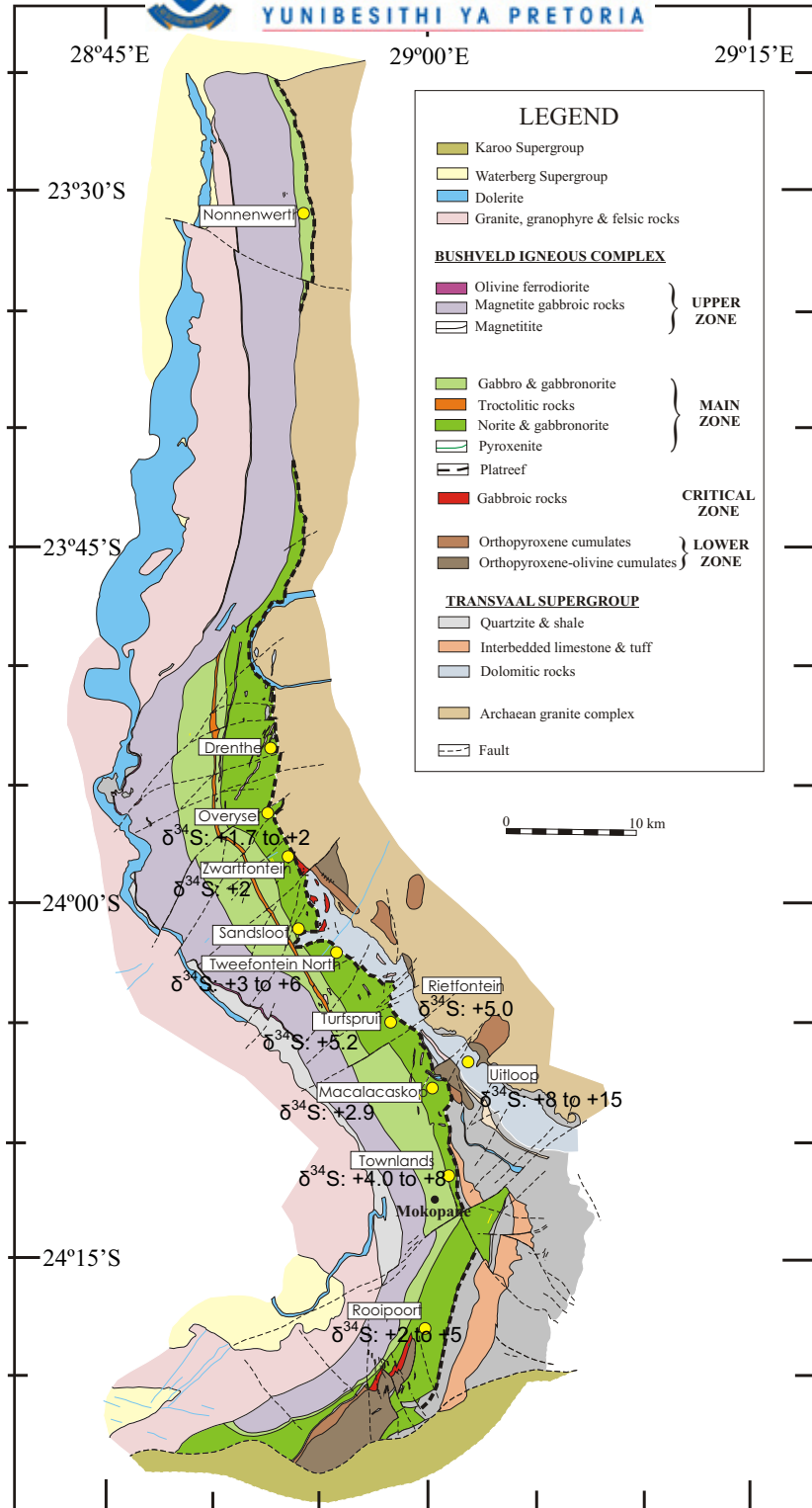


Fig. 10.1: Regional geological map of the northern limb with results of S isotope analyses superimposed. Data from Townlands are from Manyeruke et al. (2005), data from Macalacaskop, Rietfontein and Turfspruit are from Sharman-Harris et al. (2005), data from Tweefontein are from Buchannan et al. (1981), data from Rooipoort are from Maier et al. (2007), data from Uitloop are from Tuovila (in preparation), data from Overysel are from Holwell et al. (2005) and data from Zwartfontein are from Liebenberg (1968). (Map modified after Ashwal et al., 2005).



results are presented in Table 7b and analytical procedures are given in Appendix 1f. Sulphur isotopic compositions are reported in standard  $\delta$  notation relative to VCDT (Vienna Cañon Diablo Troilite). The analyses were performed to

- (i) determine the role of crustal contamination in the formation of the Platreef,
- (ii) compare the S-isotopic composition of the Platreef along strike, and thus to determine whether the high  $\delta^{34}\text{S}$  values of the Platreef on the farms Townlands (Manyeruke, 2003), Tweefontein (Buchanan *et al.*, 1981), Rietfontein, Turfspruit and Macalacaskop (Sharman-Harris and Kinnaird, 2004) are characteristic of the entire Platreef,
- (iii) determine whether regional trends in  $\delta^{34}\text{S}$  values can be observed,
- (iv) compare the  $\delta^{34}\text{S}$  signature of the Platreef to other examples of basal Ni-Cu-PGE mineralization elsewhere in the world (Fig. 10.2) .

Most samples from Nonnenwerth have relatively homogeneous  $\delta^{34}\text{S}$  values ranging from +0.73 to +1.87 ‰ which is within the mantle range (Ripley, 1999). This suggests minute or no recognizable addition of crustal sulphur to most of the Platreef rocks examined. One sample from the base of the Platreef (MOX36) has  $\delta^{34}\text{S}$  of +5.24 ‰, suggesting that localized assimilation of heavy crustal sulphur may have occurred in this sample.

Notably, the Nonnenwerth data are similar to those of Holwell *et al.* (2005) in the Platreef at Overysel where  $\delta^{34}\text{S}$  values range from +1.7 to +2.0 ‰ and where the floor rocks equally consist of granite gneiss. Broadly similar values of  $\delta^{34}\text{S}$  are also found on Zwartfontein, where the floor rocks are constituted by dolomite. In contrast,



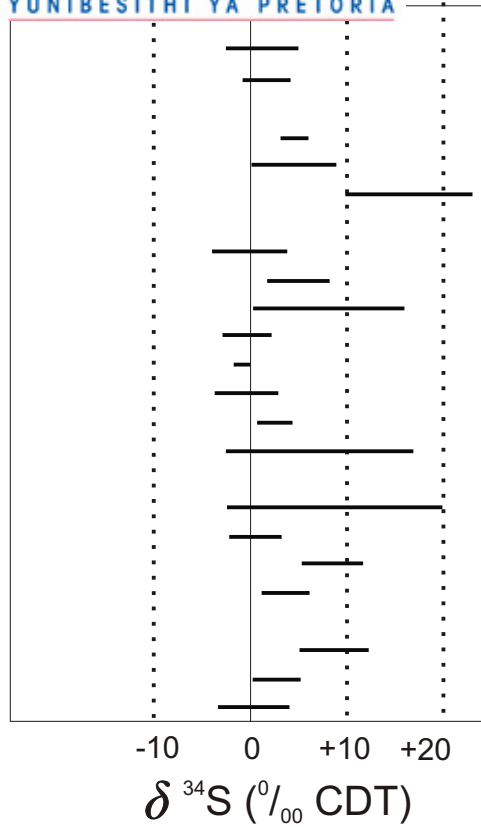
Sample	Borehole	Distance above base of Platreef (m)	$d^{34}\text{S}$ (‰VCDT)	Rock unit
MOX9	2121	111.32	1.33	recrystallized gabbronorite
MOX10	2121	91.10	1.22	recrystallized gabbronorite
MOX14	2121	35.77	1.87	melagabbronorite
MOX27	2199	184.95	1.33	anorthosite
MOX29	2199	163.82	0.73	pegmatoidal gabbro
MOX33	2199	88.81	1.22	norite
MOX36	2199	31.94	5.24	altered gabbronorite

Table 7b: S-isotopic analyses of samples from the Platreef at Nonnenwerth.

at the localities where the floor rocks consist of shale and quartzite,  $d^{34}\text{S}$  values tend to be strongly positive. These data are generally interpreted to suggest that the Platreef magma assimilated external S from the shales and granites (Manyeruke, 2003). In contrast, the dolomitic floor rocks may have either contributed insignificant amounts of external S to the magma, or the sulphur within the dolomites and granites was unfractionated. The model is supported by the S isotopic data on metasediments of the Silverton Formation (Manyeruke, 2003; Manyeruke *et al.*, 2005) that show  $d^{34}\text{S}$  values of +2.6 to +10.1 ‰. Unfortunately, no data on sulphides within the dolomites underlying the northern lobe is yet available. Cameron (1982b) analysed dolomite of the Malmani sub-group in the Fochville area and found  $d^{34}\text{S}$  between -8 and +10 ‰. It remains unclear whether the dolomites of the study area have similar S isotopic signatures.



- Archean komatiites
  - Canadian
  - Australian
- Proterozoic komatiites
  - Cape Smith
  - Pipe Thompson
- Kabanga
- Deer Lake Complex
  - Intrusion
  - Chilled margin
- Fox River Sill
- Molson Dykes
- St Stephen intrusion
- Voisey's Bay
- Kunene anorthosite
- Crystal Lake gabbro
- Duluth
  - sulfide-rich
  - sulfide-poor
- Mellon Complex
- Coldwell Complex
- Noril'sk
  - mineralized
  - unmineralized
- Insizwa



- Uitloop
- Bushveld Complex
  - Platreef (Nonnenwerth)
  - Platreef (Townlands)
  - Vlakfontein
  - Merensky
  - Uitkomst Complex
- Muskox
- Finnish deposits
  - norite-peridotite
  - graphite-bearing
- Rana Complex
  - mineralized
  - graphite-bearing
- Montcalm intrusion
- Sudbury
- East Bull Lake
- Moxie Pluton
- Mount Prospect int.
- Warren intrusion
- Plaisades sill
- Glenn Mountains layered complex
- Acoje Massif
- kimberlites

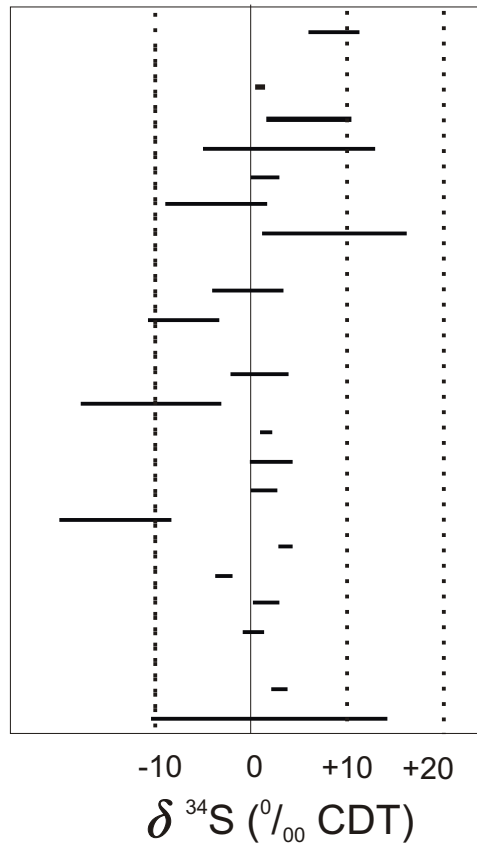


Fig. 10.2:  $\delta^{34}\text{S}$  values of sulphidic rocks and sulphides in selected mafic/ultramafic intrusions (modified from Ripley, 1999). Kabanga and Kunene data from Maier (unpublished), Uitloop data from Touvila, (personal communication) and Townlands data from Manyeruke (2003).



## 10.1 Summary

This study has shown that the sulphur isotope compositions of the Platreef at Nonnenwerth, where floor rocks are granite gneiss, are mantle-like ( $d^{34}\text{S}$  values mostly in the range from +0.73 to +1.87 ‰). At Overysel, the Platreef is also underlain by granite gneiss and  $d^{34}\text{S}$  values range from +1.7 to +2.0 ‰ (Holwell *et al.*, 2005). The distinct positive sulphur isotope values at Townlands (Manyeruke, 2003; Manyeruke *et al.*, 2005), and in the lower parts of the Platreef on Rietfontein, Turfspruit and Macalacaskop (Sharman-Harris and Kinnaird (2004); Sharman-Harris *et al.* (2005)), indicate that the Platreef assimilated external S from the Transvaal Supergroup floor rocks underlying the areas. Therefore, the variation of the footwall along strike was critical in determining the  $d^{34}\text{S}$  signature of the Platreef.

Importantly, this study and previous investigations by Holwell *et al.* (2005), Sharman-Harris and Kinnaird (2004), Sharman-Harris *et al.* (2005) show that the Platreef-style PGE-sulphide mineralization is associated with floor rocks containing variable S contents and S-isotopic signatures. Thus, assimilation of external S during magma emplacement was apparently not the principal controlling factor in sulphide genesis. Sulphur saturation probably occurred prior to intrusion in a deep staging chamber (Lee, 1996). Subsequently, assimilation of S may have merely modified already existing sulphide melt. This would have resulted in lowering the tenor of the sulphides by dilution due to low R-factors of assimilated sulphides, particularly in areas where the floor rocks consisted of sulphidic shales, between Townlands and Tweefontein.





## CHAPTER ELEVEN: O-ISOTOPE GEOCHEMISTRY

The  $d^{18}\text{O}$  of most crustal rock types are in excess of +8.0 ‰ compared to oxygen isotope values of mantle-derived mafic magmas which fall in a restricted range of +5 to +7 ‰ (Ripley, 1999). Thus oxygen isotope measurements offer a great potential as a tracer of crustal contamination of mantle-derived basaltic melts.

Pristine, mantle-derived tholeiitic melts are characterised by  $d^{18}\text{O}$  values of +5.7 to +6.0 ‰ (Ripley, 1999). Mafic igneous rocks crystallizing from such magmas should thus also show the same range of oxygen isotopic values. Deviations from the above oxygen isotopic range require explanation that may include hydrothermal alteration and exchange with a fluid phase, derivation from anomalous  $^{18}\text{O}$ -zones in the mantle related to crustal recycling, or assimilation of crustal material (Ripley, 1999).

The magma that gave rise to the eastern and western Bushveld Complex has been found to have  $d^{18}\text{O}$  values of +6.9 ‰ (Schiffries and Rye, 1989 and Reid *et al.*, 1993, respectively), approximately 1 ‰ higher than values expected for rocks crystallizing from mantle-derived basaltic magma. Furthermore, the oxygen isotopes do not display any systemic variation with stratigraphic height and the authors attributed this and the higher  $d^{18}\text{O}$  values to contamination and well mixing in a staging chamber before emplacement. The model was supported by Harris *et al.* (2005) who also found slightly elevated  $d^{18}\text{O}$  values and no stratigraphic variation.



Orthopyroxene  $d^{18}\text{O}$  values for the eastern Bushveld Complex range from +6.12 to +6.97 ‰ (average +6.6 ‰) and for the western Bushveld Complex +6.2 to +6.8 ‰ (average +6.5 ‰) (Schiffries and Rye, 1989).

Harris and Chaumba (2001) carried out oxygen isotope analyses on plagioclase and pyroxene separates for Upper Zone and Main Zone from the Bellevue core and the Platreef. The Upper Zone and Main Zone from Bellevue core show a restricted range in  $d^{18}\text{O}$  values, from +7.0 to +8.3 ‰ and +6.1 to +7.6 ‰, respectively, indicating crystallisation from a well-mixed, already contaminated, magma having  $d^{18}\text{O}$  values of +7.5 ‰, whereas Platreef samples have generally higher and more variable  $d^{18}\text{O}$  values (+7.4 to +10.3 ‰ in plagioclase and +6.0 to +8.9 ‰ in pyroxene) indicating assimilation of a crustal component, probably Transvaal Supergroup rocks. The authors also noted that some Platreef samples have plagioclase and pyroxene not in oxygen isotope equilibrium at magmatic temperatures, suggesting the Platreef fluid was a mixture of predominantly magmatic water with a minor component derived from the footwall.

Harris et al. (2005) showed that plagioclase, pyroxene and olivine of the Rustenburg Layered Suite have  $d^{18}\text{O}$  values indicating that the magmas from which they crystallized had  $d^{18}\text{O}$  values that were about 7.1‰, that is, 1.4‰ higher than expected for mantle-derived magmas, suggesting extensive crustal contamination. The authors also found no systematic change in  $d^{18}\text{O}$  value with stratigraphic height and interpreted this to suggest that contamination occurred in a 'staging chamber' before emplacement of the magma(s) into the present chamber.



This was followed by isotopic studies by Sharman-Harris *et al.* (2005) on samples from the southern Platreef at Turfspruit, Macalacaskop and Rietfontein, where floor rocks are Duitschland Formation metasediments. The authors reported  $d^{18}\text{O}$  values of +6.5 to +8.5 ‰ for plagioclase, +6.5 to +8.5 ‰ for pyroxene and slightly higher  $d^{18}\text{O}$  values (maximum values of +11.5 ‰) for cordierite from hornfels rafts. However, a calc–silicate from the direct footwall displayed a similar  $d^{18}\text{O}$  values as that of the Platreef itself (+8 ‰).

For the present study, oxygen isotope analyses were carried out on orthopyroxene separates and whole rock samples from Platreef gabbro-norites and a dolomite xenolith, at Indian University, Bloomington, U.S.A. Only three rock samples were analysed, therefore the data and interpretations thereof should be treated with caution. Analytical results are presented in Table 8 and analytical procedures are given in Appendix 1g. This was done to document the  $d^{18}\text{O}$  values of orthopyroxene separates from the Platreef at Townlands and Nonnenwerth and to compare the data to available oxygen isotope data on the Platreef (Harris and Chaumba, 2001; Harris *et al.*, 2005; Sharman-Harris *et al.*, 2005), and the eastern and western Bushveld Complex (e.g. Schiffries and Rye, 1989).

The gabbro-norites and pyroxene separates from the Platreef on Nonnenwerth show  $d^{18}\text{O}$  values that vary from +6.3 to +7.2 ‰ and +4.4 to +5.2 ‰, respectively. These values are within the range for mantle-derived mafic magmas (+5 to +7 ‰) (Ripley, 1999) suggesting little or no contamination in Nonnenwerth rocks. However, the Platreef on Townlands has generally higher  $d^{18}\text{O}$  values (+8.0 to +8.3 ‰ in whole



Sample	Borehole	Distance above base of Platreef (m)	$\delta^{18}\text{O}$ ( $^{\circ}/_{\text{oo}}\text{V-SMOW}$ )	Rock unit
MOX9 bulk	2121	111.32	7.2	recrystallized gabbronorite
MOX9 (PYX)	2121	111.32	5.2	recrystallized gabbronorite
MOX10 bulk	2121	91.1	6.4	recrystallized gabbronorite
MOX10 (PYX)	2121	91.1	4.4	recrystallized gabbronorite
MOX14 bulk	2121	35.77	6.3	melagabbronorite
MOX14 (PYX)	2121	35.77	4.8	melagabbronorite
P15 bulk	TL1-03	57.45	8.1	Middle Platreef gabbronorite
P15 (PYX)	TL1-03	57.45	7.2	Middle Platreef gabbronorite
P19 bulk	TL1-03	44.65	8.0	Middle Platreef gabbronorite
P19 (PYX)	TL1-03	44.65	11.2	Middle Platreef gabbronorite
P25 bulk	TL1-03	8.62	8.3	Lower Platreef gabbronorite
P25 (PYX)	TL1-03	8.62	5.4	Lower Platreef gabbronorite

Table 8: S-isotopic analyses of samples from the Platreef at Nonnenwerth and Townlands. SMOW = standard mean ocean water.

rock samples and +5.4 to +11.2 ‰ in pyroxene) indicating assimilation of a crustal component, probably Transvaal Supergroup rocks. It should be noted that the pyroxene separates and whole rock give different  $\delta^{18}\text{O}$  values probably resulting from post-crystallisation processes. The above would generally be investigated by evaluating the degree of oxygen-isotope equilibrium between coexisting minerals and/or whole rocks, using so-called d-d plots (Gregory and Criss, 1986; Gregory *et al.*, 1989), but unfortunately, only pyroxene separates were analyzed for O-isotopic composition in this study.



This study also shows that  $d^{18}\text{O}$  values on Nonnenwerth are lower and uncontaminated compared to  $d^{18}\text{O}$  values of the Main Zone and Upper Zone from the Bellevue borehole (Harris *et al.*, 2005), eastern and western Bushveld Complex has (Schiffries and Rye, 1989 and Reid *et al.*, 1993, respectively). However the data on both Townlands and Nonnenwerth is in agreement with the trace element and S-isotope data which showed that the Platreef on Nonnenwerth experienced little or no contamination compared to Platreef on Townlands which interacted and was contaminated by floor rock shales. Finally, the data on Townlands is in agreement with previous published O-isotope data on the Platreef (e.g. Harris and Chaumba, 2001; Sharman-Harris *et al.*, 2005; Harris *et al.*, 2005).

### 11.1 Summary

The present study has established that  $d^{18}\text{O}$  values on Nonnenwerth are lower and uncontaminated compared to  $d^{18}\text{O}$  values of the Platreef at Townlands, Sandsloot (Harris and Chaumba, 2001), Main Zone and Upper Zone from the Bellevue core (Harris *et al.*, 2005), eastern and western Bushveld Complex has (Schiffries and Rye, 1989 and Reid *et al.*, 1993, respectively). This may suggest that local contamination with dolomite did not play a role in the mineralization process at Nonnenwerth. Thus, the occurrence of mineralization close to the dolomite xenoliths at Nonnenwerth may be due to the dolomite forming an impermeable layer that forced the magma below into sulphide saturation. Dolomite assimilation may however have played part in other parts of the Platreef e.g. at Sandsloot.



## CHAPTER TWELVE: DISCUSSION AND CONCLUSIONS

### **12.1 Compositional and lithological variation of the Platreef in the northern lobe**

PGE-sulphide mineralization has been known to occur in the Platreef since ca. 80 years. Much of the publicly available data has been generated on localities in the southern and south central portions of the northern lobe, between Grassvally and Drenthe (e.g. Buchanan *et al.*, 1981; Gain and Mostert, 1982; Hulbert, 1983; Barton *et al.*, 1986). Additional data was generated by mining companies in the form of drilling and analyses, but much of these data remained unavailable to the public until recently. Thus, there was a perception that the Platreef occurs only in the south and that it consists of heterogeneous rocks dominated by pyroxenites enriched in xenoliths, as seen at Sandsloot (McDonald *et al.*, 2005), Tweefontein, Turfspruit, and adjacent localities (e.g., Kinnaird, 2005). This has influenced models on the origin of the mineralization during the last decades. The present study describes for the first time the occurrence of the Platreef in the north, and provides a detailed lithological and chemical description. This allows making comparisons of the Platreef along strike, to establish how the reef changes along strike, and ultimately constrains how the mineralization has formed.

#### **12.1.1 Nature of the floor rocks to the Platreef**



Along the nearly 100 km separating the southernmost portions of the northern lobe from its northernmost portions, the Bushveld Complex has transgressed through several kilometers of Transvaal sedimentary rocks. Thus, in the south the floor consists largely of shales of the Timeball Hill Formation on Townlands and Macalacaskop (Manyeruke *et al.*, 2005; Kinnaird *et al.*, 2005), sulphidic shales and limestone of the Deutschland Formation on Turfspruit and Tweefontein (Kinnaird *et al.*, 2005), and Penge iron formation in the northern parts of Tweefontein (Buchanan *et al.*, 1981). From northern Tweefontein through Sandsloot to Zwartfontein, the Platreef rests on dolomite of the Malmani sub-group (White, 1994; Harris and Chaumba, 2001). Interestingly, this is where the peak mineralization occurs at Sandsloot. Some authors e.g., De Waal (1977) proposed that devolatilization of dolomite may increase the O fugacity of the magma, thereby decreasing the activity of  $\text{Fe}^{2+}$  and the S solubility. Finally, from Overysel to Nonnenwerth and adjoining farms, the floor to the Bushveld consists of granite-gneiss basement rocks (Stevens, 2004; Manyeruke, in preparation). Dolomite may have been present based on abundant and occasionally very large and laterally persistent dolomite layers (e.g., at Nonnenwerth and Drenthe), but if so has been largely ingested by the magma.

### **12.1.2 Platreef Lithologies**

Previous studies in the south have shown that the Platreef consists of a variety of rock types, including fine-, medium- to coarse grained gabbronorites, norites, anorthosites, pyroxenites, peridotites and chromitites (Kinnaird *et al.*, 2005, and references therein). At several localities, ultramafic rocks appear to be dominant (e.g., Turfspruit; Kinnaird, 2005). The present study documents that at Nonnenwerth, the



Platreef is essentially gabbro-noritic, with very minor quantities of ultramafic rocks. The lithologies at Nonnenwerth are similar to those at Drenthe (Stevens, 2004). The available data thus suggests that there is significant lithological variation along strike, and that the rocks become less ultramafic towards the north. The observed lithological changes are most likely reflecting increased differentiation of the Platreef magma from south to north, possibly reflecting a feeder zone in the south.

### **12.1.3 Nature of xenoliths**

The xenoliths population in the Platreef includes shales, hornfels, quartzite, ironstone, dolomites of the Transvaal Supergroup and granite gneisses of the Archean granite gneiss basement. Their distribution along Platreef strike seems to be controlled by the nature of the floor rocks immediately underlying the Platreef at different localities. In the south, the xenolith population is variable whereas the northern portions of the northern lobe from Tweefontein and Nonnenwerth have dolomite and calc-silicate xenoliths (e.g., Cawthorn *et al.*, 1985; Buchanan and Rouse, 1984; Holwell and McDonald, 2006) except at Drenthe which additionally has granite gneiss xenoliths (Stevens, 2004). From Rooipoort to Tweefontein, xenoliths present are dominated by hornfels, quartzite, ironstone and calc-silicate (Manyeruke, 2003; Kinnaird *et al.*, 2005) and minor dolomites (e.g., at Macalacaskop and Turfspruit; Kinnaird, 2005). Notably, dolomite xenoliths are present everywhere along the strike of the Platreef even in areas where the Platreef overlies stratigraphically more elevated sedimentary rocks of the Pretoria Group. The along strike variation of the xenoliths in the Platreef suggests the Platreef was contaminated with variable material. However, which one, if any was responsible for the sulphide segregation is unclear.





#### 12.1.4 Mineral compositions

Silicate minerals reveal a compositional break between the Platreef and Main Zone. Although the composition of the two intervals overlap, the Platreef is more heterogeneous, with several samples having high Ni, Cr and Mg# in pyroxenes and An in plagioclase. Furthermore, the Platreef pyroxenes and plagioclase become more primitive with height, whereas in the Main Zone, the silicates become more evolved with height. These compositional differences between the Platreef and the Main Zone suggest that the two units represent distinct influxes of magma.

The orthopyroxenes from the Platreef at Nonnenwerth are more difficult to correlate with other sequences in the northern lobe or elsewhere, partly because of their compositional variations. The orthopyroxenes are markedly less magnesian ( $Mg\#_{57-72}$ ) than orthopyroxenes in the Platreef on the farms Townlands ( $Mg\#_{68-82}$ ; Manyeruke, 2003), Tweefontein ( $Mg\#_{74-78}$ ; Buchanan *et al.*, 1981) and Sandsloot ( $Mg\#_{76-80}$  for the primary reef, McDonald *et al.*, 2005). Plagioclase in the Platreef at Townlands ( $An_{54-84}$ , average 71; Manyeruke *et al.*, 2005) is also more An-rich than plagioclase at Nonnewerth ( $An_{47-75}$ , average 63). The former has a composition similar to plagioclase in the Upper Critical Zone ( $An_{68-85}$ ; Cameron, 1982a; Naldrett *et al.*, 1986; Kruger and Marsh, 1985; Maier and Eales, 1997).

Past studies from south have shown that the Platreef shows important similarities to the Upper Critical Zone (e.g., Wagner, 1929; Hulbert, 1983; Maier *et al.*, 2007). Platreef orthopyroxenes on Nonnenwerth have broadly similar maximum values of Mg# as orthopyroxenes on Drenthe and Overysel ( $Mg\#_{65-77}$ ; Gain and Mostert, 1982;



Cawthorn *et al.*, 1985), where the reef is equally underlain by granite-gneiss and dolomite. These compositions are less magnesian than those of Upper Critical Zone orthopyroxenes ( $Mg\#_{78-84}$ ; Cameron, 1982a; Naldrett *et al.*, 1986; Eales *et al.*, 1993; Cawthorn, 2002). The closest compositional match exists with the central Main Zone and the lower Main Zone seems to be missing. Thus there is trend of reef becoming more differentiated towards the north.

#### **12.1.5 Lithophile whole rock data**

The Nonnenwerth Platreef shows unfractionated trace element patterns, with similarities to the Main Zone at Union Section. Major element data also overlap with central Main Zone. This suggests the Platreef has a B2/B3 magmatic lineage with little contamination or some dolomite contamination. Dolomite contamination is not easily detectable by using major and trace elements due to the paucity of the Transvaal dolomite in most trace elements (Klein and Beukes, 1989). In the south, trace elements are more fractionated, more similar to Upper Critical Zone, and probably also contain some crustal contaminant because the concentrations of the REE are too high to be explained by a trapped melt component of either B1 or B2 Bushveld lineage. Thus, the data shows again that there is a systematic variation along strike, partly due to contamination with variable footwall rocks and possibly because the magma from which the Platreef crystallised became more differentiated from the south northwards along the Platreef strike.

#### **12.1.6 Sulphides and chalcophile elements**



Firstly, the Nonnenwerth Platreef contains broadly similar amounts of sulphides than elsewhere along the Platreef, but the PGE are more fractionated, with higher Pd/Ir ratios. This is in agreement with a more differentiated magma, suggested by the mineral and major elements chemistry and the absence of pyroxenite and chromitite. In addition, laurite is present at Townlands, but not in the northern portions of the northern lobe. Secondly, the present study has established a broad positive correlation amongst those PGE that could behave in a mobile manner (in particular Pd, Hsu *et al.* 1991) and those that are believed to be immobile under most conditions (e.g., Pt and Ir; Fig. 6.9b and e) and between individual PGE and S (for samples with > 0.1 % S), suggesting that magmatic sulphides were the primary PGE collector and that PGE are largely hosted by sulphides. However, there is also considerable scatter, notably in samples from borehole 2199, suggesting some localized secondary mobility of S, Cu, Pt and Pd. Textural evidence for the mobility of these elements is shown by discrete, euhedral grains of moncheite forming a linear trail emanating from the chalcopyrite-plagioclase grain boundary into plagioclase (Fig. 9.1j & k). A similar pattern has been observed at Overysel (Holwell, *et al.*, 2005), Drenthe (Gain and Mostert, 1982) and at Townlands (Manyeruke, 2003; Manyeruke *et al.*, 2005).

At Sandsloot and Turfspruit, sulphides and platinum-group elements are decoupled and the PGE appear to be largely controlled by PGM (Armitage, *et al.*, 2002). Here, the floor rocks consist of dolomite and shale, respectively, which may release fluids in response to heating by the intrusives (e.g. Wallmach *et al.*, 1989). The fluids could potentially have resorbed the sulphides and remobilised S resulting in the formation of



secondary sulphides (chalcopyrite, pyrite and millerite) and PGM. Pd also seems to have locally behaved in a mobile manner, as indicated by the fact that Pt/Pd ratios at Sandsloot and Turfspruit are significantly higher than at Nonnenwerth.

At Townlands, where floor rocks are quartzites and shales, magmatic sulphide assemblages were not identified. The sulphide assemblage is characterized by chalcopyrite > millerite > pyrite > pentlandite. Pyrrhotite occurs locally only and galena and molybdenite are further accessories. Notably, this is the first time that such a sulphide assemblage is reported from the Platreef. This type of mineralization was detected in one drill hole only and therefore, must at this stage be regarded as exceptional and probably local only. This sulphide assemblage differs from being “typical magmatic” and came into existence through syn- to post-magmatic modification including formation of millerite from pentlandite, and pyrite replacing pyrrhotite. It is envisaged that the sulphide assemblage at Townlands originally also developed from immiscible magmatic sulphide droplets and an association pyrrhotite – pentlandite – chalcopyrite. However, this early formation was overprinted and converted to pyrite – millerite – chalcopyrite. The observed sulphide assemblage gives evidence that the conversion took place at elevated fugacity of sulphur ( $fS_2$ ) as will be shown below. This conversion was not completely pervasive, as evidenced by relict pyrrhotite – pentlandite assemblages (Table 3). Furthermore, no direct replacements (millerite after pentlandite and pyrite after pyrrhotite) were observed in situ.



The relative timing of this remobilization and replacement is hard to constrain; it probably took place early on the down-temperature path of the mineralization. Probably, syn- to post-emplacement fluids were also involved as evidenced by amphibole needles crosscutting sulphide grains (Fig. 8.4a).

Sulphide contents in any Unit increase towards the base from disseminated (< 2 vol. %) to semi-massive and disseminated (up to 30 vol. %.) The disseminated sulphides towards the top of each Unit probably formed under moderate  $fS_2$  and low  $fO_2$  conditions whereas those towards the floor probably formed under high  $fS_2$  and  $fO_2$  conditions. The gradients in the S-fugacity in Platreef rocks from Townlands are in agreement with the S-isotope study of the Platreef on Townlands (Manyeruke, 2003; Manyeruke *et al.*, 2005). The authors showed that  $\delta^{34}S$  values from Townlands are distinctively heavier (+2.6 to +10.1 ‰) and increase towards the base of the Middle and Upper Platreef, a phenomenon they attributed to enhanced assimilation of crustal S towards the floor of each layer, perhaps by continued degassing of the floor rocks during crystallisation of the Platreef or by S loss towards the top of each Unit.

The current study distinguishes three different associations of sulphide at Nonnenwerth i.e. the magmatic sulphides, secondary sulphides replacing magmatic sulphides and sulphides associated with secondary silicates. Magmatic sulphides represent the dominant sulphide assemblage. They are represented by composite grains of pyrrhotite often intergrown with chalcopyrite and pentlandite, chalcopyrite and polycrystalline fragmented pentlandite grains along pyrrhotite fractures or pentlandite and chalcopyrite included in pyrrhotite towards pyrrhotite grain margins.



Pentlandite may occur as flame-like exsolution lamellae in pyrrhotite. These magmatic sulphides represent fractionated blebs of sulphide. During crystallization, magmatic sulphide liquid crystallizes to a monosulphide solid solution (mss) with the residual sulphide liquid forming intermediate solid solution (iss) (Barnes *et al.*, 2006). The former recrystallizes to pyrrhotite and pentlandite on cooling and the latter to chalcopyrite and some pentlandite (Barnes *et al.*, 2006) in agreement with the textures displayed by magmatic sulphides.

Secondary sulphides, as defined here, replace magmatic sulphides and lack the zoned, fractionated textures displayed by magmatic sulphides and have a 'rugged' outline. They are dominated by chalcopyrite, pyrite, and minor pentlandite. Pyrrhotite includes subrounded vermicular intergrowths of pyrite and chalcopyrite, in places with a remnant pentlandite suggesting replacement of pentlandite by the two phases. Pentlandite may be altered and replaced by coronas of violarite with relict pentlandite forming islands in violarite suggesting that the pentlandite is relictic and that most of the primary pentlandite has been replaced by violarite. It should be noted that recrystallized gabbronorite samples with high pyrrhotite contents have no pyrite and vice versa. The absence of pyrrhotite may suggest an increase in S fugacity ( $fS_2$ ) resulting in pyrrhotite being transformed to or replaced by pyrite. Minor phases are fine, flame-like exsolutions of mackinawite and small disseminated sphalerite grains in chalcopyrite.

Sulphides associated with secondary silicate assemblages are rare in the Platreef at Nonnenwerth. They are represented by fine disseminated chalcopyrite grains



intergrown with alteration minerals in replacement of primary silicates adjacent to coarse composite sulphides, deuteritic veinlets of pyrite that cut through the plagioclase or pyrite replacing clinopyroxene along cleavage planes and cracks. The sulphides do not display well defined sulphide zonation.

Platinum-group elements and S display good correlation, a pattern also observed at Overysel (Holwell, *et al.*, 2005; Holwell and McDonald, 2006) and Drenthe (Gain and Mostert, 1982) suggesting the mineralization at these localities is magmatic. Thus the degree of S mobility is dependant on the nature of the floor rocks to the Platreef. Where the floor rocks consist largely of relatively unreactive granite e.g., at Nonnenwerth, the platinum-group elements are controlled by sulphides and decoupling of base metal sulphides and platinum-group elements is prevalent where floor rocks are reactive e.g., at Sandsloot and Turfspruit.

With the exception of pentlandite from Nonnenwerth (see below), Pd, Pt and Rh are below the detection limits of the electron microprobe in the sulphides analysed from Nonnenwerth and Townlands. Pentlandites as part of the “typical magmatic” sulphide assemblage at Nonnenwerth constantly contain appreciable amounts of Pd (range from ~ 140 – 700 ppm). This finding is in accordance with literature data (e.g. Gervilla *et al.*, 2004) that pentlandite may carry even up to some % of Pd (substituting for Ni) in its crystal lattice. Accordingly, the Pd contents in Nonnenwerth pentlandite probably reflect a primary magmatic signature.



In contrast, pentlandites from Townlands have Pd contents below the detection limit (20 ppm Pd) of the method. This lack of measurable Pd contents in pentlandite may find the following explanations: (i) Pd in pentlandite was analysed in one sample (P 13) only, and therefore, the results may not be representative. (ii) Pd-bearing PGM could have been mobilized during replacement of 'primary' sulphides by pyrite dominated assemblages into the surrounding silicates (Prichard *et al.*, 2001). (iii) The Townlands sulphide assemblage differs from being "typical magmatic" and has experienced severe syn- to post-magmatic modification as described above. Therefore, the relatively rare pentlandite at Townlands may either represent a second generation of pentlandite, or is a relict primary phase that has suffered an overprint that extracted lattice-bound Pd. Arguments for the latter possibility are provided by the presence of abundant Pd-minerals in sample P 13 (see Table 3).

The analytical work presented here has shown marked differences in Pd contents in pentlandites from the Platreef for the first time. It is suggested that systematic research in this topic would be a worthwhile undertaking to improve our understanding of the distribution of the PGE in Platreef ores. The nature and distribution of the PGM from Nonnenwerth and Townlands are discussed below in section 12.1.7.

#### **12.1.7 Platinum-group mineral, tellurides and trace minerals**

The present study has established that Pd-rich phases account for approximately 70 and 76 % of the PGE-bearing phases at Nonnenwerth and Townlands, respectively and IPGE-bearing phases predominantly occur in the south. The Pd-bearing PGM are





dominated by merenskyite and kotulskite which range in size from <5 to 40  $\mu\text{m}$  in size, averaging 20  $\mu\text{m}$ . Three subhedral to anhedral grains of sperrylite were identified at Townlands.

At Nonnenwerth, The PGM occur predominantly at the contact between sulphide (mostly chalcopyrite, minor pyrrhotite and rare pyrite) and secondary silicate (mostly chlorite and albite after plagioclase) or enclosed in sulphides. Importantly, Pd-rich PGM (Pd-bismuthotellurides) are mostly enclosed in silicates. However, even these PGM enclosed in silicates retain a strong spatial relationship with the base metal sulphides, mostly chalcopyrite, and are associated with secondary minerals (mostly chlorite and albite which replace plagioclase, or rarely amphibole which replaces orthopyroxene and base metal sulphides). The above observation may result from dissolution of the base metal sulphides hosting Pd, and leaving isolated insoluble Pd-PGM behind (Barnes *et al.*, 2007), or Pd may have been remobilized from the sulphides into the surrounding silicates. Based on textural evidence, the latter model is preferred. In contrast, at Townlands, the PGM assemblage is dominated by **Pd-rich** bismuthotellurides, minor sperrylite, rare stibiopalladinite and isomertieite. The PGM occur predominantly enclosed in sulphides (mostly pyrite and minor chalcopyrite and millerite), or locally at the contact between sulphide and secondary silicate (amphibole after orthopyroxene).

In general, there are no dramatic differences between the PGM assemblages at Nonnenwerth and Townlands, also in comparison to descriptions from most other Platreef occurrences (e.g. Kinloch, 1982; Holwell *et al.*, 2006). Bismuthotellurides



predominate followed by rarer arsenides and antimonides. One obvious difference, however, is the wide compositional range of Pt-Pd bismuthotellurides and the presence of Pt-rich bismuthotellurides at Nonnenwerth only, whereas at Townlands, only Pd-rich bismuthotellurides are present. The significance of this finding cannot be evaluated conclusively. The variability may be related to local factors like different host rocks; footwall lithologies, down-temperature re-equilibration, activity of fluids, and other possible causes.

The observation that most of the PGM at the studied Platreef intersections occur mostly intergrown with secondary silicate minerals close to sulphides suggests the PGM formed or re-equilibrated at moderately low temperature conditions. The above is in agreement with the observed resorption of primary sulphides and the occurrence of secondary sulphides e.g. violarite. Low temperature conditions for PGM formation are also supported by the abundance of Pd-rich and Pt-rich bismuthotellurides, the significant substitution of Te by Bi, which are in agreement with the low thermal stability of Merenskyite (Kim *et al.*, 1990) and michenerite (Hoffman and MacLean, 1976). The above data indicate that the (Pt,Pd)-bismuthotellurides formed at temperatures below 500<sup>0</sup>C (Hoffman and MacLean, 1976), which is consistent with their textural sitting in the ore. The above model finds support in the studies on Sandsloot, north of Townlands and south of Nonnenwerth (Holwell *et al.*, 2006) and Turfspruit, north of Townlands and south of Nonnenwerth (Hutchinson *et al.*, 2004). The authors of these previous studies suggest the PGM formed in response to considerable S and chalcophile metals in metasomatic fluids and felsic melts, leading



to the formation of a non-sulphide assemblage dominated by chalcopyrite particularly near the floor contact.

At Sandsloot, the PGM assemblage is dominated by PGE-alloys and tellurides and no PGE-sulphides were identified (Armitage *et al.*, 2002). The abundance of PGE-alloys here is notable as there scarce in the north and south of the northern lobe. In the latter, PGM are dominated by tellurides, bismuthotellurides and antimonides (e.g., Kinloch, 1982; Viljoen and Schürmann, 1998; Holwell *et al.*, 2006; Hutchinson and Kinnaird, 2005). This may indicate considerable sulphide resorption or hydrothermal remobilization where floor rocks are fusible dolomite.

Thus the PGE were most likely initially scavenged by immiscible sulphide liquid within the Platreef magma. During crystallisation of the magmatic sulphide liquid, Pd, Pt, Cu, Ag and Au are incompatible in the mss (Barnes and Maier, 1999) and thus are partitioned into the fractionated Cu-rich liquid in solid solution or exsolved from the sulphide melt. The exsolved PGE may then form PGM on the margins of the crystallised pyrrhotite and pentlandite or when retained in solid solution in the Cu-rich melt, are exsolved and form thin merenskyite lamellae in chalcopyrite, explaining the observed occurrence of merenskyite laths in chalcopyrite. However, on Townlands, the merenskyite exsolution is thicker and occurs in pyrite. The thin nature of the merenskyite lamellae in chalcopyrite may be due to low temperature exsolution and due to lower diffusion speeds in low-S sulphides (chalcopyrite) when compared to high-S sulphides (pyrite) (Peregoedova, *et al.*, 2004). The coarser grains of PGM on the margins of sulphides may suggest preferential distribution of the PGE into the



metal phase (Peregoedova, *et al.*, 2004). The occurrence of the bismuthotellurides close to each other together with silver tellurides and lead tellurides may indicate that these minerals crystallised almost at the same time. This was followed by variable remobilization and secondary redistribution of the PGE in secondary silicates close to partially resorbed sulphides. The remobilization and redistribution PGE may be attributed to various factors among them assimilation of crustal S where floor rocks are of Transvaal Supergroup, devolatilization of dolomite xenoliths which are present along the whole strike length of the northern lobe or interaction of primary magmatic sulphides with late stage magmatic fluids. The involvement of late magmatic/hydrothermal fluids is supported by the occurrence of violarite which is probably of hydrothermal origin.

Addition of floor rock crustal S is supported by the studies of Manyeruke *et al.* (2005). The PGM are dominated by lower temperature Pd-rich bismuthotellurides and minor Bi-, Sb- and Te-bearing phases (Kim *et al.*, 1990), as opposed to the Merensky Reef, where PGE sulphides may constitute a substantial proportion of the overall PGM assemblage (e.g. Kinloch, 1982; Mostert *et al.*, 1982). Therefore, the PGM assemblages at Nonnenwerth and Townlands support the suggestion that the PGM are “secondary” in the sense of Cawthorn *et al.* (2002).

The model of sulphide control for the PGE is supported by the broad positive correlation between Pt and Pd and between PGE and S, and abundance of magmatic sulphides at Nonnenwerth suggesting that sulphides were the primary PGE collector. Even though the base metal sulphides do not host the PPGE (Pt, Pd and Rh) –



except for a certain proportion of Pd in pentlandite – the PGM that do host them maintain a close spatial relationship with the base metal sulphides, underlining the initial control of PGE by sulphides.

### **12.1.8 S and O- isotopes**

S isotopes in the northern sections of the northern limb where floor rocks are granite gneiss are mantle-like e.g., at Nonnenwerth ( $d^{34}\text{S}$  values from +0.73 to +1.87 ‰) and Overysel ( $d^{34}\text{S}$  values from +1.7 to +2.0 ‰; Holwell et al, 2005). This suggests little assimilation of external S at Nonnenwerth, which is in agreement with the available Nd isotopic data from Drenthe ( $\epsilon\text{Nd}$  –6.9 to –7.7; Stevens, 2004). In contrast, in the south where the floor rocks consist of shale and quartzite,  $d^{34}\text{S}$  values are strongly positive suggesting significant assimilation of external S. The observations are supported by the S-isotopic composition of the floor rocks e.g.  $d^{34}\text{S}$  values of –12 to –18 ‰ for the Timeball Hill shale (Cameron, 1982b) and  $d^{34}\text{S}$  values of +2.6 to +10.1 ‰ for metasediments of the Silverton Formation (Manyeruke, 2003; Manyeruke *et al.*, 2005).

The data indicate that Platreef-style PGE-sulphide mineralization may be associated with floor rocks containing variable S contents and S-isotopic signatures. Thus, assimilation of external S during magma emplacement was apparently not the principal controlling factor in sulphide genesis since PGE mineralisation occurs at Nonnenwerth where the Platreef overlies granite gneiss. Instead, significant assimilation of S may have merely modified already existing sulphide melt, essentially diluting the tenor of the sulphides, particularly in areas where the floor rocks consisted of



sulphidic shales, between Townlands and Tweefontein (Manyeruke *et al.*, 2005; Hutchinson and Kinnaird, 2005) and the formation of the lower temperature semi-metal PGM e.g. (Pt,Pd)-bismuthotellurides.

$d^{18}\text{O}$  values on Nonnenwerth are lower and uncontaminated compared to  $d^{18}\text{O}$  values of the Platreef at Townlands, Sandsloot (Harris and Chaumba, 2001), Main Zone and Upper Zone from the Bellevue core (Harris *et al.*, 2005), eastern and western Bushveld Complex has (Schiffries and Rye, 1989 and Reid *et al.*, 1993, respectively). This may suggest that local contamination with dolomite did not play a role in the mineralization process at Nonnenwerth. Thus, the occurrence of mineralization close to the dolomite xenoliths at Nonnenwerth may be due to the dolomite forming an impermeable layer that forced the magma below into sulphide saturation. Dolomite assimilation may however have played part in other parts of the Platreef e.g. at Sandsloot. The data on both Townlands and Nonnenwerth is in agreement with the trace element and S-isotope data which showed that the Platreef on Nonnenwerth experienced little or no contamination compared to Platreef on Townlands which interacted and was contaminated by floor rock shales. Finally, the data on Townlands is in agreement with previous published O-isotope data of the Platreef (e.g. Harris and Chaumba, 2001; Sharman-Harris *et al.*, 2005; Harris *et al.*, 2005).

## **12.2. Magmatic lineage of the Platreef**

The data summarized in the preceding section suggest that the Platreef is very variable along strike, probably due to processes including contamination and



differentiation. The question thus is whether there is a specific magmatic lineage of the Platreef. Or does the Platreef represent magmas of variable composition that were variably contaminated with variable floor rocks?

The Nonnenwerth data clearly indicate overlap with Main Zone, in terms of the lithologies, mineral and whole rock compositions. Thus, the rocks are gabbro-norites, orthopyroxene has Mg# mostly 60 - 70, and plagioclase has An mostly 50 – 75, REE patterns are relatively unfractionated, with Ce/Sm ratios between 5.7 and 10.6 (averaging 8) i.e., a B2 signature. This is in agreement with the data of Stevens (2004) who provided Nd isotopic data on the Platreef at Drenthe which indicate crustal values very similar to the Main Zone of the western Bushveld Complex ( $\epsilon_{Nd} - 6.9$  to  $-7.7$ ). But even at Nonnenwerth, the Platreef is more variable, more PGE enriched, more S enriched, and contains more xenoliths than the Main Zone. Thus one could propose a model of contamination of an initial surge of B2/B3 Bushveld parental magma with dolomite, followed by more B2/B3 magma that was less contaminated with dolomite and formed the Main Zone.

In the south, the Platreef is more variable than in north. At Sandsloot (McDonald *et al.*, 2005) and Drenthe (Maier *et al.*, 2007), there are similarities to Nonnenwerth in terms of the trace element (average Ce/Sm 8 at Nonnenwerth, 9.03 at Drenthe, 7.51 at Sandsloot) and REE patterns, with relatively lower La/Yb<sub>N</sub> (Fig. 9.5) and low total element abundances. At Townlands (Manyeruke *et al.*, 2005) and Rooipoort (Maier *et al.*, 2007), the data indicate mixed B1-B2 signature i.e., higher and more fractionated REE contents (average Ce/Sm 12.6 at Townlands) with relatively higher La/Yb<sub>N</sub>.



Moreover, the high concentration of the trace elements in some samples clearly indicates contamination with shale. It is possible that the entire crustal component is due to contamination with shale, and thus the importance of B1 is uncertain. On the other hand, the presence of dunites, harzburgites and orthopyroxenites below Platreef at Rooipoort (de Klerk 2005) could suggest some B1 influence in Platreef. Magmatic serpentinites are also present at Nonnenwerth, Turfspruit and south of Tweefontein (Hutchinson and Kinnaird, 2005) which could suggest that some B1 magma surges may have reached the north, but this is uncertain as the rock is altered. Alternatively, the serpentinite could also be a cumulate of B2 Bushveld parental magma.

In summary, the Platreef seems predominantly B2 related. This model is supported by close spatial association of the Platreef with the Main Zone. Compositional variation of the Platreef is partly due to variable contamination with various floor rocks, and also to variable state of differentiation of the Platreef and Main Zone magma. The latter is shown by Mg# and Cr content of orthopyroxene, An of plag and variation in Pd/Ir which indicate significantly more differentiation of the Platreef and Main Zone magma towards the northern portions of the northern lobe of the Bushveld Complex. This could reflect distance to a feeder zone in the south. Some localized influence of B1 magma is possible, notably at Turfspruit where Kinnaird reports abundance of peridotite.

### **12.3 Origin of the Mineralization**





Basal sulphides are common in layered intrusions underlain by various floor rocks e.g., Portimo, Finland (Alapieti and Lahtinen, 2002) and East Bull Lake, Canada (Peck *et al.*, 2002). This could suggest that local contamination does play some role in the mineralization process. However, my data show that Platreef is present above variable floor rocks and assimilates variable floor. S isotopes are mantellic in places, trace elements unfractionated. This could suggest that the presence of mineralization is not controlled by assimilation of any specific lithology, or external sulphides. The only common factor at all localities is the presence of dolomite xenoliths. Calc-silicate xenoliths are found at all Platreef localities throughout the northern lobe, suggesting that dolomites formed part of the country rock assemblage during intrusion of the Platreef magma. Thus, the magma may have reached S-saturation in response to assimilation of dolomite which may have lowered the S solubility of the magma in response to devolatilization and oxidation (e.g. de Waal, 1975), which could be supported by the peak mineralization at Sandsloot where floor is dolomite. The importance of dolomite assimilation in causing sulfide saturation in the Nonnenwerth contact rocks is highlighted by the concomitant paucity of sulfides in most other Main Zone rocks elsewhere in the Bushveld. The presence of a dolomite component in the magma is difficult to detect using major and trace element geochemistry, due to the paucity of the Transvaal dolomite in most trace elements (Klein and Beukes, 1989). However, O isotope data from Sandsloot (Harris and Chaumba, 2001) clearly indicate significant assimilated dolomite. At Nonnenwerth, dolomite is absent as floor rocks probably due to effective erosion and assimilation of much of the dolomitic floor rocks at this locality. However, the dolomite xenoliths present have mantellic  $d^{18}\text{O}$  values, possibly ruling out assimilation of dolomite as a trigger to mineralization here.



Additional factors could be enhanced cooling rate along base of intrusions (suggested by occurrence of fine grained contact phases), and perhaps differentiation (differentiated magmas are more close to S saturation, and it is also notable that most basal sulphide reefs are associated with gabbroic rather than ultramafic rocks). Finally, some authors (Lee, 1996) have suggested that sulphides were entrained based on the tenor of Cu and Ni in the sulphides and the concentration of PGE in the Platreef which is difficult to reconcile with local floor-derived sulphur source. Sulphide saturation could have been triggered by mixing of compositionally contrasting magmas (e.g. Naldrett and von Gruenewaldt, 1989; Li and Ripley, 2005). I consider this model unlikely because at Nonnenwerth, Ce/Sm ratios of the rocks are relatively constant, indicating the predominance of one type of magma, namely the tholeiitic B2/B3 Bushveld type.

Where floor rocks were assimilated, devolatilization of the host rocks and xenoliths possibly occurred during or prior to the assimilation process. The resulting fluids, which may have introduced some S as indicated by crustal S-isotopes at some localities, percolated through the semi-consolidated Platreef rocks and would separate as a separate phase once they reach saturation. Ultimately, hydrous phases such as amphibole and chlorite crystallized from this hydrous component, generally in association with sulphides (see Fig. 8.4a). With the cooling of the sulphide- and volatile-saturated Platreef portion of the magma, a sulphide/volatile phase separated from the magma (first boiling). As saturation is approached, coarse/pegmatitic textures start to proliferate. This is followed by precipitation of sulphides and hydrous silicates from the hydrothermal fluid. Where the floor rocks are pelitic e.g., at



Townlands (Manyeruke, 2003; Manyeruke et al., 2005), Macalacaskop and Turfspruit (Hutchinson and Kinnaird, 2005), H<sub>2</sub>O-rich fluids would dominate and hydrous silicates would be common. Where carbonate rocks occur in the floor, CO<sub>2</sub>-rich fluids would dominate e.g. at Sandsloot (Armitage *et al.*, 2002; Holwell *et al.*, 2006). Where the floor rocks are granitic e.g., at Nonnenwerth, Drenthe (Stevens, 2004) and Overysel (Holwell, 2005) the volatile phase would be less prevalent than further south.