

# Platinum-group elements in the Pyroxenite Marker, Bushveld Complex: implications for the formation of the Main Zone

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## ABSTRACT

Concentrations of platinum-group elements and sulphides in the Pyroxenite Marker of the upper Main Zone are variable, but generally low (up to 100 ppb PGE and 0.2 weight % S). The metal patterns may mostly be explained by sulphide segregation from PGE depleted residual Upper Critical Zone magma, but they are inconsistent with sulphide segregation from a replenishing influx of undepleted Critical Zone magma. Instead, we favour a model whereby a relatively cool and dense Main Zone crystal mush intruded the Bushveld chamber during the later stages of the deposition of the Upper Critical Zone and displaced warmer and lighter residual magma depleted in chalcophile metals (Sharpe, 1985). Based on the metal contents and textural evidence such as the occurrence of ophitic textures, we hypothesize that the Pyroxenite Marker formed in response to localized supercooling and the suppression of plagioclase crystallization. The model implies that the layer represents a poor target for PGE mineralization in the upper portions of the Bushveld Complex.

## Introduction

The Pyroxenite Marker is a prominent ultramafic layer located within the predominantly mafic Main Zone of the Bushveld Complex. It is commonly interpreted as a major replenishment to a relatively evolved Bushveld chamber with less differentiated magma (von Gruenewaldt, 1973; Molyneux, 1974; Mitchell, 1990; Kruger, 1994). Based on a laterally continuous PGE anomaly in a regional soil and stream sampling survey (Wilhelm *et al.*, 1997), there has been some speculation about the presence of a PGE-enriched layer in the upper Main Zone particularly in view of the recent discovery of a PGE- and Au-rich horizon in the upper portion of the Skaergaard (Andersen *et al.*, 1998) and Rincon del Tigre (Prendergast, 2000) intrusions. Visible sulphides in some samples from the Pyroxenite Marker suggest that the latter may be a potential target for such a PGE-enriched horizon. However, as yet no PGE data on the Pyroxenite Marker has been published apart from one analysis of a PGE-poor noritic sample reported by Harney *et al.* (1990).

Here, we provide noble metal data from 8 samples of the Pyroxenite Marker and 5 samples of its host rocks at 6 different localities in the western, eastern, and northern lobes of the Bushveld Complex (Figure 1), to evaluate the economic potential of the layer, and to reassess existing models on its origin. Further, we briefly discuss some implications on the emplacement and crystallization of the Main Zone of the Bushveld Complex.

## Previous work

The layered suite of the Bushveld Complex is generally sub-divided into 5 distinct stratigraphic intervals, the Marginal, Lower, Critical, Main, and Upper Zones. The Marginal Zone is largely noritic in character and may represent composite sills or rapidly cooled derivatives of the parental magmas to the Complex (Eales and Cawthorn, 1996). The Lower Zone and the lower portions of the Critical Zone consist of ultramafic rocks (mainly harzburgites and orthopyroxenites containing massive chromitite layers), which become increasingly diluted by norite and anorthosite towards the top of the Critical Zone. The Main Zone is a 3000-3300m package of noritic and gabbro-noritic rocks, with lesser anorthosites (von Gruenewaldt, 1973; Molyneux, 1974; Mitchell, 1990). It is commonly subdivided into subzones A-C (von Gruenewaldt, 1973), based on the composition of the Ca-poor pyroxenes. The basal 1200m subzone A consists of norite, anorthosite and gabbro-norite, and the Ca-poor pyroxene is orthopyroxene. Subzone B is 1000m thick and consists of lithologically and compositionally relatively homogenous gabbro-norite, with pigeonite (now inverted to orthopyroxene) joining primary orthopyroxene as the Ca-poor pyroxene. The base of the 700-800m thick noritic to gabbro-noritic subzone C is, in many parts of the Bushveld Complex, defined by the 0.4-6m Pyroxenite Marker, where primary orthopyroxene may appear again as the sole Ca-poor pyroxene (Marais, 1977; Cawthorn *et al.*, 1991).

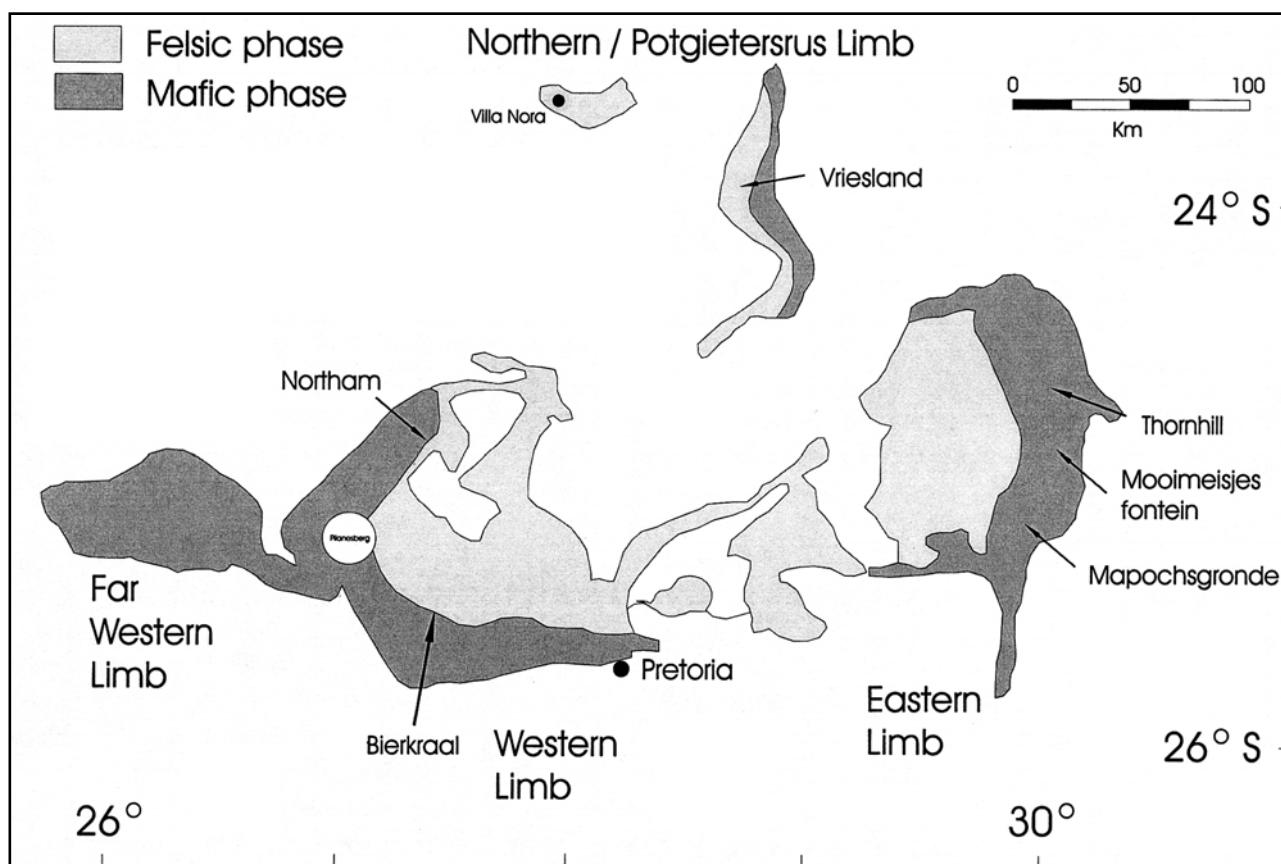


Figure 1. Simplified geological map, indicating sampling localities

However, there appears to be considerable regional variation in the nature of the Pyroxenite Marker. At some localities in the eastern and northern lobes of the Complex, there may be 2 orthopyroxenite layers developed (*e.g.* at Vriesland, Figure 1), at other localities the layer is a mela-gabbro, and yet elsewhere (*e.g.* at Northam mine) the Pyroxenite Marker is a clinopyroxenite. In the Villa Nora and Bon Accord areas the layer does not appear to be developed at all (Gold Fields in-house reports).

The mineralogical change occurring at the level of the Pyroxenite Marker is commonly accompanied by a compositional reversal, such as in Mg# and Cr content of orthopyroxenes (Table 1) and in initial Sr isotopic ratio (Kruger *et al.*, 1987; Cawthorn *et al.*, 1991), towards values more typical of the upper Critical Zone. Notably, in several profiles, the reversal in differentiation index appears to occur over an interval several 100 metres in thickness bracketing the Pyroxenite Marker (von Gruenewaldt, 1973; Cawthorn *et al.*, 1991).

### Field relationships

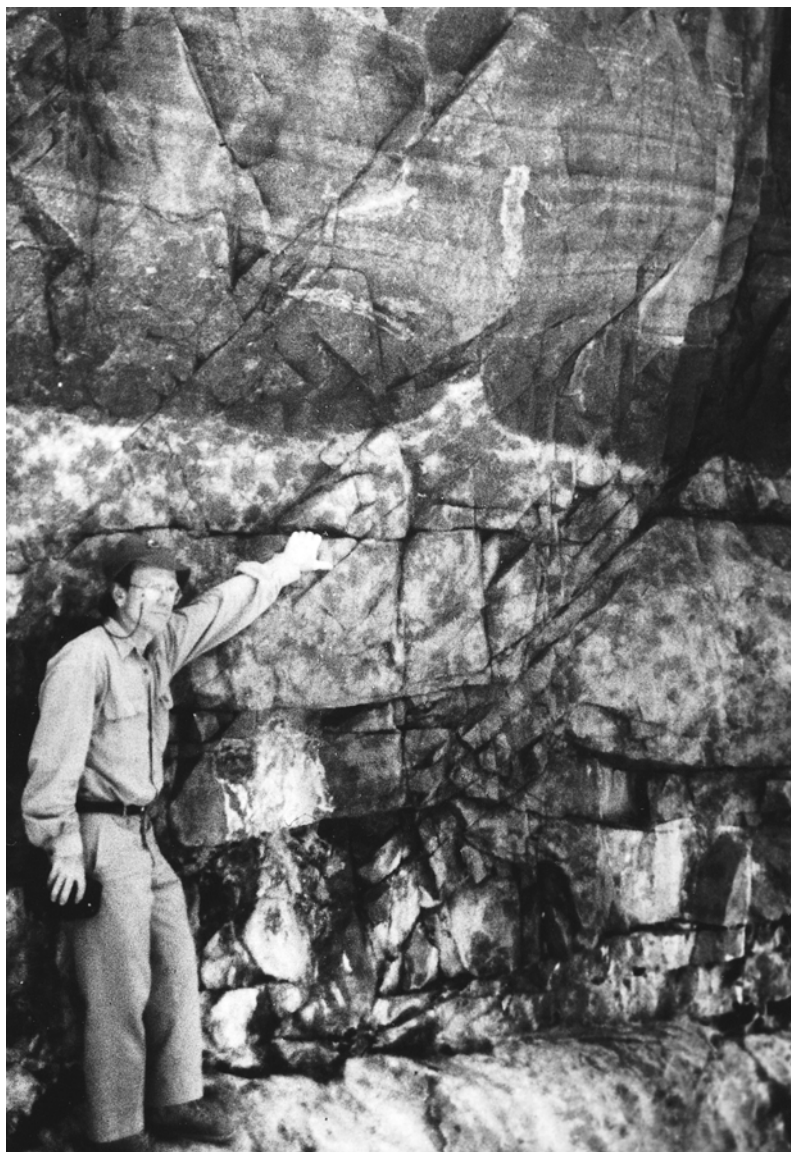
Outcrop of the Pyroxenite Marker is generally relatively poor, except on the farm Mooimeisjesfontein, where the layer is well exposed in a cliff bordering the Mosohlotse stream (Figure 2). This exposure is remarkable because there are structures developed that we interpret to be the result of gravitational instability between relatively light basal anorthosite and overlying denser melanorite

(load structures). The contact between the pyroxenite and the anorthosite forms a lobate surface with apices of the cusps reaching some 10cm in height and spaced at intervals of *ca.* 1 to 3 metres. Flame-like anorthosite veins of up to 10 cm in width extend from the cusps into the overlying pyroxenite and gabbro, without deforming the layering in the mafic rock. This suggests upward percolation of an anorthositic magma or crystal mush in response to compaction. Lobate contacts between basal felsic and overlying mafic-ultramafic layers are also observed in the Upper Critical Zone, below the Merensky Reef, where they are either interpreted as erosional features (Lee, 1981; Eales *et al.*, 1988) or

Table 1. Composition of orthopyroxene in the Pyroxenite Marker and its host rocks (data compiled from Marais, 1977)

	Thornhill	Steelpoortpark	Roosenekal	Tonteldoos
Mg#(opx)				
above PM	0.7	0.7	0.7	0.65
PM	0.74	0.74	0.74	0.62
below PM	0.66	0.65	0.69	0.56
Cr (opx, in ppm)				
above PM	506	775	400	300
PM	541	825	625	350
below PM	212	200	459	75

Notes: PM = Pyroxenite Marker; opx = orthopyroxene



**Figure 2.** The Pyroxenite Marker as exposed on Mooimeisjesfontein. Note the lobate contact between the pyroxenite and the underlying mottled anorthosite, as well as the flame-like anorthosite veins extending from the cusps into the overlying pyroxenite.

reaction replacement phenomena (Nicholson and Mathez, 1991). Further, Parsons and Becker (1987) described load structures very similar in appearance to those described here from the Klokken intrusion of Greenland.

### Sample description

Samples of the Pyroxenite Marker were obtained from 6 localities in the western, eastern and northern lobes of the Bushveld Complex (Figure 1). Sample 1 (Table 2) was obtained from borehole BK2 in the Bierkraal area near Rustenburg, within the basal 10cm of the Pyroxenite Marker. At this locality, the layer is hosted by gabbro-norites (see Kruger *et al.*, 1987; Cawthorn *et al.*, 1991, for a description of the core). Sample 2 was obtained from the base of the Pyroxenite Marker in borehole VB1 at Northam platinum mine in the western Bushveld Complex. Five additional borehole samples from Northam mine (samples 9 to 13) are from the

gabbro-noritic hanging- and footwall of the layer. The eastern Bushveld Complex is represented by 4 surface samples from 3 different localities. Samples 3 and 4 were collected on the farm Mooimeisjesfontein, with sample 3 derived from the cliff shown in Figure 2, some 5cm above the base of the layer, which is approximately 40cm in width at this locality. Sample 4 was collected from poorly exposed Pyroxenite Marker, on a hill slope some 100 to 200m to the north-east of the cliff. The Pyroxenite Marker at Mooimeisjesfontein is underlain by mottled anorthosite, but the hanging wall is gabbro-norite. The remaining two samples (5 and 6) are from the farms Mapochsgronde (next to the Roossenekal-Lydenburg road at km stone 58.0) and Thornhill. For both samples their precise stratigraphic position within the layer, as well as the thickness of the layer is not known. Samples 7 and 8 are also surface samples that were collected on the farm Vriesland in the northern lobe. They represent 2 layers of melanoritic

**Table 2.** Selected element concentrations in samples from the Pyroxenite Marker and its adjacent hostrocks

Pyroxenite Marker		Host rocks												
Sample		1	2	3	4	5	6	7	8	9	10	11	12	13
Locality		Bierkr	Northam VB1 1223	Mooi	Mooi	Mapoch	Thornh	Vriesl upp.layer	Vriesl low.layer	Northam VB1 1214	Northam VB1 1250	Northam VB1 1268	Northam RY5 1473	Northam RY5 1511
Cr	(ppm)	793	na	139	411	640	974	na	na	na	140	41	192	24
Ni	"	410	194	170	270	552	480	147	133	na	95	142	104	79
Cu	"	4	42	15	14	123	100	59	22	16	26	17	27	25
S	"	na	430	113	150	1963	100	<50	<50	870	63	<20	85	80
La	"	2.41	na	na	2.06	1.35	1.16	0.77	0.82	na	1.65	0.9	10.8	6.1
Ce	"	4.9	na	na	4.2	2.54	2.7	1.5	1.3	na	3.24	1.6	22.7	11.4
Nd	"	3.3	na	na	1.3	1.44	1.5	<0.64	1.1	na	1.1	1.7	7.87	4.3
Sm	"	1.21	na	na	0.62	0.53	0.64	0.19	0.17	na	0.41	0.35	1.58	1.17
Eu	"	0.15	na	na	0.31	0.15	0.06	0.38	0.26	na	0.5	0.3	0.7	0.65
Tb	"	0.26	na	na	0.15	0.11	0.12	0.08	0.07	na	0.1	<0.2	0.2	0.2
Yb	"	1.34	na	na	0.76	0.72	0.81	0.48	0.41	na	0.47	0.36	0.74	0.71
Lu	"	0.22	na	na	0.12	0.13	0.14	0.08	0.072	na	0.08	0.07	0.17	0.14
Th	"	0.17	na	na	0.31	0.24	0.05	<0.04	<0.05	na	<0.2	<0.2	2.1	1.4
Hf	"	0.32	na	na	0.34	0.23	0.25	<0.12	0.13	na	<0.3	<0.3	1.3	0.65
Os	(ppb)	0.5	<0.7	<0.2	<0.4	0.2	<0.3	<0.3	<0.5	<0.7	<1.0	<1.2	0.8	<1.0
Ir	"	1.27	0.87	0.05	0.20	0.87	0.18	0.04	0.02	0.07	0.07	0.09	0.07	0.14
Ru	"	2	2	3	2	4	1	<2	<3	<2.3	<2	2	2	<5
Rh	"	4.0	0.2	0.1	0.5	4.7	0.9	0.4	<0.3	0.3	<0.2	0.2	0.54	0.36
Pt	"	82	<3	2	9	8	15	<2	<1	<3	<4	8	<4	19
Pd	"	21	<4	<1	2	15	15	<4	<2	<3	2	1	6	<6
Au	"	2.4	0.8	0.7	0.3	4.3	1.2	0.6	0.5	0.5	0.2	0.8	0.2	0.2

**Notes:** Mooi = Mooimeisjesfontein; Map = Mapochsgronde; Bierkr = Bierkraal; Thornh = Thornhill, Vries = Vriesland; na: not analysed.

Pyroxenite Marker, each being approximately 1m thick and separated from each other by some 2m of anorthosite. Both the foot- and hanging wall of this doublet also consist of anorthosite.

Based on petrographic observations and the concentration of highly incompatible trace elements to be discussed below, the Pyroxenite Marker is an orthopyroxene meso- to orthocumulate at Mapochsgronde, Thornhill, Bierkraal and in sample 4 from Mooimeisjesfontein, containing subhedral and anhedral orthopyroxene (70 to 90 volume %), anhedral interstitial plagioclase (10 to 20 volume %) and clinopyroxene (5 to 15 volume %). Sample 3 from Mooimeisjesfontein is a melanorite and has between 20 and 40% subhedral and anhedral plagioclase, 10% clinopyroxene, and 40 to 60% large anhedral poikilitic orthopyroxene, giving the rock a sub-ophitic texture. The sample from Northam is a clinopyroxenite, with 83% clinopyroxene, 1.7% plagioclase, 14.8% orthopyroxene and 0.5% opaques. The two samples from Vriesland are norites with a similar texture to sample 3 from Mooimeisjesfontein and approximately even proportions of large (up to 1cm) poikilitic orthopyroxene and finer grained (up to 1mm) plagioclase partly included in the orthopyroxene.

Biotite is generally rare, but secondary magnetite is present in serpentinized zones of alteration within orthopyroxene. The sample from Mapochsgronde contains in excess of 0.5% sulphides (pyrrhotite, with lesser chalcopyrite and pyrite), but in the other samples no visible sulphides are present. Mineral compositions of the samples have not yet been determined by us, but summarized data of Marais (1977) from some localities in the eastern Bushveld Complex are given in Table 1.

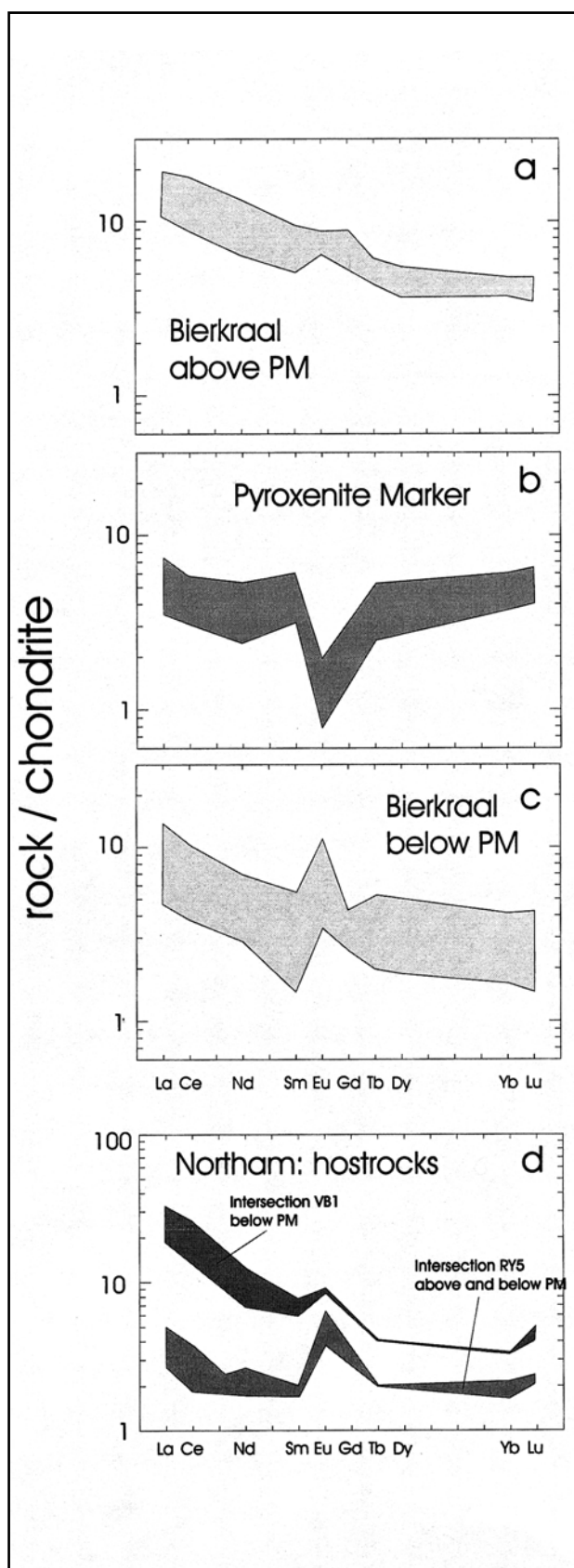
### Analytical results

Concentrations of the platinum-group elements, Au, Cu, Ni, S, and a number of other elements in the analysed samples are listed in Table 2. In the case of sample 1, insufficient sample material was available to perform a S analysis. However, no sulphides were visible in hand specimen. The PGE were determined by instrumental neutron activation (INAA) at the University of Quebec at Chicoutimi (UQAC) after collection of the metals in a Ni-sulphide bead. The analytical procedures and conditions are summarized in Maier and Barnes (1999). Cu was determined by atomic absorption at UQAC, Ni by XRF at the University of Pretoria, and S by LECO titration, at UQAC. The other elements listed were determined by INAA on 2g of whole-rock powder (see Bédard and Barnes, 1990, for analytical methods and conditions), at UQAC.

Chondrite-normalized REE patterns for four samples of the Pyroxenite Marker are flat and have pronounced negative Eu anomalies (Figure 3b), indicative of crystallization from magma that was fractionating plagioclase. This is in marked contrast to the patterns for the over- and underlying rocks, which have positive Eu anomalies and fractionated REE patterns (Figures. 3a; c; Cawthorn *et al.*, 1991; Maier and Barnes, 1998). Concentrations of the highly incompatible elements Th, Hf and Sm indicate that the Pyroxenite Marker contains approximately 10 to 20% trapped melt, depending on whether B1 or B3 magmas are chosen as parents (unpublished data of E. Curl). Trapped melt contents in the gabbroic host rocks appear to be highly variable, based on the variation in REE contents observed at Northam (Figure 3d).

S contents of the Pyroxenite Marker vary between less than 50 and 1960ppm. The analysed host rock





**Figure 3.** Average chondrite-normalized REE patterns of (a) the over- and (c) the underlying gabbroic rocks to the Pyroxenite Marker at Bierkraal (from Cawthorn *et al.*, 1991), (b) four samples of the Pyroxenite Marker analysed in this study, and (d) the host rocks to the Pyroxenite Marker at Northam. Normalization factors are from Nakamura (1974).

gabbros have somewhat lower average S contents, generally below 100ppm (Table 2, and Maier and Barnes, 1998).

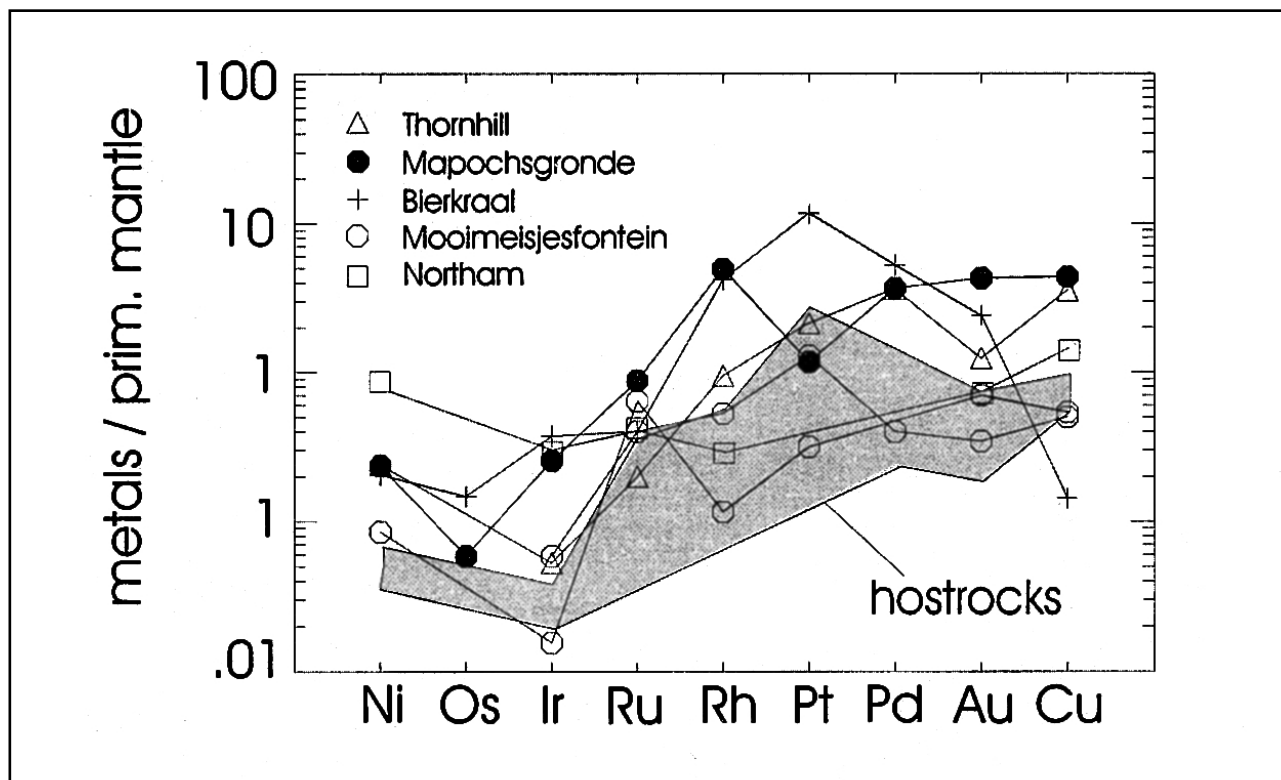
Cu contents vary between 4 and 123ppm, with the latter value coming from the S-enriched sample at Mapochsgronde. Three of the samples fall within the background values for the upper Main Zone of between 10 and 30ppm Cu (Table 2, and Maier and Barnes, 1999). The sample from Bierkraal is extremely Cu-poor suggesting low sulphide contents, while the two samples from Mapochsgronde and Thornhill contain elevated Cu contents. In view of the chalcophile nature of Cu ( $D_{\text{sulphide melt/silicate melt}} = 1000$ , Francis, 1990), there is a remarkably poor correlation between S and Cu in our samples. Ni contents range between 130 and 480ppm. Orthopyroxene in the Pyroxenite Marker contains between 300 and 400ppm Ni (Marais, 1977), accounting for the bulk of the Ni in the rock, and this explains the observed lack of correlation between S and Ni.

Five of the samples from the Pyroxenite Marker have low PGE contents similar to the average levels observed in the remainder of the Main Zone (Figure 4; Table 2; Maier and Barnes, 1999). They have noble metal patterns similar in shape to those from the remainder of the Main Zone (Maier and Barnes, 1998, and Figure 4), with a steady increase from Ir to Pd and a flattening out from Pd to Au. Cu and Ni occur mostly at higher mantle-normalized levels than the PGE ( $\text{Cu}/\text{Pd}_{\text{mantle}}$  significantly higher than unity,  $\text{Ni}/\text{Ir}_{\text{mantle}} 1.26$ ). In the three remaining samples, the PGE contents are somewhat elevated, reaching 110ppb in the sample from Bierkraal. This sample, in particular, shows the arch-shaped pattern typical of PGE-enriched cumulates in the Upper Critical Zone, with low  $\text{Ni}/\text{Ir}_{\text{mantle}}$  and  $\text{Cu}/\text{Pd}_{\text{mantle}}$  ratios (Figure 4). The average Pt/Pd ratio of the samples is 2.2, somewhat higher than that of most of the remainder of the Main Zone, but within the range of the uppermost portion of the Critical Zone (Maier and Barnes, 1999). Pd/Ir and Pt+Pd/Os+Ir+Ru ratios are too variable to allow meaningful comparisons with other portions of the Bushveld Complex.

## Discussion

### *Previous models for the origin of the Pyroxenite Marker*

Based on the compositional and mineralogical reversal observed at the level of the Pyroxenite Marker, as well as the more mafic nature of the layer relative to its host rocks, most authors argued that the chamber had been replenished by relatively undifferentiated magma at this level (von Gruenewaldt, 1973, Kruger *et al.*, 1987; Cawthorn *et al.*, 1991). The nature of the replenishing magma, however, has been poorly constrained. The most specific suggestions come from Davies and Cawthorn (1984) who proposed a magma slightly more differentiated than the B2 magma of Sharpe (1981), with lower MgO, Cr and Ni contents, and represented by fine-grained hypersthene gabbro sills in the Rustenburg area. Cawthorn *et al.* (1991) showed that this magma had



**Figure 4.** Cu, Ni and PGE contents of the analysed rocks, normalized to primitive mantle (normalization factors are from Barnes and Maier, 1999).

elevated REE concentrations compared to the magma from which the underlying cumulates crystallized, and a negative Eu anomaly. This would seem to be in accord with the negative Eu anomalies observed in the four analysed samples of the Pyroxenite Marker, although these patterns may also be explained by mixing of a primitive replenishing magma with differentiated resident magma.

There have been two alternative models proposed for the origin of the Pyroxenite Marker. (i) Klemm *et al.* (1985), while accepting the concept of magma replenishment in the upper Main Zone, suggested that the Pyroxenite Marker itself formed due to the resulting increase in pressure in the chamber, enlarging the stability field of pyroxene. (ii) Based on Sr-isotopic data, Sharpe (1985) suggested that intrusion of relatively cool and dense Main Zone magma above the level of the Bastard Reef led to upward displacement of warmer and lighter, resident, Critical Zone magma. The model of Sharpe was discarded by several other workers (Kruger *et al.*, 1987; Cawthorn *et al.*, 1991; Eales and Cawthorn, 1996), based on compositional, thermal, and density considerations. Their main argument is that, due to heating from above, the cooler basal batch of Main Zone magma could not crystallize until mixing and homogenization of the two distinct magma batches occurred, and this would eliminate the phase and compositional layering so characteristic of the Pyroxenite Marker. Further, they argued that the Main Zone, if it crystallized as an essentially closed system,

should contain more magnetite than the minor amounts observed, but Scoon and Mitchell (1994) showed that segregation of late-stage Fe-rich magma to form discordant iron-rich ultramafic pegmatites (IRUPs) in the Upper Critical, Main, and Upper Zones is a much more common phenomenon than previously thought. Perhaps more problematic is the question about how mixing between magmas that both had plagioclase on the liquidus would have driven the hybrid into the stability field of orthopyroxene alone to cause precipitation of the Pyroxenite Marker. Changes in pressure, as proposed by Klemm *et al.*, (1985), or other intrinsic conditions would offer a possible solution, but remain to be supported independently.

#### ***The Main Zone: intrusion of a plagioclase-rich crystal mush?***

Maier and Barnes (1998) showed that the average composition of the Main Zone cumulates (calculated from their REE data and the data of Mitchell, 1986) is remarkably similar to that of sills in the floor of the Main Zone thought to represent the parental magmas to the Main Zone. They therefore proposed that the Main Zone crystallized as a largely closed system. In that case, the poorly developed cryptic variation observed in large parts of the Main Zone (Mitchell, 1990) could be the result of limited crystal fractionation. Together with the distinct positive Eu anomalies but low incompatible trace element concentrations of the sills in the floor of the Main Zone relative to other high Al-tholeiitic basalts

(Harmer and Sharpe, 1985), this raises the possibility that the Main Zone magma intruded as a plagioclase-rich crystal mush. It is interesting, in this regard, to note that many of the marginal rocks identified by Sharpe (1981) to be associated with the Main Zone appear to have a coarser grain size than the B1 and B2 groups. Other petrographical evidence in support of the model comprises intense deformation textures of feldspar in Main Zone gabbro-norites in the northwestern Bushveld Complex (Eales, pers. com.), including common fracturing and breaking of grains, secondary twinning, and mortar textures. Further, the Nd isotopic data of Maier *et al.* (2000) indicate that the Main Zone magma contained up to 45% of a component of plagioclase-enriched residual crust. This would essentially demand bulk assimilation of the residual crust and would result in a magma containing a large proportion of partially or undissolved crustal material. If this model were correct, then the intruding Main Zone magma may have had an even lower temperature, and a higher density and viscosity than assumed by Sharpe (1985), lending support to his model. And finally, some workers (*e.g.* Czamanske and Bohlen, 1990) equally interpret thick anorthosite units in the Stillwater Complex as intrusions of crystal mushes.

We suggest that the intrusion of a relatively cold crystal mush led to supercooling at the base of the uplifted residual magma batch, possibly kinetic suppression of plagioclase crystallization within the latter, but continued growth of orthopyroxene, resulting in the development of ophitic textures in several of the investigated samples of the Pyroxenite Marker. Convective overturn and homogenization of the two distinct magma batches in the chamber would have been prevented by the high viscosity of the intruding crystal mush, but some resorption of plagioclase phenocrysts in the upper portions of the intruded mush layer may have occurred. The developing gravitational instability between a lower melt-rich felsic layer and an upper mafic-ultramafic layer could have caused the lobate interface and the filter pressing of anorthositic melt observed in Figure 2. Some residual magma may also have seeped down into the intruding crystal mush, explaining the diffuse nature of the compositional reversal described by von Gruenewaldt (1973) and Cawthorn *et al.* (1991).

#### **Evidence from sulphide and noble metal contents**

With the exception of two samples, the sulphide contents of the Pyroxenite Marker are relatively low and in the range of the under- and overlying rocks. The modelling of Li *et al.* (2001, this volume) indicate that cumulates from residual sulphide saturated Bushveld magmas may have S contents in excess of 800ppm S. However, this does not rule out crystallization of the Pyroxenite Marker from residual Upper Critical Zone magma. Segregating sulphide melt may remain entrained in the magma, and sulphides in cumulate rocks may be

partially resorbed by percolating intercumulus volatile-rich melts (Boudreau and McCallum, 1992).

PGE concentrations and patterns of the Pyroxenite Marker are highly variable, preventing meaningful comparisons of parameters such as Pd/Ir and Pt+Pd/Os+Ir+Ru ratios with cumulates of the Main and Upper Critical Zones. However, the Pt/Pd ratios are less variable and suggest an Upper Critical Zone lineage. Cu/Pd ratios are mainly above mantle values (*ca.* 6500, Barnes and Maier, 1999) and argue against the replenishment of the chamber by a B1 or B2 Bushveld magma. Instead, such ratios are in accord with crystallization from metal depleted residual magmas.

#### **Implications for exploration**

The combined data presented here and in Harney *et al.* (1990) suggest that the potential of the Pyroxenite Marker as an ore deposit, raised by Wilhelm *et al.* (1997), is exceedingly low. The PGE and sulphide contents of our samples are, however, relatively variable, in accord with the general lithological heterogeneity of the Pyroxenite Marker. This raises the possibility that the layer may locally contain elevated sulphide and PGE contents, but based on the petrogenetic model envisaged by us for the origin of the layer, such occurrences are likely to be sporadic.

#### **Acknowledgements**

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