

**ECONOMIC GEOLOGY
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**ISOTOPE AND TRACE ELEMENT PATTERNS
BELOW THE MERENSKY REEF,
BUSHVELD COMPLEX, SOUTH AFRICA:
EVIDENCE FOR FLUIDS?**

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. INFORMATION CIRCULAR No. 243

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by

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ABSTRACT

Mineralization in the Merensky Reef of the Bushveld Complex has recently been attributed to the ingress of fluids, possibly via channels beneath depressions in the footwall of the Reef referred to as potholes. In this study samples from immediately below three potholes and from the same horizon (a leuconorite) under normal Reef have been analyzed for oxygen and strontium isotopes, chlorine, and noble metals to investigate this possibility. Results from one pothole are interpreted as retaining the primary magmatic oxygen isotope signature, with average $\delta^{18}O$ of plagioclase and orthopyroxene being $7.1 \pm 0.1\text{‰}$ and $6.6 \pm 0.1\text{‰}$ respectively, and imply a $\delta^{18}O_{\text{melt}}$ of 6.8‰ . These results from the western lobe of the Bushveld Complex, are practically identical to those already established for the laterally equivalent horizons in the eastern lobe. A second pothole shows more variability, with the norite under the pothole Reef showing secondary alteration of plagioclase to paragonite and epidote, and orthopyroxene to serpentine and chlorite. Fresh plagioclase from these altered samples is only slightly depleted in ^{18}O , compared with normal Reef. Measured whole rock $\delta^{18}O$ values are, however, up to 1‰ lighter than those predicted from mineral modes, and suggest that the secondary assemblage contains a component depleted in ^{18}O , which could have been the result of exchange with a low $\delta^{18}O$ fluid. Secondary alteration of the footwall was accompanied by introduction of chlorine. Gold contents also appear to be slightly enriched in the footwall under pothole reef. The sporadic nature of the secondary alteration, interaction with low $\delta^{18}O$ fluids, and enrichment in volatile elements such as chlorine is emphasized.

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INTRODUCTION

Cross-cutting depressions ("potholes") in the layered units immediately underlying the Merensky Reef in the western lobe of the Bushveld Complex of South Africa represent intriguing features of this mineralized horizon. Some of the models invoked to explain potholes involve the migration of residual magma or fluids from underlying cumulates into the overlying magma in the form of fumarole- or exhalative-type emanations. The very process of melt or fluid expulsion was considered responsible for the crater-like potholes, and may in some way contribute to the formation (or at least beneficiation) of the platinum mineralization in the Merensky Reef (eg. Elliot *et al.*, 1982, Kinloch and Peyerl, 1990). Having originated through the upstreaming of melts or fluids soon after consolidation of the cumulate pile, it was further suggested that some of the potholes may have allowed later stage, lower temperature fluids to pass along channelways or chimneys through the cumulate pile, and may contribute further to mineralization of the Merensky Reef (Ballhaus and Stumpfl, 1985, 1986; Boudreau *et al.* 1986). Furthermore, the orthomagmatic model for the origin of these features in which new, superheated magma erodes the footwall also appears to require pre-existing weakness in the underlying cumulate pile, possibly caused by fluid streaming, to form major depressions.

Subsequently, geochemical and mineralogical investigations have been carried out in the search for evidence for fluid interaction beneath potholes developed in the footwall units to the Merensky Reef at Impala Platinum Mines. Cawthorn and Poulton (1988) have reported enrichments in some mobile elements (K, Rb, and Cu) in the footwall of the pothole reef, as well as petrographic evidence for alteration of the primary igneous phases (plagioclase and orthopyroxene). The above authors studied three individual potholes by comparing pairs of vertical profiles through footwall unit 3 (a cumulate norite). Profiles beneath potholes (so-called "pothole reef") were compared with profiles nearby (under so-called "normal reef"). Two of these potholes were chosen for detailed oxygen isotope analysis, whilst all three were analysed for their Cl content. One pothole has been analysed for PGE and gold abundances, although only Ir and Au yielded data of sufficient quality to be reported.

GEOLOGIC SETTING

The Merensky Reef occurs near the boundary between the Critical and Main Zones of the Bushveld Complex (Vermaak, 1976; Kruger, 1990), in a series of incompletely developed cyclic units, comprising pyroxenite, norite and anorthosite with occasional bands of chromite. Most layers within this sequence are traceable over considerable distances, although variations in thickness occur and some layers may be eliminated, possibly by erosion (Viljoen *et al.*, 1986; Eales *et al.*, 1988). The unconformable basal contact of the Merensky Reef is irregular and, in places, occurs in potholes which have been described in detail by many authors (Schmidt, 1952; Ferguson and Botha, 1963; Vermaak, 1976; Schwellnus *et al.*, 1976; Leeb-Du Toit, 1986; Viljoen *et al.*, 1986; Farquhar, 1986; Ballhaus,

1988). They range in size from a few metres to 0.5 km in diameter and may plunge from 1 to 100 m below the normal plane of the Reef. They may have sloping to steep, or even overhanging, margins, and the rocks immediately underlying the normal Reef have been totally removed prior to deposition of the Merensky Reef in these potholes. The base of the Merensky Reef was therefore deposited on an extensive unconformity.

The samples which have been studied came from Impala Platinum Mines, which are situated 10 km north-northwest of Rustenburg in the western lobe of the Bushveld Complex (Fig. 1). The detailed geology and mineralization has been documented by Leeb-Du Toit (1986), and the samples are further described in Cawthorn and Poulton (1988). The typical morphology and relation of potholes to the Merensky Reef are described in that publication and the typical cross section in Figure 2 is based on that work. Footwall lithologies under the Merensky Reef have been described as a series of layered units (numbered Footwall 1 to 6). Several potholes, well exposed during mining operations, bottom out within Footwall unit 3, and thus this unit was the best candidate for this comparative study.

PETROGRAPHY

Footwall unit 3 is a leuconorite, bounded by pure anorthosite below (Footwall unit 4) and a pyroxenite above (the base of Footwall unit 2). This leuconorite is atypical in that the proportion of pyroxene increases upwards (Cawthorn and Poulton, 1988). Cumulus orthopyroxene (En_{74-82}) and plagioclase (An_{74-82}) form the bulk of the rock, clinopyroxene being a minor interstitial phase. There are also infrequent flakes of biotite. No systematic differences exist in the mineral proportions of the rocks at any specific height in Footwall unit 3, between profiles under normal Reef, and under the potholes. However, the more pyroxene-enriched samples comprising the top of Footwall unit 3 are missing under potholes. Under normal Reef, variation with height involves a change in plagioclase content from 80-100% at the base, to 40-50% at the top. Finally, no systematic variation in mineral compositions occurs with height, or between normal and potholed profiles.

While the norites below normal Reef and potholes are similar in their mineralogy and magmatic texture, the extent of post-magmatic alteration does vary in the two settings. Under normal Reef, alteration is very minor. Occasionally, the orthopyroxene contains irregular veinlets of serpentine and the plagioclase has cloudy areas reflecting the formation of clay or zeolite minerals. Under potholes the alteration is more variable, although many samples are indistinguishable from those under normal Reef (eg. Pothole PP). In others, individual grains of orthopyroxene may be totally replaced by an extremely fine-grained alteration product identified as serpentine and chlorite by X-ray diffraction (Cawthorn and Poulton, 1988). Other grains in the same thin section are unaltered. Interstitial clinopyroxene may show variable replacement by tremolite and chlorite. Plagioclase may be replaced by clay minerals, paragonite, and occasionally epidote. The alteration is extremely localised and does not represent a regionally extensive retrograde metamorphism, and the existence of fresh and altered grains in the same thin section demonstrates that equilibrium has not been reached even at that small scale.

Despite the localised nature of the secondary alteration, it is pertinent to note that veining is more prevalent in the norite under some of the potholes (eg. Pothole LL, Poulton, 1986). When compared with

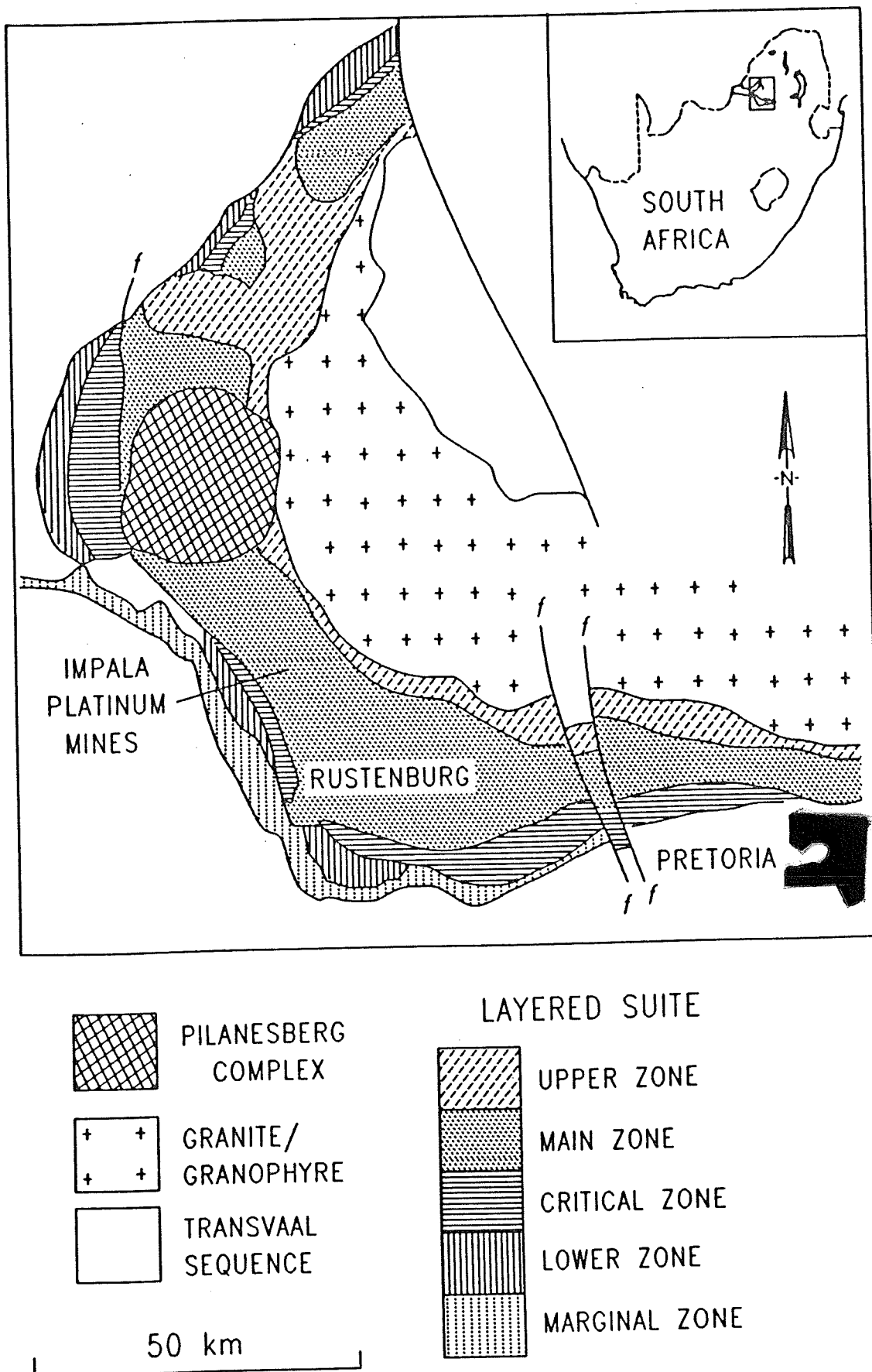


Figure 1: Location of the study area within the Bushveld Complex.

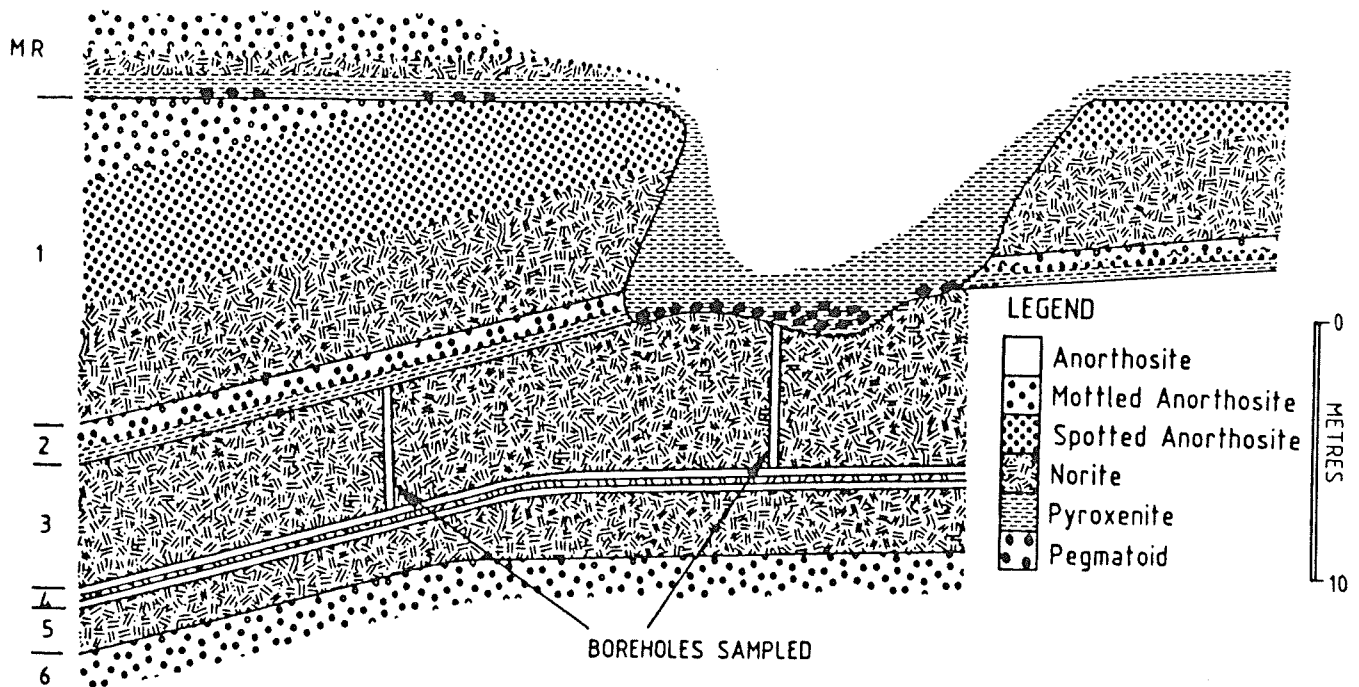


Figure 2: Schematic section of a pothole developed in the Merensky Reef, that has excavated down to footwall norite unit 3 (after Leeb-du Toit, 1986; Cawthorn and Poulton, 1988). The vertical bars in Footwall 3 illustrate schematically the positions of the profiles analysed in the present study.

the descriptions in the eastern Bushveld by Schiffries and Skinner (1987), the alteration in Footwall unit 3 appears similar to their "Middle Stage" family of veins, being characterised by greenschist facies mineral assemblages. Schiffries and Skinner (1987) did, however, stress the regionally developed nature of all their vein systems, although the differences in scale between their study and this investigation could perhaps account for the seemingly localised nature of the alteration identified at Impala.

RESULTS

Sampling and Analytical Techniques

Samples were taken from borehole core that intersected Footwall unit 3 associated with three separate potholes (labelled KK, LL, and PP). Three pairs of profiles, each consisting of a normal (K-, L-, and P-series) and pothole reef (KK-, LL-, and PP-series) section, were thus obtained. Sample positions are relative to the base of Footwall unit 3; and were selected at approximately 0.5 m intervals. Crushed rock samples and powders used in the study of Cawthorn and Poulton (1988) were utilised in the present study. The crushes were subjected to pre-treatment involving successive washings with (1) distilled water to remove dust, (2) alcohol/acetone to remove grease, and (3) 5% nitric acid to remove carbonate. Pure separates of plagioclase and orthopyroxene were obtained using conventional heavy liquid and magnetic methods, followed by hand picking under a binocular microscope. Average grain size was $\sim 200\mu$ for both minerals. Oxygen isotope analysis was carried out using techniques described in Vennemann and Smith (1990). All oxygen isotope ratios were determined by gas source mass spectrometry using a VG 602E double collector instrument in the Department of Archaeology, University of Cape Town.

Conventional delta notation (relative to V-SMOW) is used throughout, with $\delta^{18}\text{O}$ normalised to a value of 9.64 ‰ for NBS-28. All samples were analysed in duplicate, and minerals were reproducible to $\pm 0.09\text{‰}$ on average, while whole rock samples were reproducible to $\pm 0.15\text{‰}$ on average (Table 1).

Sr isotope compositions (including Rb and Sr elemental data) were determined on whole rock powders using conventional techniques described in Eales et al. (1990). The value for SRM-987 obtained during the study was 0.71022 ± 6 . Measured values have been corrected assuming an age of 2060 Ma (Walraven et al., 1990), $\lambda_{87} = 1.42 \times 10^{-11} \text{ a}^{-1}$. Analytical data are listed in Table 2.

Chlorine was determined on whole rock samples by X-Ray Fluorescence (XRF) and details of the method are covered in the Appendix.

The Ir and Au abundances were determined by NiS pre-concentration followed by neutron activation, using techniques described in Davies and Tredoux (1985).

Table 1 contains oxygen isotopic data for two potholes (called PP and LL by Cawthorn and Poulton, 1988). Normal reef samples range in height from the base to + 5 metres, while pothole reef samples are from a truncated section of unit 3 norite. The oxygen isotope composition of orthopyroxene, plagioclase, and whole rock are plotted against height above base in Figure 3.

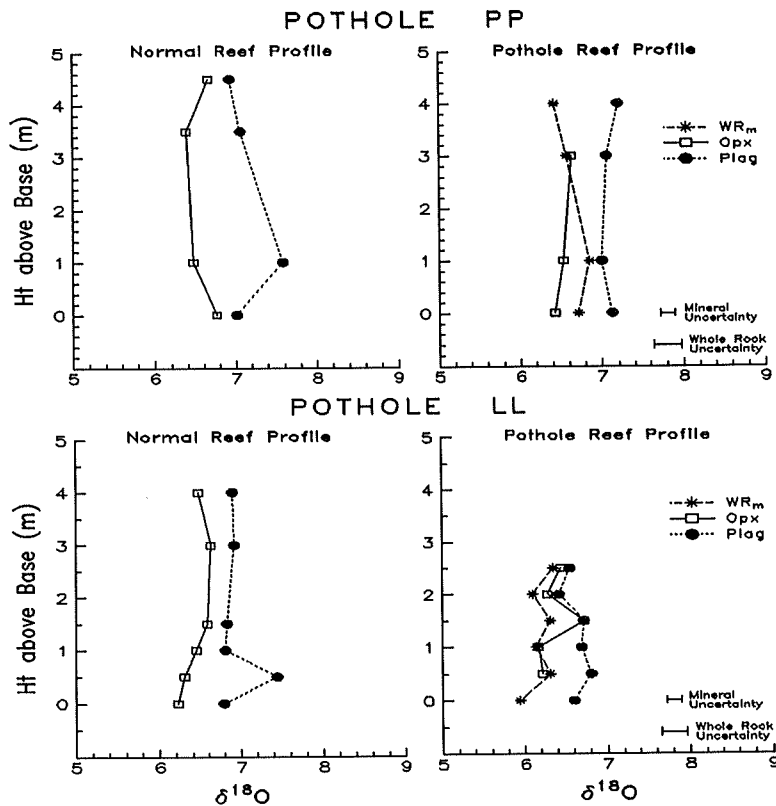


Figure 3: Variation in oxygen isotope composition with height in footwall norite unit 3.

Table 1. Oxygen isotope data for the footwall norite unit 3

Sample	Height above base (m)	$\delta^{18}\text{O}_{\text{plag}}$	$\delta^{18}\text{O}_{\text{opx}}$	$\delta^{18}\text{O}_{\text{melt}}$	Δ plag-opx	T° C	$\delta^{18}\text{O}_{\text{WR}}$ meas	$\delta^{18}\text{O}_{\text{WR}}$ calc	% Plag	LOI
POTHOLE PP										
Normal Reef										
P1	0	7.0	6.8	6.8	0.3	1260		7.0	83	0.79
P3	1.0	7.6	6.5	7.2	1.1	1052		7.2	65	0.74
P8	3.5	7.1	6.4	6.8	0.7	1157		6.8	57	0.53
P10	4.5	6.9	6.7	6.7	0.28	1253		6.8	45	0.68
Pothole Reef										
PP1	0	7.1	6.4	6.8	0.7	1155	6.7	7.1	94	0.99
PP3	1.0	7.0	6.5	6.8	0.5	1208	6.9	6.9	80	0.38
PP7	3.0	7.1	6.6	6.8	0.4	1217	6.6	7.0	78	0.46
PP9	4.0	7.2		7.0			6.4		83	1.98
POTHOLE LL										
Normal Reef										
L1	0	6.8	6.2	6.5	0.6	1184		6.7	84	2.39
L2	0.5	7.4	6.3	7.1	1.1	1048		7.2	76	0.59
L3	1.0	6.8	6.4	6.6	0.4	1232		6.6	69	1.74
L4	1.5	6.8	6.6	6.6	0.3	1260		6.7	67	1.21
L7	3.0	6.9	6.6	6.7	0.3	1250		6.8	71	0.73
L9	4.0	6.9	6.5	6.7	0.4	1217		6.7	54	0.55
Pothole Reef										
LL1	0	6.6		6.4			5.9	6.6	100	3.86
LL2	0.5	6.7	6.2	6.5	0.6	1179	6.3	6.6	66	2.56
LL3	1.0	6.7	6.2	6.4	0.5	1196	6.1	6.5	64	2.26
LL4	1.5	6.7	6.7	6.6	0.0	1320	6.3	6.7	72	2.20
LL5	2.0	6.55	6.45	6.39	0.1	1287	6.4	6.5	55	3.45
LL6	2.5	6.6	6.5	6.4	0.1	1296	6.4	6.5	58	1.75
Errors		±0.09	±0.09			±60	±0.15			

T° C = $1320 - 239(\Delta_{\text{plag-opx}})$ (Schiffries and Rye, 1989)LOI = Loss on ignition corrected for oxidation of Fe (wt % $\text{Fe}_2\text{O}_3/\text{FeO} = 0.05$) (Analytical data from Poulton, 1986)

meas = measured on whole rock powder

calc = calculated using $\delta^{18}\text{O}$ and wt % normative data for plagioclase and orthopyroxene (norms from Poulton, 1986)

Table 2: Rb and Sr concentrations, and measured and initial $^{87}\text{Sr}/^{86}\text{Sr}$ in samples from Pothole LL and adjacent normal succession

Sample	Rb ppm	Sr ppm	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{meas}}$	$^{87}\text{Sr}/^{86}\text{Sr}_{2060}$
L2	1.72	400.1	0.0124	0.706723	0.70635
L4	2.56	318.2	0.0233	0.706967	0.70628
	2.37	318.1	0.0216	0.706899	0.70626
L7	2.02	328.2	0.0178	0.706896	0.70637
L9	1.69	234.2	0.0209	0.706910	0.70629
LL3	4.67	399.6	0.0338	0.707370	0.70637
LL4	6.24	395.9	0.0456	0.707407	0.70605
LL6	3.38	266.1	0.0367	0.707245	0.70615
Errors			0.5 %	0.01%	

Pothole PP

Pothole PP shows limited variation in $\delta^{18}\text{O}$ with height. Both orthopyroxene and plagioclase vary by only 0.4 ‰ (with one sample P3 being the exception). Moreover, there is little difference between the normal and pothole reef profiles. Average data are given in Table 2, and it can be seen that plagioclase under the normal reef has an average $\delta^{18}\text{O}$ of 7.15 ± 0.29 ‰, compared with 7.10 ± 0.09 ‰ under the pothole. A similar result has been obtained for orthopyroxene, with average $\delta^{18}\text{O}$ under normal reef of 6.56 ± 0.17 ‰, and 6.53 ± 0.10 ‰ under the pothole. Since there is a large degree of overlap, it is permissible to combine the data for the two profiles, which yields average $\delta^{18}\text{O}$ for plagioclase of 7.12 ± 0.20 ‰ and orthopyroxene of 6.55 ± 0.14 ‰. Individual mineral pairs do not vary significantly, except for sample P3, where the plagioclase seems to be unusually enriched in ^{18}O , so that $\Delta_{\text{plag-opx}}$ is > 1.0 ‰. Using the average value for $\Delta_{\text{plag-opx}}$ of 0.57 ‰ and the relationship derived by Dunn (1986) and Kyser et al. (1981), a temperature of 1180° C is obtained, which is probably very close to magmatic conditions. Estimates for $\delta^{18}\text{O}_{\text{melt}}$ (also after Dunn, 1986) - assuming equilibrium with plagioclase and orthopyroxene - are also included in Table 1. With the exception of sample P3, $\delta^{18}\text{O}_{\text{melt}}$ ranges between 6.7 and 6.9 ‰, with the average calculated from both profiles being 6.86 ± 0.16 ‰ (Table 3).

Whole rock $\delta^{18}\text{O}$ values for the pothole profile compare well with those calculated from mineral modes in the lower part of the section, but appear to deviate upwards towards the contact with the pothole reef (Fig. 3). The uppermost sample (PP9) shows evidence for secondary alteration, particularly the orthopyroxene (which precluded analysis), and would appear to show the greatest deviation between measured and whole rock $\delta^{18}\text{O}$ values.

Table 3. Average stable isotope data for the two pothole profiles

	$\delta^{18}\text{O}_{\text{plag}}$	$\delta^{18}\text{O}_{\text{opx}}$	$\delta^{18}\text{O}_{\text{melt}}$	$\Delta_{\text{plag-opx}}$	T °C
POTHOLE PP					
Normal Reef	7.2±0.3	6.6±0.2	6.9±0.2	0.6±0.4	1180±100
Pothole Reef	7.1±0.1	6.5±0.1	6.6±0.2	0.6±0.1	1190±40
Overall Average	7.1±0.2	6.6±0.1	6.9±0.2	0.6±0.3	1180±80
POTHOLE LL					
Normal Reef	7.0±0.3	6.4±0.2	6.7±0.2	0.5±0.3	1200±80
Pothole Reef	6.7±0.1	6.4±0.2	6.5±0.1	0.3±0.3	1250±60
Overall Average	6.8±0.2	6.4±0.2	6.6±0.2	0.4±0.3	1220±80
Main Zone ^a	7.0±0.2	6.6±0.2	6.8±0.2	0.4±0.2	1220±40
Critical Zone ^a	7.1±0.1	6.7±0.2	6.8±0.2	0.5±0.1	1210±20

a = Data for the eastern Bushveld after Schiffries and Rye (1989)

The altered nature is also reflected in the high LOI value of 1.98 %, compared with loss on ignition (LOI) values < 1 % in the other samples. Displacement of the whole rock to lower $\delta^{18}\text{O}$ suggests presence of a ^{18}O - depleted component, presumably in the secondary mineral assemblages replacing primary orthopyroxene.

Pothole LL

The variation in $\delta^{18}\text{O}$ in the normal reef profile compares with the patterns observed in Pothole PP. With the exception of sample L2, which again appears to contain plagioclase slightly enriched in ^{18}O , the pattern of variation in both minerals is slight and the average $\delta^{18}\text{O}$ values for plagioclase ($6.95 \pm 0.25 \text{ ‰}$) and orthopyroxene ($6.44 \pm 0.16 \text{ ‰}$) are within error of the overall averages obtained for the other pothole. The average $\Delta_{\text{plag-opx}}$ of 0.41 yields a temperature of 1220° C. Estimates for $\delta^{18}\text{O}_{\text{melt}}$ range from 6.4 to 6.7 ‰ (excluding sample L2), with an average of $6.70 \pm 0.20 \text{ ‰}$.

The profile under the pothole shows more variation, particularly in $\Delta_{\text{plag-opx}}$, and compared with the normal reef profile, the pothole reef profile is displaced to slightly lower $\delta^{18}\text{O}$, albeit by only about 0.4 ‰. The lowermost sample (LL1) is practically devoid of orthopyroxene, and is effectively an anorthosite. It is also highly altered, with the original igneous texture strongly disrupted by brecciation of plagioclase crystals and intense veining. The LOI value of 3.86 % is the highest encountered in all samples analysed. Hand-picked plagioclase, free of veins and alteration, has a $\delta^{18}\text{O}$ of 6.60 ‰, which is slightly lower than the average obtained in the normal reef profile. The altered whole rock sample, however, has a significantly lower $\delta^{18}\text{O}$ of 5.94 ‰, indicating perhaps more strongly the presence of a low $\delta^{18}\text{O}$ component in the alteration assemblage.

Mineral Patterns

Oxygen isotope data for coexisting orthopyroxene - plagioclase pairs are plotted in Figure 4. The clustering of values close to the isotherm corresponding to $\Delta_{\text{plag-opx}} \sim 0.5$, is evident. Also plotted on Figure 4 are fields occupied by samples analysed by Schiffries and Rye

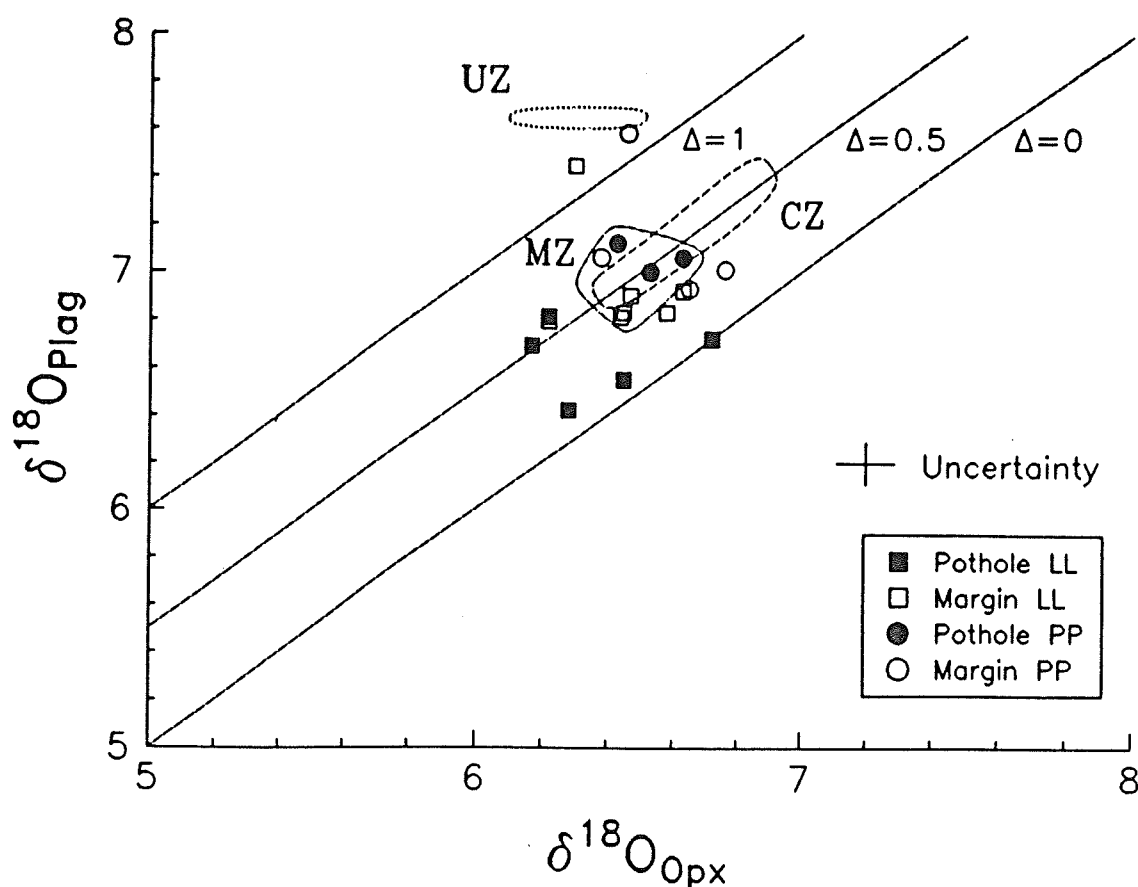


Figure 4: Plot of $\delta^{18}\text{O}$ in coexisting cumulus plagioclase and orthopyroxene in footwall norite unit 3. Dashed lines indicate constant $\Delta_{\text{plag-opx}}$ (or temperature). Fields labelled CZ (Critical Zone), MZ (Main Zone) and UZ (Upper Zone), represent data for the eastern Bushveld from Schiffries and Rye (1989).

(1989), which mainly represent the eastern lobe of the Bushveld Complex. Data for both the Critical and Main Zones of the eastern lobe appear practically identical with those obtained in the present study. Two samples from the western Bushveld analysed by Schiffries and Rye (1989) come from the Merensky Reef itself, and do not differ significantly from the present data, which have been obtained from the footwall.

Data which plot outside the fields established above include the profile under Pothole LL, all which appear to show displacement to low $\delta^{18}\text{O}_{\text{plag}}$, and two samples from each of the normal reef profiles, which have already been alluded to as having high $\delta^{18}\text{O}_{\text{plag}}$. These latter two samples have $\delta^{18}\text{O}$ compositions very similar to those reported by Schiffries and Rye (1989) for Upper Zone rocks from the eastern lobe.

Strontium isotopes

The Rb-Sr isotopic data for samples from Pothole LL are listed in Table 2 and plotted in Figure 5, which reveals small differences between the normal and pothole reef profiles. Pothole reef samples have slightly

higher Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those under the normal reef. There appears to be some alignment such that when regressed using the errors listed in Table 2, the data yield an isochron (MSWD=1.26, F-value=2.25) with an "age" of 1513 ± 322 Ma. The very high error in the age is caused by the small dispersion in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This Rb-Sr age is younger than that assigned by Walraven et al. (1990) for the Bushveld layered rocks (2060 Ma). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio obtained from the Rb-Sr isochron is 0.70648 ± 13 , which is barely distinguishable from the average initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70625 ± 10 calculated assuming an age of 2060 Ma.

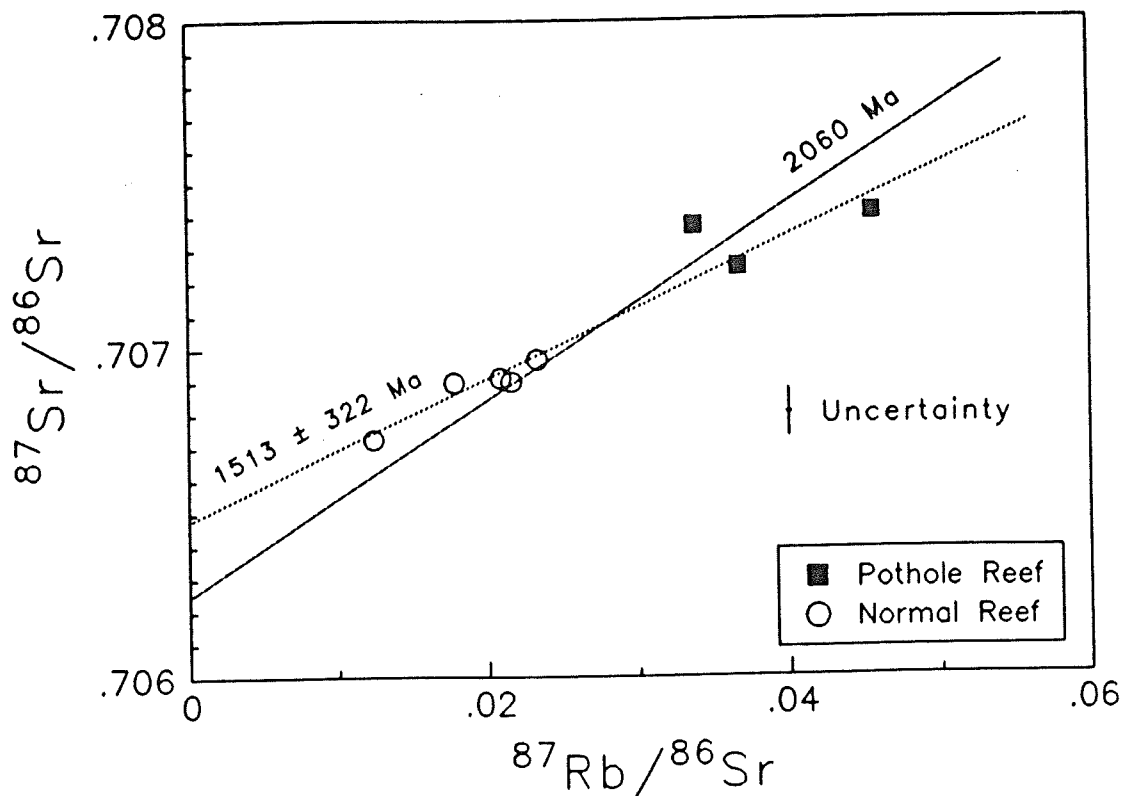


Figure 5: Plot of Rb-Sr isotopic data for samples from Pothole LL. Normal reef (L-series) and potholed reef (LL-series) are distinguished. Reference isochrons correspond to the assigned emplacement age of the Bushveld layered rocks (2060 Ma after Walraven et al., 1990), and the best fit line through the data (1513 ± 322 Ma, MSWD = 1.26, F-value 2.25).

Chlorine Contents

The concentration of Cl in all samples is extremely high compared to typical basaltic rocks (Mitchell and Schilling, 1989). As the Bushveld samples are adcumulates (as evidenced by their very low incompatible element abundances of Rb, K, and Zr) the abundance of Cl (Table 4) relative to magmas is remarkable. There is no correlation between the P_2O_5 (Cawthorn and Poulton, 1988) and Cl contents to suggest that the Cl is largely trapped in Cl-rich apatite (Boudreau and Kruger, 1990), and so the mineral setting of the Cl is unknown.

The chlorine abundances have been plotted against measured $\delta^{18}\text{O}_{\text{WR}}$ and LOI (recalculated assuming a fixed $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio) in Figure 7. Chlorine appears to show a negative correlation with $\delta^{18}\text{O}$, but correlates positively with LOI. While it could be debated that since Cl is a volatile element, it would by definition, influence the LOI, the big difference in abundance levels (eg. 1% LOI against 100 ppm Cl) seen in Figure 7b argues against any significant control.

Table 4. Chlorine contents (in ppm) in three pothole profiles through footwall norite unit 3. P,K,and L samples from normal Reef intersections. PP, KK,and LL samples from below pothole Reef

Sample	Height above base (m)	P	PP	K	KK	L	LL
10	4.5	204					
9	4.0	186	319	188	142	68	
8	3.5	166	336	136	105	73	
7	3.0	195	94	149	100	84	190
6	2.5	226	147		103	92	204
5	2.0	131	119	125	128	118	284
4	1.5	120	74	77	74	109	277
3	1.0	145	80	111	167	97	398
2	0.5	158	76	68	110	95	380
1	0	147	110	125	118	159	363
Average		168	150	122	116	92	300

Iridium and Gold Contents

The only platinum group element for which good quality data are available is Ir, while Au was also determined satisfactorily. Analytical data are listed in Table 5. As is predictable for adcumulate norites, the Ir and Au levels are very low (≤ 10 ppb), and reflect the lack of significant trapped melt component. It can be seen from the normal reef profile (P-samples) that average Ir and Au levels are 0.9 ± 0.7 ppb and 1.4 ± 0.8 ppb respectively. This suggests that abundance variability is of the order of 1.0 ppb for both elements, and real differences would have to exceed this value. In the case of Ir, the pothole reef profile (PP-samples) is slightly enriched relative to the normal reef, although the higher average value (2.0 ± 2.8 ppb) of the former is effectively controlled by the single elevated value in sample PP1. Previous work on PGE distribution within Bushveld rocks has shown that enrichment in PGE is sometimes related to chromite accumulation. Inspection of Cr abundances in the Pothole PP profile (Poulton, 1986) reveals that PP1 has the lowest Cr content of all the samples (262 ppm; overall range 262-1621 ppm). Chromite control on the Ir abundances does not seem to be important. More significant perhaps is the difference shown in Au contents. The pothole reef profile is consistently enriched in Au relative to normal reef, and has an average value of 4.6 ± 2.3 ppb, compared with 1.4 ± 0.8 ppb.

Table 5. Precious metal contents (in ppb) in Footwall 3 whole rock samples

Sample	Height above base (m)	Ir		Au	
		P	PP	P	PP
9	4.0	1.1	1.2	2.3	5.1
8	3.5	0.2	1.0	1.7	6.4
3	1.0	0.6	0.5	<0.1	6.9
2	0.5	0.4	0.4	1.8	1.9
1	0	2.0	7.0	1.3	2.5

DISCUSSION

Three of the four vertical profiles through the footwall norite unit 3, that underlies the Merensky Reef at Impala Platinum in the western Bushveld, seem to have retained magmatic oxygen isotope signatures. Temperatures obtained from coexisting orthopyroxene and plagioclase in this cumulate horizon, are in the range 1180 - 1200°C, and point to limited post-magmatic disturbance. This contrasts with the ^{18}O - depleted nature of some other layered mafic intrusions (eg. Skaergaard, Cuillin and Samail complexes), and rules out large-scale exchange with heated low $\delta^{18}\text{O}$ meteoric waters (Taylor and Forester, 1979; Forester and Taylor, 1977; Gregory and Taylor, 1981). Retention of magmatic $\delta^{18}\text{O}$ signatures is, moreover, shared by the Stillwater Complex (Dunn, 1986), with which the Bushveld is often compared (eg. Campbell *et al.*, 1983).

An estimate for $\delta^{18}\text{O}_{\text{melt}}$ in equilibrium with the cumulus plagioclase and orthopyroxene that form the bulk of the norite unit is 6.8‰, and compares well with that estimated by Schiffries and Rye (1989) for Critical and Main Zone rocks in the eastern lobe of the Bushveld Complex. It follows that correlation of the eastern and western Bushveld rocks also applies to the $\delta^{18}\text{O}$ of the parental magmas.

Oxygen isotope data for mineral pairs from a profile under Pothole LL show displacement from the magmatic field in Figure 4, and requires explanation. Possible causes of variation in $\delta^{18}\text{O}$ are illustrated in Figure 6, and include (1) sub-solidus re-equilibration, (2) variation in magma composition, and (3) open system exchange with an externally derived aqueous fluid. Sub-solidus re-equilibration could occur between coexisting phases in response to dropping temperature during cooling. If closed system transfer applies, then the final oxygen isotope composition will be controlled in part by modal composition. Re-equilibration vectors for two modal compositions (40% and 80% plagioclase) are shown in Figure 6 for reference, and represent the range observed in the Footwall unit 3 norite. It is possible that part of the variation in the magmatic field could reflect a response to cooling, although final closure (at $\sim 1000^\circ\text{C}$) is not much lower than the inferred liquidus temperatures. The two mineral pairs with $\Delta \text{plag-opx} > 1\text{‰}$ could perhaps be an extreme case of re-equilibration, and the high plagioclase/orthopyroxene ratio would be consistent with the position of the samples (P3 and L2) being near the anorthositic base of Footwall unit 3. A similar argument could perhaps be proposed for the Main Zone samples analysed by Schiffries and Rye (1989), although these authors suggest that some unspecified secondary alteration processes may have been operative.

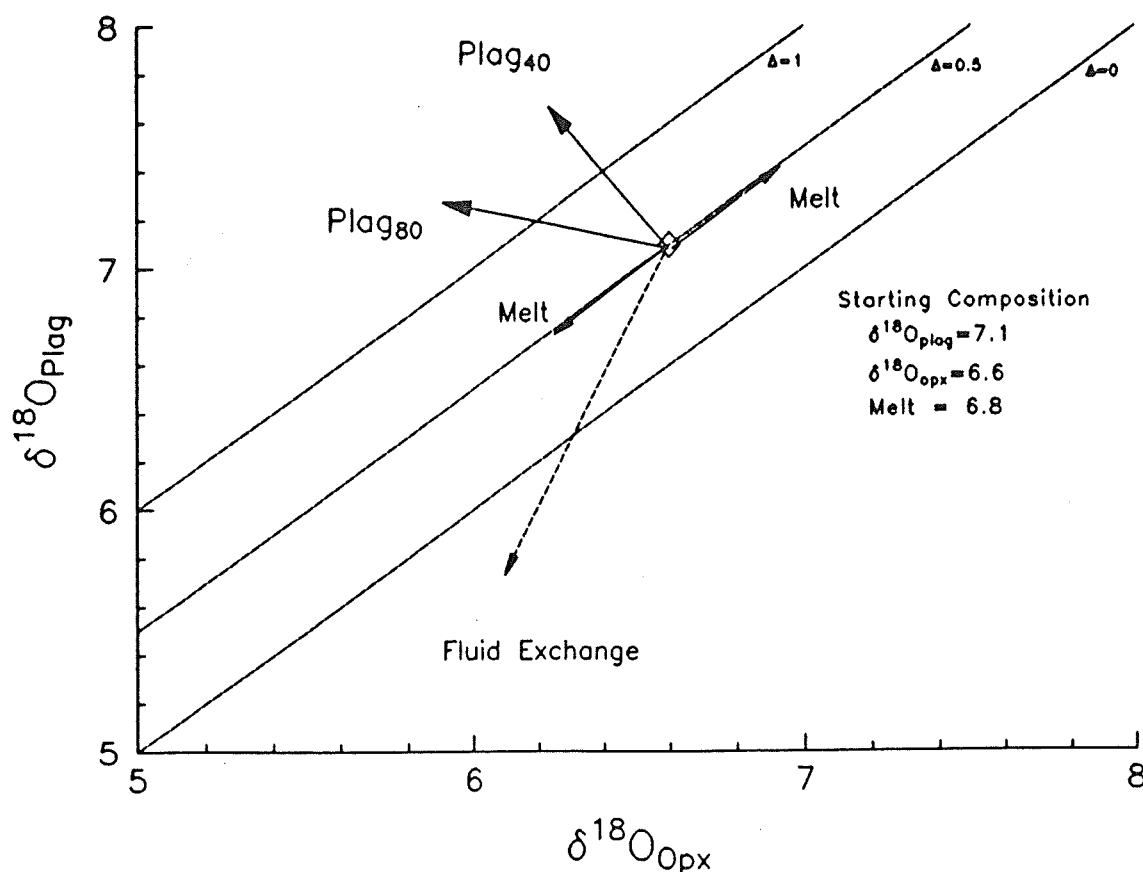


Figure 6: Possible causes of variation in $\delta^{18}\text{O}$ of plagioclase and orthopyroxene in the footwall norite unit. Vectors labelled with Plag_{40} and Plag_{80} correspond to closed system, sub-solidus re-equilibration of orthopyroxene and plagioclase in response to lowering temperature. Vector direction corresponds to rocks composed of 40% and 80% plagioclase respectively. Vectors labelled with "Melt" correspond to possible variation in ^{18}O of the magma from which orthopyroxene and plagioclase co-precipitated at the same temperature. The vector labelled "Fluid Exchange" represents the effect of sub-solidus exchange between the norite and heated meteoric waters strongly depleted in ^{18}O (Gregory and Criss, 1986).

Variation in primary magma composition can be ruled out in this particular case as the samples come from a single norite unit, showing little change in mineral composition or initial Sr-isotope composition vertically or horizontally. However, this does not rule out the possibility that variation in $\delta^{18}\text{O}_{\text{melt}}$ may occur over a greater thickness of Bushveld rocks. The dispersion along the $\Delta_{\text{plag} - \text{opx}} = 0.5\text{‰}$ isotherm observed for the Critical Zone in the eastern Bushveld could perhaps reflect such a variation, although Schiffries and Rye (1989) did not specifically discuss this feature of their data.

Exchange between primary igneous minerals and heated meteoric waters has been demonstrated in several layered mafic complexes (Gregory and Taylor, 1986). The most salient result of this interaction is illustrated in Figure 6, where displacement along a steep vector to lower $\delta^{18}\text{O}$ is caused by differing susceptibilities of orthopyroxene and plagioclase. The degree of displacement is, in part, controlled by the contrast in $\delta^{18}\text{O}$ between the minerals and fluid. It is possible that while

large-scale exchange with heated low $\delta^{18}\text{O}$ fluids can be ruled out, the small displacement observed for the norite profile under Pothole LL could reflect small degrees of fluid interaction, although uncertainty in fluid composition limits any constraint on the degree of exchange.

The fine grain size and sporadic development of the alteration products in the studied samples preclude efficient separation, and the writers were left with comparing the whole rock $\delta^{18}\text{O}$ data as measured, with those calculated using mineral modes. Both profiles under the potholes studied showed differences between measured and calculated $\delta^{18}\text{O}$ values, but the profile under Pothole LL showed deviation practically throughout. Sample LL1, for example, has a whole rock $\delta^{18}\text{O}$ of 5.94 ‰, compared with a probable primary value of ~ 7.1 ‰, judging by the results obtained from unaltered samples. The differences suggest the presence of a low $\delta^{18}\text{O}$ component in samples showing alteration, as evidenced by greater modal alteration observed in thin section, as well as elevated LOI. There also seems to be a rough correlation between the degree of secondary alteration and the displacement of the whole rock $\delta^{18}\text{O}$ value. It is strongly suggestive of the secondary alteration products (serpentine, chlorite, paragonite, epidote) having very low $\delta^{18}\text{O}$, presumably due to exchange with ^{18}O - depleted fluids, which were responsible for their development.

Results of the oxygen isotope study indicate that little post-magmatic disturbance has taken place in Footwall 3, either under normal or pothole Reef. However, in some localities where there is petrographic evidence for secondary alteration, in the form of medium-low temperature hydrous phases (including serpentine and chlorite replacing orthopyroxene, and paragonite and epidote replacing plagioclase), there is also evidence for exchange with fluids depleted in ^{18}O . The degree of exchange, as may be indicated by the lowering of $\delta^{18}\text{O}$ in plagioclase, appears to be slight, although the secondary assemblages are probably characterised by very low $\delta^{18}\text{O}$. The sporadic nature of this alteration and interaction with low $\delta^{18}\text{O}$ fluids is emphasized. The mineralogy (serpentine, chlorite, tremolite, paragonite, epidote) and texture (irregular fine veinlets and variable alteration even on the scale of a thin section) suggest that this alteration took place at low temperatures in the greenschist facies as suggested by Schiffries and Rye (1989). This is at much lower temperatures than suggested for the fluids by Elliot *et al.* (1982), Ballhaus and Stumpfl (1986) and Boudreau *et al.* (1986).

The inferred low temperature of alteration under the potholes does suggest that it occurred some time after emplacement of the layered rocks. Just how long after emplacement could perhaps be forthcoming from the Sr-isotope data. Although only one pothole has been investigated, it is the one showing the greatest degree of alteration (Pothole LL). The alignment of the data in Figure 5 may be an artefact of alteration, in that the high Rb/Sr data points may have been caused by alteration, since Cawthorn and Poulton (1988) have reported enrichments in Rb (and other mobile elements) under the potholes. Introduction of Rb alone will have no effect on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, but could cause the type of pattern observed in Figure 5, in which case the errorchron has no age significance. This explanation would imply that the time of Rb introduction (and hence the alteration) was very late, in order to cause clockwise rotation of the Rb-Sr isochron. No quantitative estimate of the age can be made however.

Another possible explanation is that the Rb-Sr array does in fact have some age significance, in that a discrete alteration event did indeed occur long after emplacement of the layered rocks. The Rb-Sr age of

1513 \pm 322 Ma overlaps within error of the \sim 1300 Ma Pilanesberg Complex and associated dykes (Ferguson, 1973), which intrude the western Bushveld Complex (Fig. 1). Hydrothermal fluids associated with this alkaline complex may have been responsible for the introduction of Rb, and other mobile elements such as K and Cl. A closer look at alteration of Bushveld layered rocks in the aureole around the Pilanesberg Complex is perhaps warranted.

If the slight increase in ^{87}Sr seen in the pothole reef samples is neglected, then the average initial $^{87}\text{Sr}/^{86}\text{Sr}$ calculated at 2060 Ma of the seven samples is 0.70625 ± 10 , and compares closely with previously published data for the upper Critical Zone (Kruger and Marsh, 1982; Sharp, 1985; Eales *et al.* 1990). This shows that the fluid responsible for the alteration observed either did not carry a significant amount of Sr relative to the altered assemblage, or the Sr had the same isotopic composition as the surrounding cumulates. This is in strong contrast to the cross-cutting ultramafic pegmatites which are common in the succession and appear to have exchanged totally with their host rocks (Kruger, 1989). This is a significant observation as the ultramafic pegmatite bodies favour areas of greater pothole density, suggesting the control by pre-existing channels.

In one pothole (LL) the Cl abundance is very much higher than the adjacent normal section; while for the other pothole there is no difference in the average Cl content in the two profiles (P and PP). However, the variance in Cl content in the pothole section is far greater than the normal section. Greater variance for the mobile incompatible elements in pothole environments was also recorded by Cawthorn and Poulton (1988).

The covariation between Cl and LOI displayed in Figure 7b suggests that Cl may have been controlled by the same process that increases LOI. In other words, since LOI is probably predominantly H_2O , introduced as hydrous phases during secondary alteration, Cl must have been introduced at the same time. The negative correlation between Cl and measured $\delta^{18}\text{O}_{\text{WR}}$ (Figure 7a) further indicates the close relationship between secondary alteration, introduction of H_2O and Cl, with depletion in ^{18}O . The strong correlation between these values suggest that H_2O and Cl were introduced by the same event. The steady decrease in $\delta^{18}\text{O}_{\text{WR}}$ with increasing Cl and LOI further supports the idea of the involvement of a low $\delta^{18}\text{O}$ fluid. One pothole section enriched in Cl, Cu, Rb, and K; and two others with highly variable values for these elements, suggest that redistribution does not prove that fluid migration has been focussed on pothole environments; but is consistent with this model.

The pothole chosen for Ir and Au analysis shows little variation in Cl, $\delta^{18}\text{O}$, and LOI, as well as little development of secondary hydrous phases. Yet the pothole reef is definitely enriched in Au and maybe in Ir. A clearer picture may emerge after further PGE analyses of more altered profiles (such as the LL-samples) which show high Cl, LOI abundances and depletion in ^{18}O . At this stage, it can only be noted that noble metal abundances do indeed vary within the footwall norite unit studied, and there exist circumstantial evidence that such variation is associated with the development of potholes in the Merensky Reef.

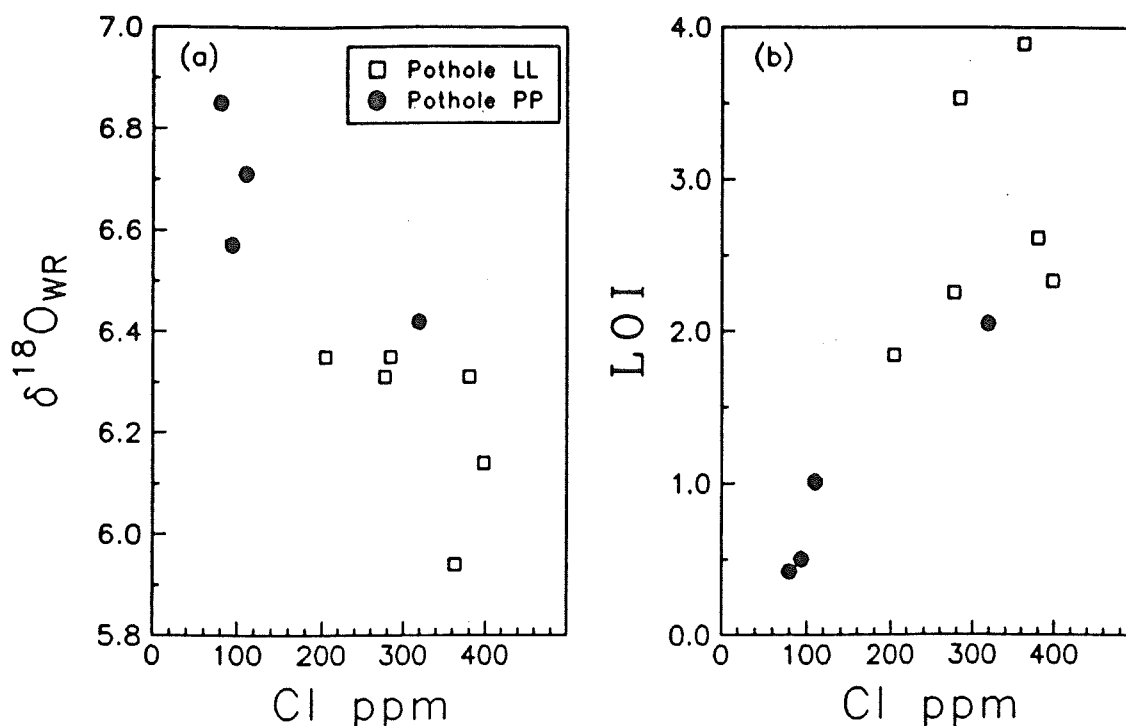


Figure 7: Variation of Cl with (a) measured $\delta^{18}O$ and (b) LOI in Footwall unit 3 norite under potholes PP and LL.

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APPENDIX

Analytical techniques for chlorine in whole rock powders using XRF spectrometry followed those of Leake et al. (1969), who also presented a recommended set of values for international standards. The following standards (which cover the range of Cl concentrations in this study) gave a reasonable working curve (contents in ppm):

RGM (recommended by Leake et al., 1969)	540	(this study)	520
AGV-1	185		150
GSP-1	330		301
G-2	100		107

Others were inconsistent. It is uncertain whether this is because the data of Leake et al. (1969) are inaccurate or whether contamination of the standards had occurred. Some samples were analysed in duplicate. First, the pressed pellet used for trace element analysis (Poulton, 1986) was analysed. Subsequently, further samples of rock powder were washed in distilled water and pressed pellets prepared with different volumes

of binding agent (Mowiol) dissolved in acetone. Differences of up to 20 ppm were recorded, but were not consistently lower for the samples prepared with distilled water, nor did they increase systematically with larger volumes of binding agent. For these reasons, the data are **probably** only reliable to ± 20 ppm. Sixteen replicate analyses of standard RGM run as an unknown during a three month period gave a precision of 520 ± 27 ppm. Few previous analyses of Cl are available in the literature, and Mathez (1990) has pointed out that it is difficult to draw inferences about Cl in mineralised horizons because of this lack of data.

However, in order to test the significance of these results the writers have also analysed some fresh samples from the Karoo Igneous Province for comparison. The samples chosen were cumulates (to be more comparable with the Bushveld samples) from the Mount Ayliff Intrusion (Cawthorn *et al.*, 1988), a 500 m-thick differentiated sheet. The range in values obtained from this Karoo intrusion was from 47 - 174 ppm with an average of 85 ppm, and so are considerably lower than those determined from the Bushveld Complex. For further comparison, samples from the lower Critical, Main, and Upper Zones of the Bushveld Complex were analysed. Chlorine contents throughout the intrusion appear extremely high, although randomly variable. The average for 219 samples is 246 ppm. Hence, the writers conclude that the entire intrusion is enriched in Cl, and not merely in proximity to the Merensky Reef.

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