

Oxygen and Hydrogen Isotope Stratigraphy of the Rustenburg Layered Suite, Bushveld Complex: Constraints on Crustal Contamination

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New $\delta^{18}\text{O}$ values for plagioclase, pyroxene and olivine, and limited whole-rock δD values are presented for samples from the Rustenburg Layered Suite of the Bushveld Complex, South Africa. In combination with existing data, these provide a much more complete composite O-isotope stratigraphy for the intrusion. Throughout the layered suite, mineral $\delta^{18}\text{O}$ values indicate that the magmas from which they crystallized had $\delta^{18}\text{O}$ values that were about 7–1‰, that is, 1.4‰ higher than expected for mantle-derived magmas, suggesting extensive crustal contamination. More limited H-isotope data suggest that the OH present within whole rocks, regardless of the degree of alteration, is of magmatic origin and not an alteration phenomenon. There appears to be no systematic change in $\delta^{18}\text{O}$ value with stratigraphic height and this requires the contamination to have taken place in a ‘staging chamber’ before emplacement of the magma(s) into the present chamber. Large amounts (30–40%) of contamination by the lower to middle crust are needed to explain these $\delta^{18}\text{O}$ values, which is in general agreement with previous estimates based on Sr- and Nd-isotope data. Alternatively, smaller amounts of contamination (~20%) by sedimentary rocks, or their partial melts, represented by the country rock can explain the data, but it is not apparent how such material could have been present at the depth of the ‘staging chamber’ in the lower to middle crust.

KEY WORDS: Bushveld Complex; Rustenburg Layered Suite; oxygen isotopes; hydrogen isotopes; crustal contamination

INTRODUCTION

The mafic–ultramafic component of the Bushveld Complex of South Africa is the largest such igneous intrusion on Earth (e.g. Eales & Cawthorn, 1996) and contains some of the most important magmatic ore deposits yet discovered. The intrusion covers an area of roughly 65 000 km² (e.g. Tankard *et al.*, 1982) and lies almost entirely within the bounds of the sedimentary rocks of the Transvaal Supergroup (Fig. 1). The layered mafic–ultramafic rocks of the Bushveld complex have been designated the Rustenburg Layered Suite [South African Committee on Stratigraphy (SACS), 1980], henceforth abbreviated to RLS, and were emplaced at 2058.9 ± 0.8 Ma (U/Pb date on titanite, Buick *et al.*, 2001). The RLS is most commonly subdivided using a zonal stratigraphy into a norite Marginal Zone, an ultramafic Lower Zone (LZ), an ultramafic to mafic Critical Zone (CZ), a gabbro-noritic Main Zone (MZ), and a ferrogabbroic Upper Zone (UZ). The boundaries between the zones are not always defined in the same way by different researchers, but the exact position of boundaries is not of great significance to the present paper. A schematic stratigraphic column is shown in Fig. 1. Despite the large amount of existing data, no consensus has yet been reached on the

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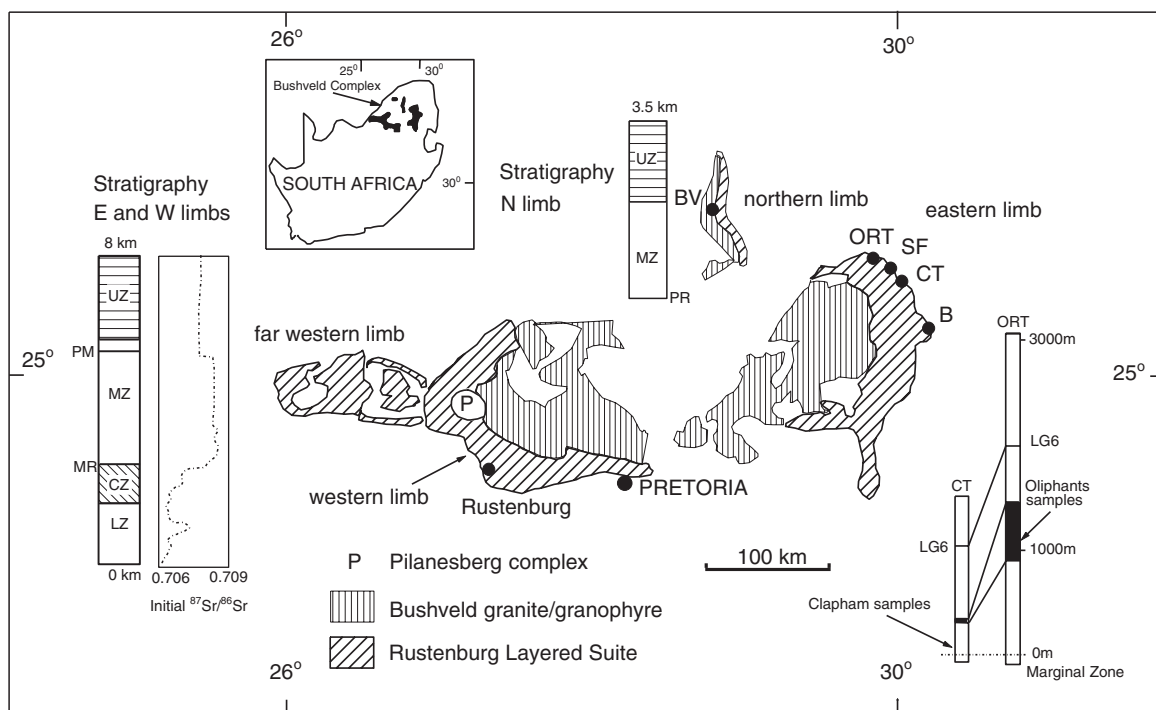


Fig. 1. Sketch map of the Bushveld Complex showing its location in South Africa (inset), and its three main limbs (eastern, western and northern). The location of the Bellevue borehole (BV), the Oliphants River and Clapham Troughs (ORT, CT), the Schwerin fold (SF), and Burgersfort (B) are shown. Also given are the generalized lithological stratigraphy and the variation of initial Sr-isotope ratio (from Kruger, 1994) with stratigraphic height for the western and eastern limbs and the lithological stratigraphy of the northern limb (UZ, Upper Zone; MZ, Main Zone; CZ, Critical Zone; LZ, Lower Zone; PM, Pyroxenite Marker; MR, Merensky Reef; PR, Platreef). The stratigraphy of the LZ and CZ at Clapham (Lee & Tredoux, 1986) and the Oliphants River (Cameron, 1978), and the location of samples analysed are also indicated.

petrogenesis of the Bushveld magma(s). Most workers (e.g. Davies *et al.*, 1980; Cawthorn *et al.*, 1981; Sharpe, 1981; Kruger, 1994; Eales & Cawthorn, 1996) are agreed that the Rustenburg Layered Suite appears to have crystallized from at least three distinct magma types, and that these magmas were affected by a significant amount of crustal contamination.

A large number of stratigraphic profiles have been compiled through different sections of the layered rocks; these include studies on the changes in mineral proportion and cryptic variations recorded in mineral compositions (e.g. von Gruenewaldt, 1973; Cameron, 1978; Teigler & Eales, 1996). One of the most significant stratigraphic datasets, which has greatly influenced ideas concerning the origin and evolution of the magma(s), is that of initial Sr-isotope ratio (Hamilton, 1977; Kruger & Marsh, 1982; Harmer & Sharpe, 1985; Sharpe, 1985; Kruger, 1994). The base of the LZ records the lowest initial Sr-isotope ratios (0.7048) and thereafter the LZ shows considerable variability, reaching a high of 0.707 (Fig. 1). The CZ is also highly variable, with a sudden increase from 0.7065 to 0.7075 at the level of the Merensky Reef (Kruger & Marsh, 1982) just below the contact between the CZ and the MZ. The lower part of the MZ has variable initial

Sr-isotope ratios (0.7075–0.709) before becoming fairly constant (0.7085) through its upper part. At the Pyroxenite Marker (Fig. 1), just below the contact between the MZ and UZ, there is a sudden shift to lower initial Sr-isotope ratios (0.7073), which remain at a similar value throughout the UZ. The Pyroxenite Marker (von Gruenewaldt, 1973) represents an important event, because it marks a reversal in composition of both plagioclase and pyroxene, and a reversal in pyroxene mineralogy in that primary orthopyroxene reappears at this layer, whereas there is inverted pigeonite below. Together with the Sr-isotope break, these observations suggest a significant role for magma recharge. Kruger (1994) suggested that the variable Sr-isotope ratios from the LZ to the lower MZ represent an open-system 'integration stage' with numerous influxes of magma, whereas the upper MZ and UZ represent a closed-system 'differentiation stage' where the evolution of the magmas was dominated by fractional crystallization with infrequent addition of new magma or *in situ* contamination.

In contrast to the Rb–Sr system, there are comparatively few Sm–Nd isotope data for the Bushveld Complex. Maier *et al.* (2000) demonstrated that the ϵ_{Nd} stratigraphy of a 4700 m section of the LZ to MZ in the

western limb follows an inverse relationship to that of initial Sr-isotope ratio, and that there is a negative (although not especially strong) correlation between ϵ_{Nd} and initial Sr-isotope ratios. Those workers concluded that the parental magmas that fed into the lower part of the intrusion had assimilated a relatively small amount of a partial melt of the crust, whereas the magmas parental to the upper part of the complex had assimilated a higher proportion of an incompatible element poor residue of that previous partial melting event.

Like Nd-isotopes, oxygen-isotope data for Bushveld mafic rocks are comparatively scarce. Previous work has shown that the $\delta^{18}\text{O}$ values of Bushveld magmas, estimated from mineral $\delta^{18}\text{O}$ values (Schiffries & Rye, 1989; Reid *et al.*, 1993; Harris & Chaumba, 2001), are typically about 1.5‰ higher than the value of 5.7‰ expected for a mantle-derived basaltic magma (Ito *et al.*, 1987; Eiler, 2001). Unlike Sr-isotopes, the oxygen-isotope data appear to show no systematic change with stratigraphic height. The constancy of these data was taken by those workers to suggest that the parental magmas had already assimilated a significant amount of crust before emplacement and that progressive contamination of the magma *in situ* did not occur to a significant degree.

At present, it is not easy to reconcile models explaining the radiogenic isotopes in terms of the influx of different magmas that had experienced variable degrees of contamination and/or different contaminants, with the lack of change in the O-isotope composition. Nevertheless, it ought to be possible to use O-isotope data in combination with existing radiogenic isotope data to produce a well-constrained model for the types of contamination process and the various contaminants involved. Oxygen isotopes have one important advantage over radiogenic isotopes in that the concentration of oxygen in the various end-members would not be expected to vary significantly. Modelling of contamination processes using oxygen isotopes produces inherently better constrained solutions than is the case for radiogenic isotopes (e.g. Sr and Nd) because the Sr and Nd concentrations are generally not known in all end-members. In the case of the Rustenburg Layered Suite, modelling of radiogenic isotopes is problematic because the rocks are cumulates. Although the initial isotope ratios in the cumulates and the liquids from which they crystallized ought to be the same, it is not a simple matter to determine the elemental concentration of Sr and Nd in the liquids based on the cumulate compositions because of the trapped liquid effect (e.g. Cawthorn, 1996). This is compounded by the problem of estimating element concentrations in the proposed contaminant, which for some zones may be a partial melt of a crustal rock.

PURPOSE OF STUDY

Our first aim is to produce a more detailed O-isotope stratigraphy of the Rustenburg Layered Suite. The existing data comprise samples ($n = 24$) from the eastern limb (Schiffries & Rye, 1989) with additional data for the northern limb from Harris & Chaumba (2001). Existing data for the LZ and Marginal Zone are particularly sparse (only one sample of LZ), whereas the Merensky Reef and its immediate footwall and hanging wall have been comparatively thoroughly analysed by Schiffries & Rye (1989) and Reid *et al.* (1993). It is clearly important to improve the density and distribution of sampling, and in this paper we combine the existing data with mineral analyses of 25 additional samples from the northern limb (Fig. 1), and 14 samples of LZ and Marginal rocks from the eastern limb. We regard the acquisition of data from the Marginal Zone and the LZ of particular importance, as they potentially provide information on the composition of the earliest magma(s) that were intruded. The resulting dataset, although composite, gives a much more complete view of the O-isotope stratigraphy.

Our second aim is to produce a model for crustal contamination that can explain both the Sr- and Nd-isotope data and the O-isotope data for the Bushveld layered rocks. In particular, it is important to explain why the radiogenic isotopes apparently vary systematically with stratigraphic height whereas O-isotopes apparently do not. Although, as discussed above, O-isotope studies permit well-constrained crustal contamination models, they are more susceptible than Sr- and particularly Nd-isotopes to change during alteration processes. The approach used in this, as in previous papers (Schiffries & Rye, 1989; Reid *et al.*, 1993; Harris & Chaumba, 2001), has been to analyse separated minerals as opposed to whole-rock powders. The use of mineral data has several advantages over whole rocks; only fresh mineral grains are selected for analysis, and the difference in $\delta^{18}\text{O}$ value of coexisting plagioclase and pyroxene ($\Delta_{\text{plagioclase-pyroxene}}$) indicates whether or not the minerals are in oxygen-isotope equilibrium at magmatic temperatures.

It is important for this study that the effects of secondary alteration are well understood and can be eliminated as a possible cause of O-isotope variation. With this in mind, a subset of samples have been analysed for their hydrogen-isotope composition.

GEOLOGY AND SAMPLE SELECTION

The Rustenburg Layered Suite (SACS, 1980) can be divided into eastern and western limbs of approximately the same size, and a smaller northern limb (Fig. 1). The far western limb consists mainly of Marginal Zone rocks

and the Bethal limb is situated under the cover of Karoo Supergroup rocks. The oxygen-isotope data of Schiffries & Rye (1989) are for samples collected predominantly in the eastern limb. Our new analyses are for LZ and Marginal Zone rocks from the Olifants River Trough (Cameron, 1978) and the Clapham Trough (Valigy, 1998) of the eastern limb. The location and a summary of the stratigraphic position of the samples are given in Fig. 1. These data are combined with new and existing data for samples from a 3 km core through the northern limb at Bellevue. The stratigraphy of the Bellevue core has been described by Knoper & von Gruenewaldt (1992), Ashwal *et al.* (2004) and Barnes *et al.* (2004), and is not repeated here. An important difference between this section through the northern limb and similar sections through the eastern and western limbs is the absence of the Pyroxenite Marker, and its associated reversal in mineral compositions and changes in pyroxene mineralogy. The core, drilled from the top of the UZ, does not extend as far as the Platreef, which is the mineralized zone found at the base of the MZ in the northern limb (Buchanan *et al.*, 1981; Lee, 1996; Harris & Chaumba, 2001).

To relate the samples in a composite stratigraphy, the Bellevue core data and the data of Schiffries & Rye (1989) were combined using the appearance of cumulus magnetite at the UZ–MZ boundary as a common reference. The Clapham Trough samples were related to the base of the LZ, with Marginal Zone samples (i.e. stratigraphically lower than the LZ) being assigned negative height (the Marginal Zone being of the order of 220 m thick here). Two samples are from the Burgersfort area and sample 382 was taken 1 m above the contact with metasedimentary rock. The ultramafic rocks above this contact were considered by Sharpe & Hulbert (1985) to be a sill formed by ejection of an olivine-rich mush expelled from the LZ. The Olifants River Trough samples are from the middle harzburgite unit of the LZ (Cameron, 1978) and have been assigned a height of 1100 m. It should be noted that the LZ section at Clapham Trough is compressed relative to that of Olifants River Trough, suggesting that each developed as a separate 'basin' (e.g. Uken & Watkeys, 1997) separated by the Schwerin fold (Fig. 1).

PETROGRAPHY

Modal proportions for the samples from Bellevue, Clapham Trough and Olifants River Trough sections are presented in Tables 1 and 2. The petrography and mineral chemistry of samples analysed from the Bellevue core (Fig. 1) were described by Knoper & von Gruenewaldt (1992) and Ashwal *et al.* (2004). The samples include gabbros, norites, gabbro-norites and anorthosites. Magnetite

and Fe-rich olivine are present in some of the UZ samples and up to 10% modal quartz is present in some of the uppermost samples of the UZ. In the case of some anorthosites, it was not possible to separate sufficient pyroxene for analysis. The proportion of modal plagioclase in the analysed samples (Table 1) varies from 46 to 98% (mean 71%). Just over 400 m below the MZ–UZ boundary in the Bellevue core (at 1970.8 m), there is a feldspathic clinopyroxenite layer about 1 m thick (here termed the Pyroxenite Horizon). This horizon is not equivalent to the Pyroxenite Marker of the western and eastern limbs (Ashwal *et al.*, 2004), as there are fundamental differences. It does not mark a reversal in mineral compositions, and it coincides with a change from primary orthopyroxene (below) to primary (now inverted) pigeonite (above), i.e. in the reverse sense to the Pyroxenite Marker (Ashwal *et al.*, 2004). Although there is no *a priori* evidence to link this horizon to an input of new magma, by analogy with the western and eastern limbs, it must be close to the level where the input of new (UZ) magma occurred. Ashwal *et al.* (2004) suggested that up to 500 m of the uppermost MZ (including the Pyroxenite Marker), is missing from the northern limb, possibly as a result of thermal and/or mechanical erosion of the uppermost MZ by the emplacement of UZ magmas. The two lowest samples from the Bellevue core (2849.4 and 2901; Table 1) contain significant quantities of olivine (10% and 12%, respectively) and as such are atypical for the MZ, which elsewhere contains no olivine. The olivine-bearing rocks comprise four troctolitic layers found near the base of the core. The two samples analysed are from the uppermost and lowermost of these layers, which are of the order of 50 m in thickness. Ashwal *et al.* (2004) suggested that the primitive nature of mineral compositions in these troctolites (An_{70-80} , En_{80-83} , Fe_{75-78}) is more akin to the CZ, suggesting that the troctolitic horizons might represent a sliver of CZ rocks dismembered by the intrusion of MZ magmas.

The samples from the Clapham Trough and Olifants River Trough, being from the LZ, are considerably more mafic and comprise norites, and feldspathic harzburgites and pyroxenites. The Olifants River Trough samples come from a short section that is rich in olivine (30–90%). In four samples (1352, 1532, 1535 and 1582; Table 2) it was possible to separate fresh olivine for analysis, although these olivines showed minor serpentinization along cracks and at grain boundaries. The Clapham Trough samples contain no olivine, but have much higher amounts of orthopyroxene (65–92%) than the Olifants River Trough samples. The Marginal Zone norites consist of orthopyroxene and plagioclase with variable proportions of clinopyroxene, magnetite, quartz and biotite, the latter two minerals (which are not found in the LZ, CZ or MZ rocks) suggesting some degree of local crustal contamination.

Table 1: Oxygen- and hydrogen-isotope data for Bellevue core samples

Depth (m)	Ht (m)	Type	% plag	% opx	% pig	% cpx	% ol	% op	% bi	% amp	% qz	% ap	$\delta^{18}\text{O}$ plag	$\delta^{18}\text{O}$ pyrox	$\delta^{18}\text{O}$ qz	$\delta\text{D wr}$	H_2O^+	% An	
<i>Upper Zone</i>																			
106-2	7949	Olivine ferrodiorite	40	0	0	4	20	5	4	15	5	2				-117	0.27	42	
352	7712	Quartz anorthosite	83	0	0	0	0	3	4	0	10	0	7.6					47	
375-1	7690	Granite vein													8.7		0.35	45	
417	7649	Quartz anorthosite	87	0	0	0	0	1	0	2	10	0	7.4	6.1				45	
462-7	7640	Olivine gabbro	46	3	0	18	15	10	5	0	0	3	6.9	5.9		-88	0.64	44	
612	7461	Magnetite anorthosite	62	0	0	0	0	30	5	3	0	0	7.8					54	
689-5	7386	Mgt olivine gabbro	57	0	0	23	8	10	2	0	0	0	6.9	5.8		-95	0.21	47	
847-4	7234	Mgt gabbronorite	55	15	0	16	0	12	2	0	0	0	6.1	6.0		-79	0.27	53	
894	7189	Mgt leucogabbro	74	0	10	5	0	8	2	1	0	0	8.0					56	
969	7116	Anorthosite											8.3					58	
969-5	7115	Mgt gabbronorite	66	0	10	7	0	14	3	0	0	0	8.0	6.7		-69	0.65	58	
1046	7042	Quartz anorthosite	87	0	0	0	0	2	1	0	10	0	7.5					57	
1146	6945	Mgt leucogabbro	81	0	0	3	0	8	5	0	3	0	7.6					57	
1211-9	6881	Mgt gabbronorite	68	9	0	7	0	15	1	0	0	0	9.1	6.3		-74	0.41	55	
1318	6799	Mgt leucogabbro	81	6	0	3	0	9	1	0	0	0	7.5	6.3				56	
1402	6698	Mgt gabbronorite	82	0	0	3	0	13	2	0	0	0	7.8					57	
1510	6594	Mottled anorthosite	97	0	0	2	0	0	0	0	1	0	7.2	6.6				57	
1547-9	6557	Leucogabbronorite	73	0	6	12	0	9	0	0	0	0	7.3	6.4		-49	0.25	55	
1558-8	6546	Mgt leucogabbronorite	82	0	3	4	0	11	0	0	0	0	8.4	6.2		-59	0.23	55	
1560	6545	Mgt gabbronorite	83	0	7	3	0	7	0	0	0	0	10.4					55	
Depth (m)	Ht (m)	Type	% plag	% opx	% pig	% cpx	% ol	% op	% ol	% op	% qz	% ap	$\delta^{18}\text{O}$ plag	$\delta^{18}\text{O}$ pyrox	$\delta\text{D wr}$	H_2O^+	% An		
<i>Main Zone; MZ-UZ boundary at 1575-81 m</i>																			
1594-5	6511	Gabbronorite	55	0	30	15	0	0	0	0	0	0	7.2	6.3		-59	0.18	55	
1618	6489	Gabbronorite	45	0	45	10	0	0	0	0	0	0	7.3	6.5				54	
1693-9	6416	Gabbronorite	55	0	25	20	0	0	0	0	0	0	7.1	6.4		-71	0.16	54	
1745	6367	Gabbronorite	49	0	35	15	0	0	0	0	1	0	13.1	6.4		-40	0.28	55	
1790-5	6323	Gabbronorite	60	0	27	13	0	0	0	0	0	0	7.6	6.4				56	
1843-3	6272	Gabbronorite	50	0	35	15	0	0	0	0	0	0	6.6	5.9		-75	0.28	54	

Table 1: Continued

Depth (m)	Ht (m)	Type	% plag	% opx	% pig	% cpx	% ol	% op	% qz	$\delta^{18}\text{O}$ plag	$\delta^{18}\text{O}$ pyrox	$\delta\text{D wr}$	H_2O^+	% An
1870-6	6245	Gabbroanorthite	50	0	35	15	0	0	0	6.9	6.4	-55	0.18	56
1912-3	6205	Norite	58	0	35	7	0	0	0	7.1	6.5	-87	0.28	55
1934-6	6183	Anorthosite	95	0	0	0	0	0	5	7.1				55
1955-7	6163	Leuconorthite	80	0	15	5	0	0	0	7.0	6.2	-76	0.29	56
1966	6153	Melanorite	46	0	50	4	0	0	0	6.9	6.5			58
<i>Pyroxenite Horizon 1969–1973 m</i>														
1975	6144	Mottled anorthosite	94	0	4	1	0	0	1	7.0	6.6			60
1980-1	6139	Gabbroanorthite	58	20	0	20	0	0	0	7.1	6.5	-94	0.18	60
1994-6	6126	Leuconorthite	88	0	10	2	0	0	0	7.0	6.6			59
2021-1	6100	Gabbroanorthite	50	30	0	20	0	0	0	6.8	6.3	-85	0.23	60
2046	6076	Gabbroanorthite	60	25	2	13	0	0	0	7.3	6.3	-52	0.15	59
2093-2	6030	Leucogabbroanorthite	76	0	14	10	0	0	0	6.7	5.8	-73	0.20	60
2115	6009	Mottled anorthosite	90	0	0	4	0	4	2	7.2	7.6			60
2307	5824	Leuconorthite	94	3	0	3	0	0	0	7.4	6.4			65
2446	5689	Leucogabbroanorthite	88	1	0	10	0	0	1	7.2	6.6			70
2516	5622	Mottled anorthosite	89	5	0	6	0	0	0	7.8	6.6			73
2703	5441	Anorthosite	98	0	0	2	0	0	0	7.1				75
2849-4	5300	Olivine gabbroanorthite	60	13	0	7	20	0	0	6.8	7.0	-79	0.23	75
2901	5250	Troctolite layer + opx	86	1	0	1	12	0	0	7.2	7.5			76

Geology of core, mode and plagioclase composition data from Ashwal *et al.* (2004). Depth is in metres measured along the core, height is the estimated height in the intrusion as a whole (see text). The dip of the magmatic layering in the area of the borehole varies from 10 to 20° (dip assumed to be 15° for correction purposes). plag, plagioclase; pyrox, bulk pyroxene; opx, orthopyroxene; pig, inverted pigeonite; cpx, Ca-rich clinopyroxene; ol, olivine; op, opaque minerals; bi, biotite; amp, amphibole; qz, quartz; ap, apatite. Sample 106-2 contains an additional 5% alkali feldspar. Biotite and apatite <1% or absent in all samples below UZ–MZ contact.

Table 2: Oxygen-isotope data for Marginal Zone, Lower Zone and Critical Zone samples

Sample	Zone	Ht (m)	Type	% plag	% opx	% cpx	% ol	$\delta^{18}\text{O}$ plag	$\delta^{18}\text{O}$ pyrox	$\delta^{18}\text{O}$ oliv	δD wr	H_2O^+
<i>Burgersfort</i>												
382	LZ	1	Harzburgite	0	70	0	30		6.2		−65	3.92
									6.3			
384			Harzburgite								−76	1.94
<i>Oliphants River Trough</i>												
1352	LZ	1100	Harzburgite	tr	70	0	30		6.4	5.6	−92	0.23
1532	LZ	1100	Pyroxenite						5.7	6.3	−79	0.50
									5.7			
									6.0			
1535	LZ	1100	Harzburgite	0	20	0	80		6.8	6.5	−86	3.56
1582	LZ	1100	Dunite	0	10	0	90			6.5	−77	6.86
1943	LZ	1100	Harzburgite	tr	45	10	45		5.9		−97	0.21
<i>Schwerin fold</i>												
1581	Marginal	0	Norite					7.8			−84	0.53
<i>Clapham Trough</i>												
C11	LZ	53	Norite					7.3	7.5			
C14	LZ	45	Pyroxenite	15	80	5		7.4	7.6			
C17	LZ	35	Pyroxenite	5	92	3		7.3	7.0			
C20	LZ	10	Pyroxenite	30	65	5			6.7			
C22	Marginal	−43	Norite	65	30	5		7.8	7.0			
C25	Marginal	−11	Norite	60	30	10		7.7	6.9			
C28	Marginal	−206	Norite	60	25	15		7.3	6.6			
<i>Brakspruit (Merensky Reef)</i>												
B85-14(-10)	CZ		Norite					6.7	6.2			
B85-14(+4)	CZ		Pegmatoid					6.7	6.5			
B85-21	CZ		Pegmatoid					6.8	6.3			
B85-17(-80)	CZ		Norite					7.1	6.4			
B85-23	CZ		Norite					7.1	6.2			

Olivine by laser fluorination; pyroxene and plagioclase by conventional fluorination. Mineral modes obtained by visual estimation using thin sections. Ht is stratigraphic height above the base of the LZ, hence Marginal Zone samples have negative height. The Brakspruit data are unpublished analyses, courtesy of E. A. Mathez and P. Agrinier.

ANALYTICAL METHODS

Mineral separates were prepared by hand picking clean sieved material under a binocular microscope, in some cases after initial magnetic separation. Oxygen-isotope ratios of the silicate minerals were determined at the University of Cape Town (UCT) and Université Jean Monnet (UJM) after drying powdered material in an oven at 50°C, and degassing under vacuum on conventional silicate lines at 200°C for 2 h. The silicate minerals were reacted with ClF_3 (UCT) or BrF_5 (UJM) and the O_2 was converted to CO_2 using a hot platinumized carbon rod. Stable isotope ratios were measured using either a Finnigan MAT252 (UCT) or a Micromass Isoprime

(UJM) mass spectrometer and are reported in the familiar δ notation where $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$ and $R = {}^{18}\text{O}/{}^{16}\text{O}$. Duplicate splits of an internal standard (Murchison Line quartz, MQ) were run with each batch of samples in both laboratories. The $\delta^{18}\text{O}$ of MQ has been accurately determined to be 10.1‰ after calibration against the NBS-28 quartz standard, assuming a value for NBS-28 of 9.64‰ (Coplen *et al.*, 1983). The average value obtained for MQ was used to normalize the raw data to the SMOW scale. The average difference between duplicates of MQ analysed during the course of this work was 0.11‰ (UCT, $n = 8$) and 0.20‰ (UJM, $n = 15$). These are equivalent to 1σ values of 0.06 and 0.17, respectively, and represent the typical precision of

the analyses. Further details of the methods employed for extraction of oxygen from silicates at UCT have been given by Vennemann & Smith (1990) and Harris & Erlank (1992); the UJM extraction procedure has been described by Gerbe & Thouret (2004). The yields of CO₂ produced from each mineral were measured to confirm complete reaction. The average yield of the conventional extraction method was 98%. A smaller number of mineral separates (including all olivine samples) were analysed using laser fluorination methods at UJM using the same equipment as described by Harris *et al.* (2000), but with BrF₃ as reagent. Replicate analyses of the Monastery garnet standard (Harris *et al.*, 2000) suggest that the precision is comparable with that of the conventional fluorination data. Unlike the conventional analyses, which comprise many individual grains, the laser data were obtained on 1–3 individual mineral grains. The average yields for laser fluorination during the course of this work were plagioclase 97%, quartz 94%, pyroxene 97% and olivine 96%.

Hydrogen isotopes were determined at UCT using the method of Vennemann & O'Neil (1993). Whole-rock samples were degassed on the vacuum line at 200°C prior to pyrolysis. An internal water standard (CTMP; $\delta D = -9\text{‰}$) was used to calibrate the data to the SMOW scale and a second water standard (DML; $\delta D = -300\text{‰}$) was used to correct for scale compression (e.g. Coplen, 1993). Typical reproducibility of internal biotite standards during the period of analysis was $\pm 2\text{‰}$ (1σ). Water contents were determined either from the voltage measured on the mass 2 collector or (in the case of large samples) from the pressure measured during sample inlet using identical inlet volume to standards of known number of micromoles. Repeated measurements of water standards of known mass suggest that the typical relative error for the water content is 3%. However, it should be noted that many of the whole-rock samples analysed contain very little H₂O⁺ and in these samples the errors might be somewhat higher. Duplicate analyses of sample 2046 gave δD values of -52 and -54‰ and H₂O⁺ values of 0.15 and 0.15 wt %.

RESULTS

The $\delta^{18}\text{O}$ values of plagioclase and pyroxene samples from the Bellevue core are given in Table 1 and presented graphically in Figs 2–4. Both plagioclase and pyroxene show a fairly restricted range in $\delta^{18}\text{O}$ values, from 6.1 to 8.4‰ (mean 7.32‰; $n = 41$) and from 5.8 to 7.6‰ (mean 6.45‰; $n = 32$), respectively. The only exceptions are three samples (1211.91, 1560, 1745) that have plagioclase of much higher $\delta^{18}\text{O}$ value (9.1, 10.4 and 13.1‰, respectively), which have not been included in the average. The per mil difference (Δ) between plagioclase and

pyroxene ranges from +0.6‰ to +1.3‰ (mean value +0.98‰; $n = 31$, not including the samples with abnormally high plagioclase $\delta^{18}\text{O}$ values), with two exceptions at -0.4 and $+0.1\text{‰}$ (samples 2115 and 847.42, respectively). A single olivine from one of the olivine-bearing zones at the base of the Bellevue core gave a $\delta^{18}\text{O}$ value of 6.4‰.

Data from the LZ and Marginal Zone of the eastern limb are given in Table 2. Pyroxene and olivine from the ultramafic rocks of the Olifants River Trough gave $\delta^{18}\text{O}$ values of 5.7–6.8‰ and 5.6–6.5‰, respectively. Replicate analyses were made of olivine from two samples and the difference (0.6‰) is somewhat larger than predicted by the normal analytical precision. This may be due to oxygen-isotope heterogeneity among olivine grains, but it is also possible that small amounts of alteration are present along cracks, which affects the $\delta^{18}\text{O}$ value of each grain to a different degree. The Marginal Zone and LZ samples from the Clapham Trough have very consistent plagioclase (mean 7.47‰) and pyroxene (mean 7.04‰) $\delta^{18}\text{O}$ values and a single Marginal Zone norite from the Schwerin fold contains plagioclase with a $\delta^{18}\text{O}$ of 7.8‰.

A comparison of conventional and laser fluorination data for selected samples from the Bellevue core is shown in Table 3. Although there is broad agreement between data obtained by the different methods for some samples (e.g. 1843.34 and 2849.40), the laser data sometimes differ considerably from the conventional data, particularly so for plagioclase. For the samples in Table 3, the mean $\delta^{18}\text{O}$ values for plagioclase and pyroxene by conventional analysis are 6.96 and 6.21‰, whereas by laser fluorination the values are 6.54 and 5.98‰, respectively. Thus it appears that the laser data are generally slightly lower than the conventional values. It is important to note that the conventional data represent an average of many grains, whereas the laser data often represent only one grain, having 5–15% of the mass of the sample analysed by the conventional method. Apart from analytical error, possible explanations for this apparent difference are, first, that individual mineral grains contain variable quantities of impurities and/or minor alteration phases and, second, that the $\delta^{18}\text{O}$ values of minerals are inherently heterogeneous. Variability in plagioclase $\delta^{18}\text{O}$ values within the same sample could be due to post-magmatic interaction with fluids, which is not petrographically visible. Pyroxene is more resistant to alteration, but unlike plagioclase there is the possibility of the presence of small magnetite inclusions, which are not always visible under the binocular microscope. A single magnetite was analysed, which has a much lower $\delta^{18}\text{O}$ value (-0.1‰ , Table 3). The observed per mil difference between pyroxene and magnetite in this sample corresponds to a temperature of 515°C [using the equations of Chiba *et al.* (1989)]. The presence of small magnetite inclusions within pyroxene grains in the UZ might

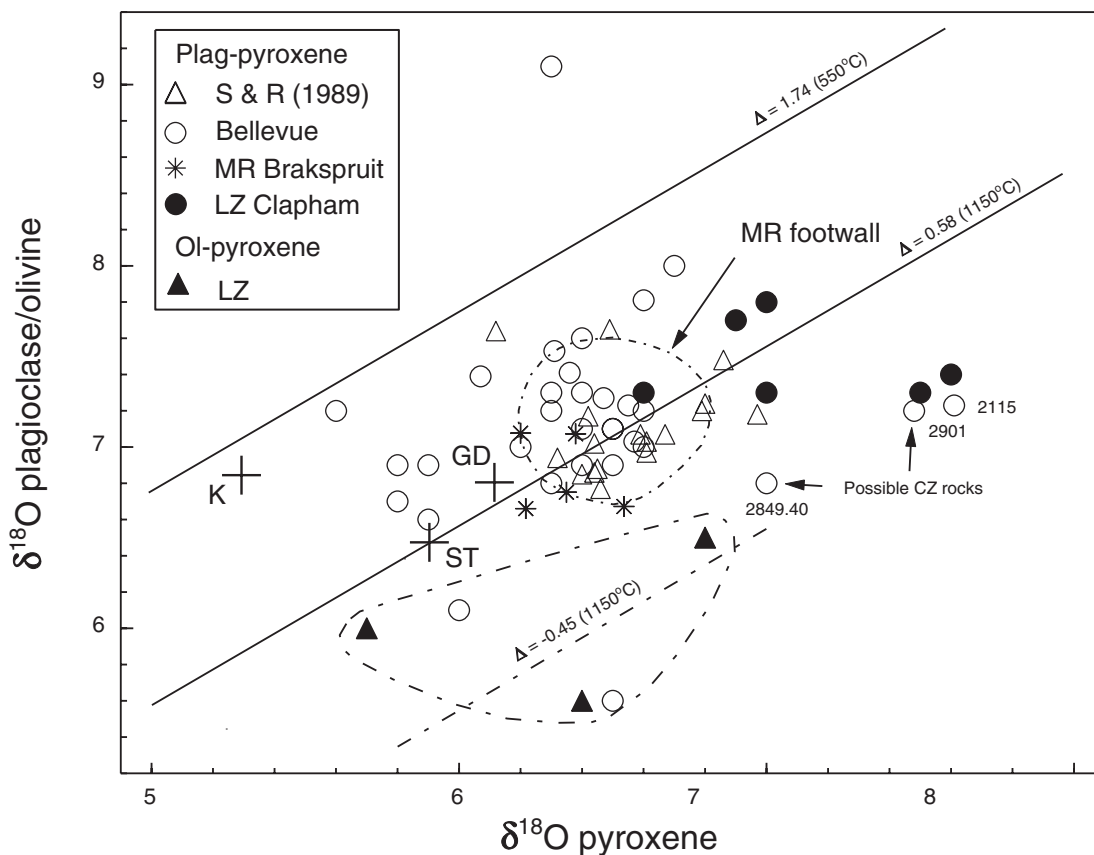


Fig. 2. Plot of the $\delta^{18}\text{O}$ value of plagioclase (or olivine) vs the $\delta^{18}\text{O}$ value of pyroxene for Bellevue and Clapham Trough (LZ) samples. The Oliphants River Trough data cannot be plotted as the rocks do not contain plagioclase. Also plotted are the Bushveld data of Schiffries & Rye (1989) and Merensky Reef data from Brakspruit (Nicholson & Mathez, 1991), in the Rustenburg section of the western limb [E. A. Mathez & P. Agrinier, unpublished data (2004) given in Table 1]. The field of data for samples from the Merensky Reef footwall at Impala Platinum, in the western limb ($n = 18$, Reid *et al.*, 1993) is also shown. The crosses mark the average for the Great Dyke (GD, Chaumba & Wilson, 1997), Kiglapait (K, Kalamarides, 1984) and Stillwater (ST, Dunn, 1986). The two olivine-bearing samples from the base of the Bellevue core that might represent CZ (see text) are indicated. Plagioclase–pyroxene isotherms for 550 and 1150°C (corresponding to values of $\Delta_{\text{plagioclase-pyroxene}}$ of 1.74 and 0.58‰, respectively) are shown, as is the olivine–pyroxene isotherm for 1150°C ($\Delta = -0.45\%$). The isotherms are calculated using the calibrations of Chiba *et al.* (1989) and for plagioclase assume a constant composition of An_{60} .

explain why the laser pyroxene analyses tend to be more variable than the conventional analyses. Variable $\delta^{18}\text{O}$ values within fresh phenocryst populations (and sometimes within individual crystals) have been recognized in volcanic rocks (e.g. Baker *et al.*, 2000) and related to crystal accumulation during contamination. In the RLS, Prevec *et al.* (2004) showed that individual rocks from the Merensky and Bastard Reefs of the RLS contain minerals with variable initial Nd- and Sr-isotope ratios. It is, therefore, possible that individual minerals in the RLS have inherently heterogeneous $\delta^{18}\text{O}$ values as a result of magmatic processes. Because of the greater variability of the laser data, we have chosen to use the conventional $\delta^{18}\text{O}$ values for pyroxene and plagioclase on all plots. A more detailed study of the intra-sample variability in $\delta^{18}\text{O}$ values within RLS rocks, combined with radiogenic isotopes, is required to resolve this issue.

Figure 2 shows a plot of plagioclase vs pyroxene $\delta^{18}\text{O}$ values for the Bellevue core samples, Clapham Trough samples, and samples from all three zones of the layered suite analysed by Schiffries & Rye (1989). Also plotted are Merensky Reef data from Brakspruit in the western limb (E. A. Mathez & P. Agrinier, unpublished data, 2004) and the range of values for Merensky Reef footwall rocks from Impala Platinum, western limb (Reid *et al.*, 1993). Most samples plot between the 550°C and 1150°C isotherms with a significant minority (including most of the Schiffries & Rye samples) having $\Delta_{\text{plagioclase-pyroxene}}$ values between 0 and 0.58‰. It should be noted that the three samples that have very high plagioclase $\delta^{18}\text{O}$ values are not plotted, and there are four samples that have values of $\Delta_{\text{plagioclase-pyroxene}}$ close to zero. The three samples for which both olivine and pyroxene have been analysed are also plotted in Fig. 2. Two of the samples

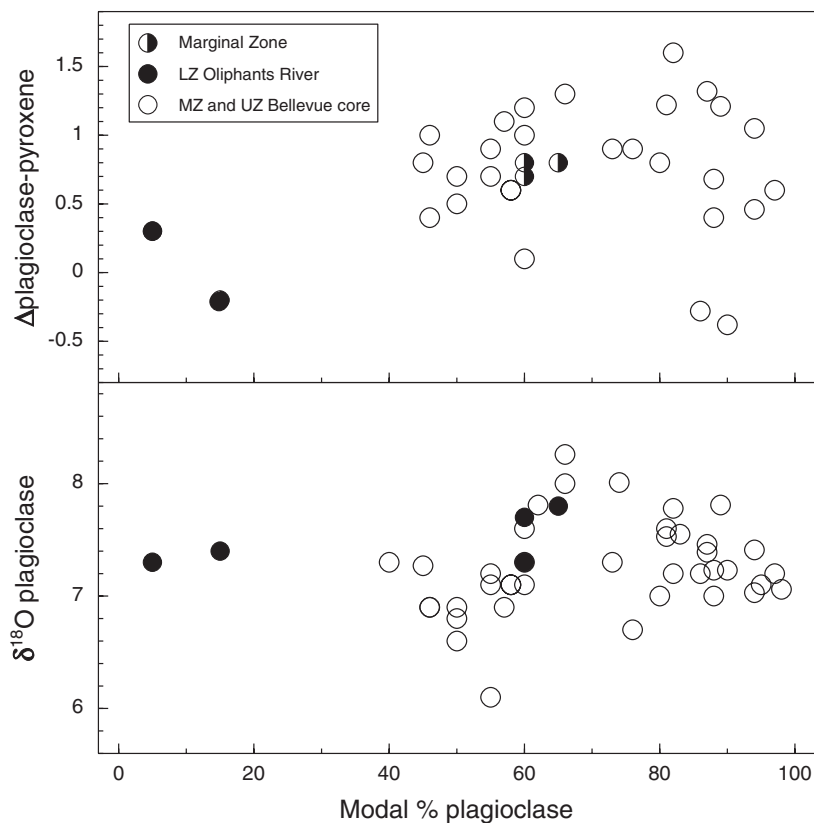


Fig. 3. Plots of the difference in $\delta^{18}\text{O}$ value of plagioclase and pyroxene ($\Delta_{\text{plagioclase-pyroxene}}$) and plagioclase $\delta^{18}\text{O}$ value vs the modal percent plagioclase. Only data from the Bellevue core, the Oliphants River Trough and the Marginal Zone are shown.

show $\Delta_{\text{olivine-pyroxene}}$ values that are close to the predicted difference of -0.45‰ at 1150°C . There is no correlation (Fig. 3) between plagioclase $\delta^{18}\text{O}$ value (or pyroxene; not shown) and the modal percent plagioclase, nor is there a correlation between $\Delta_{\text{plagioclase-pyroxene}}$ and modal percent plagioclase.

Whole-rock hydrogen-isotope compositions and water contents for selected samples are given in Tables 1 and 2, and presented graphically in Fig. 5. The range of δD values from -53 to -99‰ is similar to values previously obtained for the Bushveld (Mathez *et al.*, 1994; Harris & Chaumba, 2001; Willmore *et al.*, 2002). The Bellevue samples are notable for their relatively low whole-rock water contents (0.18 – 0.65 wt %) whereas some of the LZ samples have much higher water contents as a result of partial serpentinization. It should be noted that there is no correlation between water content and δD value or between δD value and $\Delta_{\text{plagioclase-pyroxene}}$. The highly serpentinized sample 1582 with 6.86 wt % water (equivalent to about 50% serpentine) has a δD value (-77‰) that is comparable with the δD value in comparatively unaltered samples. Those samples with $<0.5\%$ H_2O^+ have similar average δD values (-82‰) to those samples

with $>0.5\%$ H_2O^+ (-76‰). Mathez *et al.* (1994) determined the δD values in samples within a 40 m section intersecting the Merensky Reef at Atok (now Lebowa Platinum Mines) in the eastern limb. They found very low bulk-rock water contents (0.04 – 0.26 wt %, mean 0.13 , $n = 36$) and concluded that the water resided either as structural water within pyroxene, as suggested by Bell & Rossman (1992) for mantle orthopyroxenes, or as submicroscopic phlogopite along orthopyroxene cleavage planes. The data presented in Tables 1 and 2 suggest that there is little or no difference in H-isotope composition between water in high-temperature minerals such as amphibole and biotite, and water in hydrous minerals such as serpentine formed at lower temperatures, at least in the LZ.

MAGMATIC VS HYDROTHERMAL SIGNATURES

Because some layered intrusions (e.g. Skaergaard and Skye; Taylor & Forester, 1979; Taylor, 1987) show shifts in $\delta^{18}\text{O}$ associated with subsolidus hydrothermal

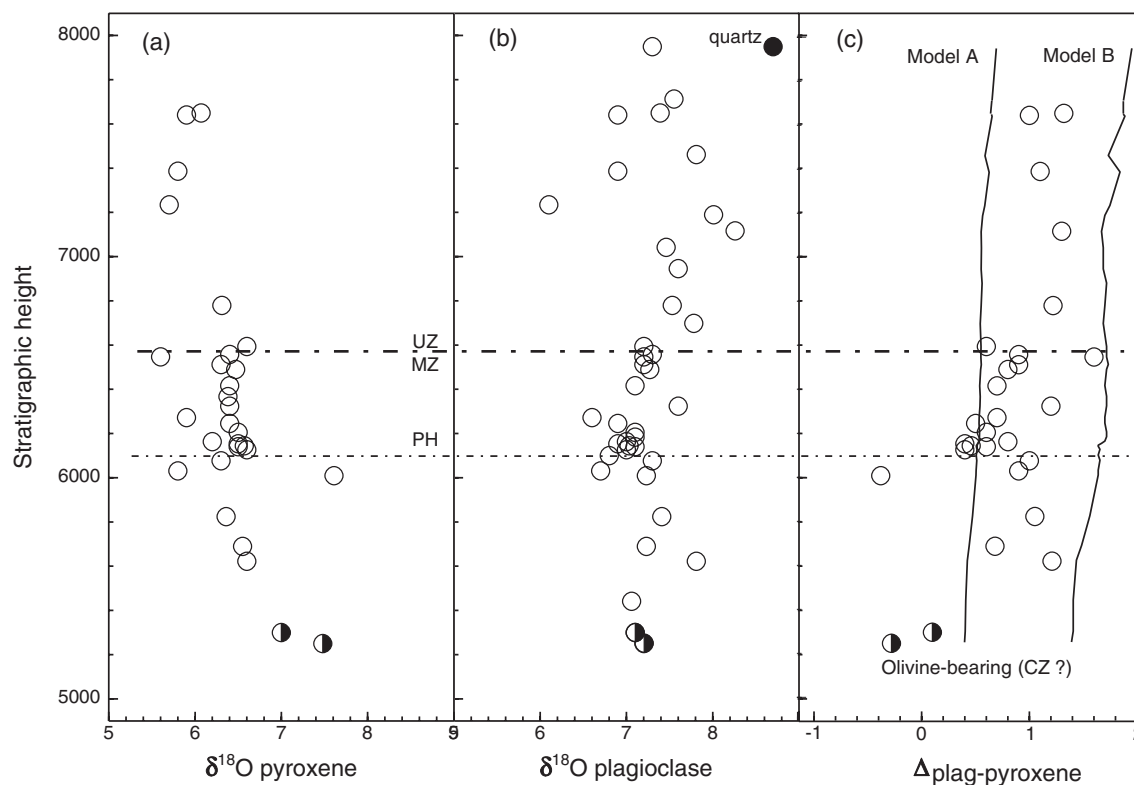


Fig. 4. Variation of (a) pyroxene, (b) plagioclase $\delta^{18}\text{O}$ values and (c) $\Delta_{\text{plagioclase-pyroxene}}$ with stratigraphic height in the Bellevue core through the northern limb. Stratigraphic height is taken to be the overall height in the intrusion calculated with reference to the MZ–UZ boundary. Conventional data only are plotted. PH, Pyroxenite Horizon (see text). In (c) calculated curves for $\Delta_{\text{plagioclase-pyroxene}}$ are shown. Model A assumes a linear decrease in crystallization temperature between 1150°C (base) and 1050°C (top) and no subsolidus re-equilibration of oxygen. Model B assumes oxygen-isotope equilibrium between plagioclase and pyroxene continued to a closure temperature of 550°C. The calibrations of Chiba *et al.* (1989) were used to calculate $\Delta_{\text{plagioclase-pyroxene}}$ using the appropriate An content of each sample (Table 1).

alteration (e.g. Gregory & Criss, 1986), it is important to establish whether or not the samples analysed here reflect the composition of the crystallizing cumulates, or result from subsequent fluid–rock interaction. In general, the effects of post-crystallization hydrothermal activity on plutonic rocks can be investigated by evaluating the degree of oxygen-isotope equilibrium between coexisting minerals and/or whole rocks, using so-called δ – δ plots (Gregory & Criss, 1986; Gregory *et al.*, 1989). The most useful δ – δ diagrams plot the $\delta^{18}\text{O}$ value of a mineral that exchanges oxygen relatively rapidly vs the $\delta^{18}\text{O}$ value of a coexisting mineral that exchanges oxygen more slowly. Minerals in equilibrium in a suite of rocks are characterized by arrays that lie on an equilibrium line of constant per mil difference between the two minerals (Δ), which are lines of constant temperature. Rock assemblages that have interacted with an external fluid will form arrays that are not parallel to these equilibrium lines because of the greater susceptibility of one of the minerals to equilibrate with the fluid.

Schiffries & Rye (1989, 1990) showed that $\Delta_{\text{plagioclase-pyroxene}}$ values for samples from the eastern

limb of the Bushveld Complex showed no evidence for interaction with hydrothermal fluids. In Fig. 2, our new data are plotted together with those of Schiffries & Rye (1989), and it can be seen that there is a relatively high degree of internal oxygen-isotope equilibrium. The new data are generally more scattered than the existing data but the overall spreads of data are similar.

Values of $\Delta_{\text{plagioclase-pyroxene}}$ between 0.58 and 1.74‰ [from 1150 to 550°C using the plagioclase–diopside fractionation curve of Chiba *et al.* (1989)] can be explained by continued oxygen-isotope exchange during slow cooling (e.g. Giletti, 1986). The plagioclase samples with high $\delta^{18}\text{O}$ values have presumably been affected by post-crystallization interaction with fluids at low temperatures, which would have raised their $\delta^{18}\text{O}$ values. The two samples at the base of the Bellevue core (2849.4 and 2901), which possibly represent large xenoliths or screens of LZ or CZ material, are notable for having plagioclase $\delta^{18}\text{O}$ values slightly lower than that of pyroxene, which plot away from the main dataset, along with two LZ samples and sample 2115 in Fig. 3. These samples with negative $\Delta_{\text{plagioclase-pyroxene}}$ values presumably indicate

Table 3: Comparison of Bellevue core data produced by laser and conventional extraction methods

Depth (m)	Type	Conventional		Laser		
		$\delta^{18}\text{O}$ plag	$\delta^{18}\text{O}$ pyrox	$\delta^{18}\text{O}$ plag	$\delta^{18}\text{O}$ pyrox	$\delta^{18}\text{O}$ other
106-20	Olivine ferrodiorite	7.3				8.7(qz)
689-49	Magnetite olivine gabbro	6.9	5.8	7.8	5.9	
847-42	Magnetite gabbronorite	6.1	6.0	7.5	5.7	
969	Anorthosite	8.0	6.7	7.5	5.6	-0.1(mgt)
1211-91	Magnetite gabbronorite	9.1	6.3			
1558-77	Magnetite leucogabbronorite	8.4	6.2	7.2, 6.6	5.6	
<i>MZ–UZ boundary at 1575-81 m</i>						
1843-34	Gabbronorite	6.6	5.9	6.6	6.0	
1912-31	Norite	7.1	6.5	5.5, 6.0	6.4, 7.0	
1955-67	Leuconorite	7.0	6.2	5.4	6.0	
1980-10	Gabbronorite	7.1	6.5	5.6, 5.4	5.9	
2021-05	Gabbronorite	6.8	6.3	6.8		
2849-40	Olivine gabbronorite	6.8	7.0	7.1	7.0	6.4 (ol)

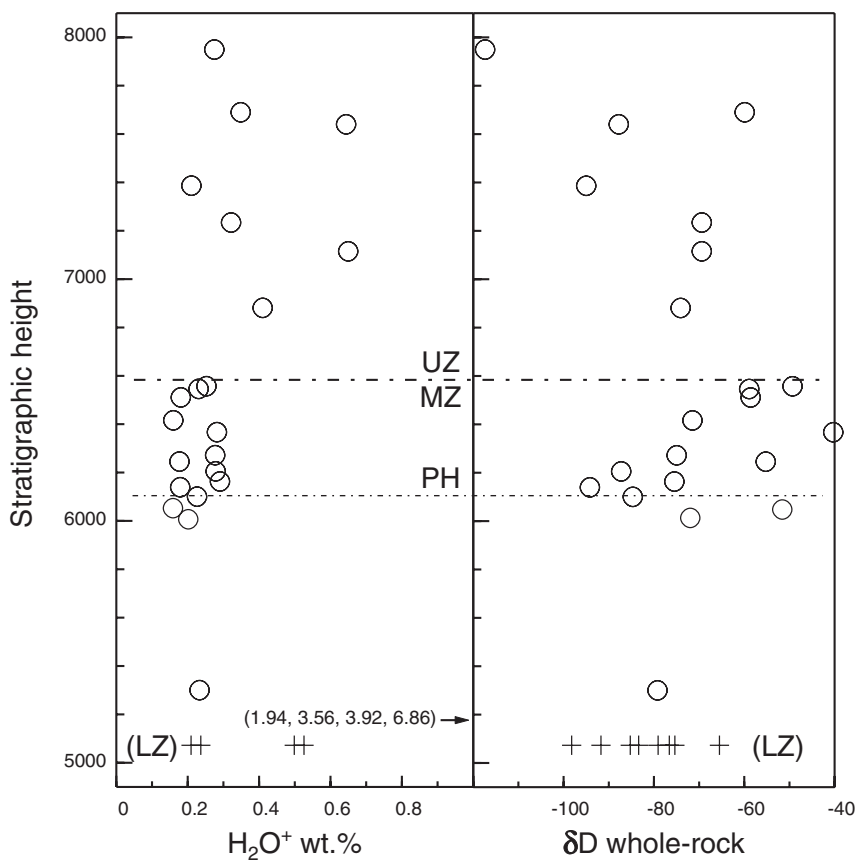


Fig. 5. Variation of whole-rock δD value and wt % H_2O^+ with stratigraphic height in the Bellevue core through the northern limb. The MZ–UZ contact and the level of the Pyroxenite Horizon are indicated. The data for the LZ are shown plotted at an arbitrary stratigraphic height for comparison. It should be noted that some LZ samples have H_2O^+ contents that are too high to be plotted, and these are indicated.

O-isotope disequilibrium as a result of alteration. Sample 2849-4 has $\Delta_{\text{olivine-pyroxene}} = -0.6\%$, which is close to the 1150°C value of 0.45% given by Chiba *et al.* (1989). These data suggest that, in at least some rocks, plagioclase $\delta^{18}\text{O}$ values have been lowered during alteration, in this case at high temperatures. The most important feature of the data, however, is that the $\Delta_{\text{plagioclase-pyroxene}}$ values of between 0.3 and 1.5% observed for the Bushveld rocks are typical of fresh gabbros worldwide (e.g. Taylor, 1968; Gregory & Criss, 1986), and imply the preservation of magmatic oxygen-isotope compositions in the vast majority of rocks of the Rustenburg Layered Suite.

The range of δD values for bulk rocks and minerals of -53 to -99% obtained by previous workers has been interpreted as magmatic in origin (Mathez *et al.*, 1994; Harris & Chaumba, 2001; Willmore *et al.*, 2002). Harris & Chaumba (2001) suggested, on the basis of palaeomagnetically determined latitude, that meteoric water interacting with the Bushveld rocks at 2050 Ma would have had a δD value of about -20% . Water of this isotope composition would have produced serpentine with a δD value of about -40% [assuming a temperature of 400°C, and the $\Delta_{\text{serpentine-water}}$ of -20% given by Suzuoki & Epstein (1976)]. The hydrogen-isotope data, therefore, do not suggest a significant role for 2050 Ma (or recent) meteoric water, even in the serpentinized LZ samples with high water content. This suggests either that the estimate for the δD value of ambient meteoric water is wrong, or that the fluids responsible for serpentinization were of magmatic rather than meteoric origin.

OXYGEN-ISOTOPE COMPOSITION OF THE PARENT MAGMA

It is important to note that the norites and pyroxenites of the Bushveld intrusion do not represent quenched liquid compositions, with the possible exception of the Marginal Zone rocks. It is, therefore, necessary to estimate the magma $\delta^{18}\text{O}$ value from mineral data. It was shown above (Fig. 2) that most of the analysed samples have plagioclase and pyroxene $\delta^{18}\text{O}$ values that are consistent with oxygen-isotope equilibrium at magmatic temperatures in that they plot between the closure (550°C) and crystallization (1150°C) isotherms. Let us consider the case of a biminerally gabbro with 71% plagioclase and 29% pyroxene, as is the case for the average Bellevue sample. At the moment of crystallization from a mantle-derived basaltic magma with, for example, a $\delta^{18}\text{O}$ value of 5.70%, this rock would have plagioclase with a $\delta^{18}\text{O}$ value of 5.90%, pyroxene with a $\delta^{18}\text{O}$ value of 5.40%, and a whole-rock $\delta^{18}\text{O}$ value of 5.76% (i.e. the cumulate has a slightly higher bulk $\delta^{18}\text{O}$ value than the magma), assuming $\Delta_{\text{plagioclase-pyroxene}} = 0.5$, appropriate for plagioclase (An₇₀) and pyroxene at 1150°C (Chiba *et al.*, 1989)

and that $\Delta_{\text{plagioclase-melt}} = +0.2\%$ (Kyser *et al.*, 1981). If this cumulate cooled slowly to about 750°C, a plausible closure temperature for pyroxene in a medium-grained igneous rock, $\Delta_{\text{plagioclase-pyroxene}} = 1\%$ (Chiba *et al.*, 1989) and the $\delta^{18}\text{O}$ values of the coexisting plagioclase and pyroxene will therefore be 6.05 and 5.05%, respectively (by mass balance, assuming equal concentrations of oxygen in both minerals, with the bulk-rock $\delta^{18}\text{O}$ value remaining at 5.76%). The change in pyroxene $\delta^{18}\text{O}$ value is larger than that of plagioclase because its modal abundance is less. Hence the pyroxene $\delta^{18}\text{O}$ value is now 0.65% less than that of the original magma.

The above approach cannot be used to relate mineral and magma $\delta^{18}\text{O}$ values exactly because the magnitude of the change in pyroxene and plagioclase $\delta^{18}\text{O}$ value during slow cooling is also dependent on parameters such as grain size and cooling rate (e.g. Gregory & Criss, 1986). Furthermore, the closure temperature to oxygen diffusion is not known and the rocks commonly depart significantly from biminerally assemblages. Nevertheless, the original magma $\delta^{18}\text{O}$ value is unlikely to differ greatly from that of the bulk rock, even for rocks with extreme modal mineralogy. In Fig. 6c the bulk-rock $\delta^{18}\text{O}$ value for the Bellevue samples has been calculated from the mineral $\delta^{18}\text{O}$ values and the modal proportions, assuming that the rocks contain only plagioclase and pyroxene. In the absence of a more rigorous approach, which is not justified, these bulk-rock $\delta^{18}\text{O}$ values are assumed to approximate those of the original magmas. The lack of correlation between modal percent plagioclase and mineral $\delta^{18}\text{O}$ values (Fig. 3) supports this assumption. For rocks where only one mineral has been analysed, and for the Schiffries & Rye (1989) data, for which no modes are available, it is assumed that $\Delta_{\text{plagioclase-rock}}$ and $\Delta_{\text{pyroxene-rock}}$ are +0.35 and -0.65% , respectively.

O- AND H-ISOTOPE STRATIGRAPHY

Upper and Main Zones (Bellevue)

Although there is a certain amount of scatter in the data, particularly for plagioclase, the following general features of the oxygen-isotope stratigraphy of Bellevue are evident. Pyroxene $\delta^{18}\text{O}$ values in the Bellevue core (Fig. 4) show an overall decrease with increasing stratigraphic height, whereas plagioclase $\delta^{18}\text{O}$ values show more scatter but do not appear to show a systematic change. This feature is also seen in the data of Schiffries & Rye (1989) through a much larger stratigraphic thickness of the eastern limb of the Bushveld. In addition, between the level of the Pyroxenite Horizon and the UZ-MZ boundary (Fig. 4), there appears to be a zone with generally lower values of $\Delta_{\text{plagioclase-pyroxene}}$.

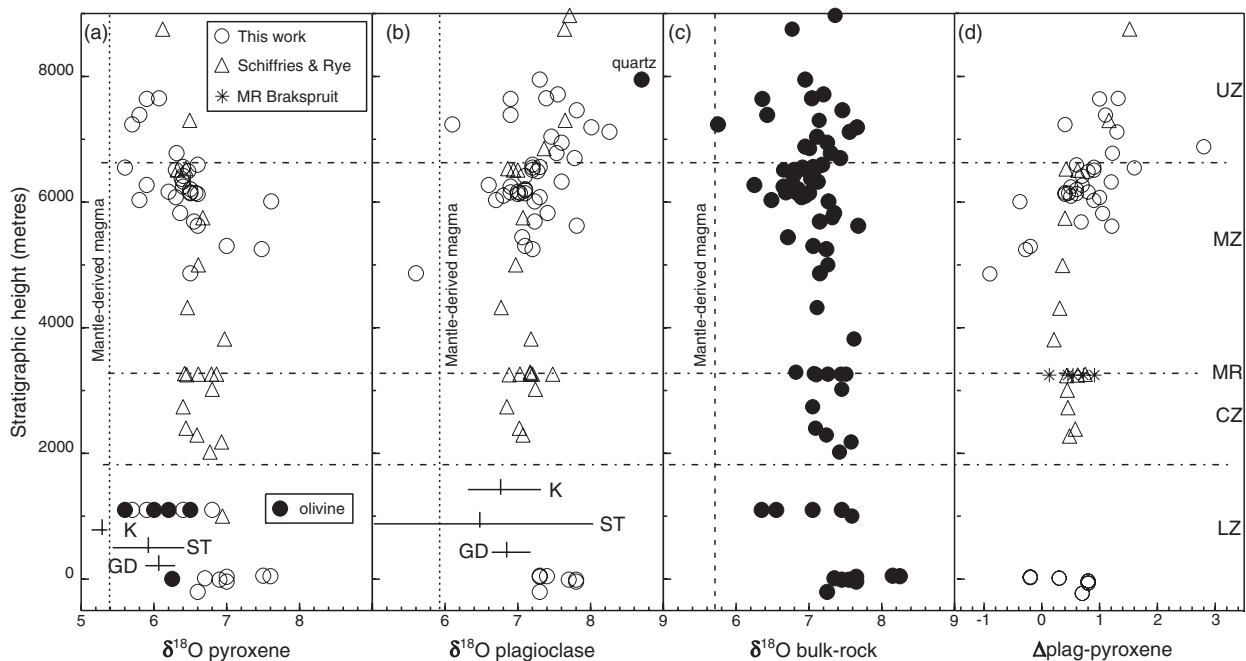


Fig. 6. Variation of $\delta^{18}\text{O}$ value of (a) pyroxene, (b) plagioclase, (c) calculated bulk rock (see text) and (d) $\Delta_{\text{plagioclase-pyroxene}}$ with stratigraphic height for the RLS. This is a composite section with data taken from different parts of the intrusion (see text) and includes published data from Schiffries & Rye (1989) and E. A. Mathez & P. Agrinier (unpublished data, 2004). Data from the Merensky Reef footwall at Impala (western limb) from Reid *et al.* (1993) show the same range as the MR data plotted here, and are omitted from the figure for clarity. Details of procedure followed for estimating stratigraphic height are given in the text. Datum is taken to be the base of the LZ, hence Marginal Zone samples have been allocated negative values for stratigraphic height. The range and average for similar rocks from the Great Dyke (GD), Kiglapait (K) and Stillwater (ST) are shown; data sources as for Fig. 2.

As a general rule, the value of $\Delta_{\text{plagioclase-pyroxene}}$ would be expected to increase with stratigraphic height for two reasons.

(1) The plagioclase becomes more sodic with height (Ashwal *et al.*, 2004; Table 3) and $\Delta_{\text{plagioclase-pyroxene}}$ is known to increase with decreasing anorthite content in the plagioclase (Chiba *et al.*, 1989).

(2) It is generally understood that the crystallization temperature in the layered suite decreased with stratigraphic height (e.g. Wager & Brown 1968) and this would have resulted in an increase in $\Delta_{\text{plagioclase-pyroxene}}$ of the primary minerals with stratigraphic height. However, post-crystallization reaction could obscure such trends.

The data presented in Fig. 4 for the Bellevue core suggest a value of $\Delta_{\text{plagioclase-pyroxene}}$ of about 0.9‰ for the lowest analysed part of the MZ (above the olivine-bearing rocks). There is no apparent systematic change in plagioclase $\delta^{18}\text{O}$ value and because plagioclase constitutes typically 80–90% of these rocks, no change in bulk-rock $\delta^{18}\text{O}$ is implied. The predicted $\Delta_{\text{plagioclase-pyroxene}}$ at crystallization temperatures is 0.53‰ [calculated from the data of Chiba *et al.* (1989) assuming An_{70} and 1150°C]. Just below the pyroxenite horizon the plagioclase composition is An_{64} . Plagioclase of this composition

and an observed $\Delta_{\text{plagioclase-pyroxene}}$ of 0.9‰ suggest final O-isotope equilibrium at 850°C. Just above the Pyroxenite Horizon, $\Delta_{\text{plagioclase-pyroxene}}$ is 0.4‰, which implies closure to O diffusion at much higher, magmatic temperatures. The value of $\Delta_{\text{plagioclase-pyroxene}}$ appears to remain constant for the remainder of the MZ (Fig. 4c). In the UZ, the $\delta^{18}\text{O}$ value of plagioclase varies significantly, probably the result of interaction with fluids, but there is no indication of a systematic change. Although the data for the upper part of the UZ are scattered, values for $\Delta_{\text{plagioclase-pyroxene}}$ are fairly constant at about 1.3‰. For a plagioclase of An_{47} (typical for the UZ, Table 1), this corresponds to a temperature of 730°C using the Chiba *et al.* (1989) fractionation factors.

The rocks between the Pyroxenite Horizon and the MZ–UZ contact are much more pyroxene rich (generally about 50% pyroxene 50% plagioclase) but the change in modal proportions in these essentially biminerals should not affect $\Delta_{\text{plagioclase-pyroxene}}$. Using the observed changes in modal proportions and assuming plagioclase and pyroxene $\delta^{18}\text{O}$ values of 6.2 and 7.1‰ (below the Pyroxenite Horizon) and 6.6 and 6.9‰ (above the Pyroxenite Horizon), it could be argued that there was a change in magma $\delta^{18}\text{O}$ value from 7.0 (below) to 6.8‰ (above) at the level of the Pyroxenite Horizon, although it

should be noted that the difference is well within the analytical errors and uncertainty in estimating magma composition from mineral $\delta^{18}\text{O}$ values.

The hydrogen-isotope stratigraphy of the Bellevue core is shown in Fig. 5. There is no obvious systematic change in δD with stratigraphic height, but it may be significant that the least negative δD values are found in the rocks between the Pyroxenite Horizon and the MZ–UZ contact. Water contents in the MZ rocks are uniformly low (0.15–0.30 wt %), although this may, in part, be due to the fact that only the freshest looking samples were analysed. The UZ rocks have variable, but generally higher water content (up to 0.65 wt %), which is often much higher than expected given the small amount of biotite and/or amphibole usually present (Table 1). This is consistent with the occurrence of significant quantities of hydroxyl-bearing minerals as very small inclusions within, for example, pyroxene and/or the presence of water within the pyroxene structure as discussed by Mathez *et al.* (1994).

Lower and Marginal Zones (Clapham and Olifants River Troughs)

The Lower Zone samples (Table 2) have more varied $\delta^{18}\text{O}$ values than the rocks from elsewhere in the Bushveld Complex. Kruger (1994) documented fairly large variations in initial Sr-isotope ratio in the LZ (0.7047–0.7072), which suggest that greater variation in magma $\delta^{18}\text{O}$ than the MZ and UZ might also have existed. Both olivine and pyroxene in the Olifants River Trough samples, and pyroxene and plagioclase in the Clapham Trough samples, have variable $\delta^{18}\text{O}$ values. The Olifants River Trough samples have pyroxene $\delta^{18}\text{O}$ values of between 5.7 and 6.8‰ and olivine $\delta^{18}\text{O}$ values that range from 5.6 to 6.5‰. Pyroxene $\delta^{18}\text{O}$ values from the Clapham Trough samples range from 6.6 to 7.6‰ (mean 7.04, $n = 7$) with plagioclase $\delta^{18}\text{O}$ values ranging from 7.3 to 7.8‰ (mean 7.47 $n = 6$). The Clapham Trough samples typically have higher $\delta^{18}\text{O}$ values than the Olifants River Trough samples. Typical $\delta^{18}\text{O}$ values of these minerals within mantle-derived volcanic rocks would be around 5.5‰ (pyroxene) and 5.2‰ (olivine) (e.g. Eiler, 2001). Thus all samples studied from the LZ have higher $\delta^{18}\text{O}$ values than expected for entirely mantle-derived magmas.

Overall stratigraphy of the RLS

A composite oxygen-isotope stratigraphy of the Bushveld layered rocks is shown in Fig. 6, which combines our data from the LZ of the eastern limb, and the MZ and UZ of the northern limb (Bellevue), with published data for the eastern limb (Schiffries & Rye, 1989) and Merensky Reef data from the western limb. As described above, these

data come from numerous different localities over a horizontal distance of over 200 km, and there is, therefore, a degree of uncertainty in how each group of samples is stratigraphically related. However, this uncertainty is relatively small compared with the total stratigraphic height of the intrusion. The following are the most important features. The LZ shows the most variation in plagioclase and pyroxene $\delta^{18}\text{O}$ values with the lowest values recorded in the Olifants River Trough samples. Although there is scatter in the data, the only systematic change in $\delta^{18}\text{O}$ value with height is a general increase in $\Delta_{\text{plagioclase-pyroxene}}$. This corresponds to little or no change in the bulk-rock $\delta^{18}\text{O}$ value (see below). Apart from some samples in the LZ, all Bushveld gabbros have $\delta^{18}\text{O}$ that are higher than typical mantle-derived magmas (or their cumulates). The variation of bulk-rock $\delta^{18}\text{O}$ value with stratigraphic height for the whole intrusion is shown in Fig. 6c. The average bulk-rock $\delta^{18}\text{O}$ value is $7.12 \pm 0.47\text{‰}$ (1σ , $n = 101$), which becomes 7.07 ± 0.34 (1σ) if three samples with anomalously high $\delta^{18}\text{O}$ values are omitted. The most important features of these diagrams are that there seems to be no evidence for systematic change in $\delta^{18}\text{O}$ value with stratigraphic height and that, on average, the RLS cumulates crystallized from magmas that had $\delta^{18}\text{O}$ values of $\sim 7.1\text{‰}$. Figure 6c suggests that there might be a slight decrease in bulk-rock $\delta^{18}\text{O}$ with increasing stratigraphic height, but the average $\delta^{18}\text{O}$ value for the UZ is 6.95 ± 0.38 (1σ , $n = 35$), which is not statistically different from the average $\delta^{18}\text{O}$ value for the MZ of 7.09 ± 0.29 (1σ , $n = 19$). The more detailed stratigraphy available for the Bellevue samples indicates that the rocks between the Pyroxenite Horizon and the top of the MZ crystallized from magmas that may have had slightly lower $\delta^{18}\text{O}$ values ($\sim 6.8\text{‰}$).

Unfortunately, our hydrogen-isotope stratigraphy for the Rustenburg Layered Suite is much less complete than that for oxygen (Fig. 5). Nevertheless, despite considerable variation in water content and degree of alteration (particularly in the LZ), there appears to be no systematic change in whole-rock δD value with stratigraphic height.

Comparison with other layered intrusions

The mean values and 1σ variation for other layered intrusions (Kiglapait, Stillwater and the Great Dyke) with similar mineralogy, are shown in Fig. 6a and b. It should be noted that all three intrusions have mineral $\delta^{18}\text{O}$ values that indicate final oxygen-isotope equilibrium at high temperatures (Fig. 2). Average plagioclase and pyroxene $\delta^{18}\text{O}$ values for Kiglapait, Stillwater and the Great Dyke are 6.84 ($n = 32$) and 5.29‰ ($n = 3$) (Kalmarides, 1985), 6.48 ($n = 28$) and 5.9‰ ($n = 10$) (Dunn, 1986) and 6.90 ($n = 5$) and 6.08‰ ($n = 5$) (Chaumba & Wilson, 1997), respectively. The average $\delta^{18}\text{O}$ values for Rustenburg Layered Suite plagioclase

and pyroxene are 7.23‰ ($n = 69$; two samples with $\delta^{18}\text{O} > 10\text{‰}$ omitted) and 6.45‰ ($n = 64$) respectively, which are slightly, but as we shall show, significantly higher than values for the other three intrusions.

DISCUSSION

Origin of high $\delta^{18}\text{O}$ values

Although the $\delta^{18}\text{O}$ values of the Bushveld magmas are not 'high' in the generally accepted sense, the fact that the gabbros appear to have crystallized from mafic magma(s) that had a $\delta^{18}\text{O}$ value around 7.1‰ indicates significant crustal contamination, as does the fact that the RLS $\delta^{18}\text{O}$ values are somewhat higher than other similar mafic-ultramafic intrusions. The Bushveld magmas have $\delta^{18}\text{O}$ values that are about 1.4‰ higher than expected from an uncontaminated mantle-derived magma (5.7‰, Ito *et al.*, 1987; Eiler, 2001). Schiffries & Rye (1989) suggested that partial melting of an ^{18}O -enriched mantle source was an unlikely explanation for the high $\delta^{18}\text{O}$ values in the Bushveld magmas. This explanation has become even less tenable since their study because mantle xenoliths from the Kaapvaal Craton show no evidence for elevated $\delta^{18}\text{O}$ values. Matthey *et al.* (1994) showed that olivine from mantle xenoliths and diamond inclusions from five kimberlite pipes in South Africa had an average $\delta^{18}\text{O}$ value of 5.19‰ ($\pm 0.28\ 2\sigma$, $n = 24$). This value is indistinguishable from that expected for olivine in equilibrium with NMORB magma assuming $\Delta_{\text{melt-olivine}} = 0.5\text{‰}$ (Eiler, 2001, p. 323). Willmore *et al.* (2002) suggested that the RLS magmas were derived by hydration partial melting in a subduction setting, on the basis of the high Cl/F ratios of CZ and LZ rocks, $\delta^{37}\text{Cl}$ values of biotites that are higher than the country rocks, and the 'boninitic arc-like character' of their magmas. However, an arc affinity, even if true, could not explain the high $\delta^{18}\text{O}$ values of the RLS magmas because Eiler *et al.* (2000) have shown that most arc-derived lavas have $\delta^{18}\text{O}$ values that are within 0.2‰ of MORB.

The other plausible explanation for higher than mantle $\delta^{18}\text{O}$ values is crustal contamination, which is the preferred model of most workers to explain the high initial Sr-isotope ratios of the RLS (e.g. Hamilton, 1977; Kruger & Marsh, 1982; Harmer & Sharpe, 1985; Kruger, 1994). The lack of any apparent systematic change in $\delta^{18}\text{O}$ with stratigraphic height for each zone suggests that the magmas became contaminated before emplacement at upper-crustal levels and were well mixed at the time of intrusion, as previously pointed out by Schiffries & Rye (1989). Sharpe *et al.* (1986) suggested that picritic mantle-derived magmas mixed with partially melted crust in a 'master AFC crystallization chamber' which then periodically fed into the Bushveld chamber to give rise to the Rustenburg Layered Suite. Although Sharpe *et al.* (1986)

suggested that this staging magma chamber was situated at the crust-mantle boundary, the exact depth is poorly constrained and, depending on the crustal level, possible contaminants could include the local country rocks (Archaean granites, and Transvaal Supergroup dolomites, metamorphosed shales, and quartzites), as well as deeper crust.

In the following sections, crustal contamination models will be discussed in terms of bulk mixing between magma and possible contaminants. This approach has also been used to model radiogenic isotope data by Maier *et al.* (2000), who discussed the limitations of using such a simple approach on the validity of their models. The fact that oxygen concentrations do not vary significantly between end-members means that bulk mixing and more complex models such as AFC (assimilation accompanied by fractional crystallization, DePaolo, 1981) do not lead to significantly different solutions. Bulk mixing can be viewed as an end-member case of an AFC process where none of the introduced material with (in this case) higher ^{18}O content is lost via the cumulates. For an AFC process, the integrated amount of contamination required to explain a given shift in $\delta^{18}\text{O}$ value is always larger than for bulk mixing.

Schiffries & Rye (1989) concluded that the rocks of the Transvaal Supergroup were the most likely contaminants because of their availability and relatively high $\delta^{18}\text{O}$ values (9–15‰). Simple mixing models indicate that between 15 and 42% contamination with such material would raise the $\delta^{18}\text{O}$ values of the magmas to 7.1‰. Pelitic rocks are present in considerable thicknesses within the Transvaal Supergroup (SACS, 1980; Ericksson & Reczko, 1995); for example, the Silverton Formation (up to 800 m) and the Timeball Hill Formation (up to 1500 m), which have easily fusible components and represent the most plausible upper-crustal material that could have contaminated the RLS magmas. Johnson *et al.* (2003) discussed partial melting in metapelites of the Silverton Formation (within the contact aureole of eastern limb). Those workers found little variation in whole-rock $\delta^{18}\text{O}$ value across a wide range of metamorphic grade ($12.2 \pm 1.0\text{‰}$, 2σ , $n = 20$) with leucosomes having $\delta^{18}\text{O}$ values only slightly higher than the host rocks (average 12.8‰, $n = 3$), which was interpreted as indicating closed-system melting. Similar partial melts could presumably have mixed with the RLS magmas, and 20% of material having a $\delta^{18}\text{O}$ value of 12.8‰ would have been required to raise the magma $\delta^{18}\text{O}$ value from 5.7 to 7.1‰.

The available $\delta^{18}\text{O}$ values for Archaean granitic rocks of the Kaapvaal craton suggest typical values of around 6–8‰ (Taylor, 1968; Barker *et al.*, 1976; Faure & Harris, 1991), and Archaean granite below the northern limb has a whole-rock $\delta^{18}\text{O}$ value of 8.3‰ (Harris & Chaumba, 2001). Because the $\delta^{18}\text{O}$ values of these granitic rocks are

only a few per mil higher than the expected value for a mantle-derived magma, they are not plausible contaminants on the grounds that very large amounts of contamination (>50%) would be required. The Malmani Dolomite in the vicinity of the northern limb (Fig. 1) has high $\delta^{18}\text{O}$ values (21–23‰, Harris & Chaumba, 2001) but is not a suitable contaminant on chemical grounds because its assimilation would have decreased the silica activity of the magma (i.e. favouring the crystallization of olivine). Thus contamination by either the granite or dolomite at shallow levels is not favoured.

If contamination took place at a much deeper level in the crust before magma emplacement, it is necessary to consider the likely oxygen-isotope composition of lower–middle crust. The closest exposures of rocks that are reasonable candidates for lower to middle crust beneath the Bushveld are in the Vredefort impact structure 150 km to the south (Hart *et al.*, 1990; Lana *et al.*, 2003) and the southern marginal zone of the Limpopo metamorphic belt a similar distance to the north. In both cases an extensive O-isotope database is available (Vennemann & Smith, 1992; La Grange *et al.*, 2000; La Grange, 2004).

Archaean basement rocks exposed in the core of the Vredefort structure have been divided by Hart *et al.* (1990) into the OGG (outer granite gneiss) and ILG (inlandsee leucogranofels). The boundary between the two appears to represent the transition between partial melt-depleted granulites (ILG) and melt-rich amphibolite-facies migmatitic gneisses (OGG) that formed during regional metamorphism of tonalitic crust at 3.1 Ga (Lana *et al.*, 2003). Geobarometry on pelitic gneisses suggests a depth of burial of about 17–20 km for the OGG (Stevens *et al.*, 1997) and at the time of formation of the Bushveld Complex at 2.05 Ga, the OGG–ILG rocks would have been typical of the middle crust in the region. A $\delta^{18}\text{O}$ profile through an 11 km section of the OGG and ILG rocks of the Vredefort structure (La Grange, 2004) shows comparatively little variation in whole-rock $\delta^{18}\text{O}$ value, with the majority of whole-rock $\delta^{18}\text{O}$ values being between 8 and 10‰. The average $\delta^{18}\text{O}$ value of the Vredefort orthogneisses is 9.15‰ ($2\sigma = 1.96\text{‰}$, $n = 35$) and the average $\delta^{18}\text{O}$ value of quartz in the analysed rocks is 9.83 ($2\sigma = 1.41\text{‰}$, $n = 6$) (La Grange, 2004). It is unlikely that any partial melt of these rocks would have had a $\delta^{18}\text{O}$ value that is more than 1‰ higher than the bulk rock. The oxygen-isotope composition of amphibolite- to granulite-facies pelitic rocks of the Southern Marginal Zone of the Limpopo Belt (Vennemann & Smith, 1992) is very similar to those of Vredefort. The Limpopo amphibolite-facies rocks have a mean $\delta^{18}\text{O}$ value of 9.59‰ ($n = 11$), which is almost identical to the average for the granulites of 9.61‰ ($n = 9$). Furthermore, the total range from 8.1 to 11.4‰ is very similar to that of Vredefort, which suggests that the

oxygen-isotope composition of the lower to middle crust does not (and did not at 2050 Ma) vary significantly beneath the Bushveld.

Mass-balance calculations assuming simple mixing show that it would require 41% contamination of the Bushveld magma by material having a $\delta^{18}\text{O}$ value equal to the average for Vredefort of 9.15‰ to raise the $\delta^{18}\text{O}$ value from 5.7 to 7.1‰. Similarly, it would require 36% contamination by material having a $\delta^{18}\text{O}$ value equal to the average for the Limpopo metapelites of 9.60‰ to raise the $\delta^{18}\text{O}$ value of the Bushveld magma from 5.7 to 7.0‰.

In summary, there are effectively two different assimilation models that can explain the high $\delta^{18}\text{O}$ values of the Rustenburg Layered Suite. The first, endorsed by Schiffries & Rye (1989) and subsequently by Harris & Chaumba (2001), favours the Transvaal Supergroup sedimentary rocks as the contaminants, the most likely mechanism being mixing with partial melts of pelitic units such as the Silverton Formation. The second model proposes that assimilation took place in a staging magma chamber(s) that was situated in the lower to middle crust. In the case of the Transvaal Supergroup, the contaminants have relatively high $\delta^{18}\text{O}$ values and about 20% assimilation would be required to raise the magma $\delta^{18}\text{O}$ value to 7.1‰. Because the $\delta^{18}\text{O}$ value of the lower to middle crust appears to be neither especially high (9.2–9.6‰) nor very variable, then it is necessary to accept that, for assimilation at these levels, the amount of contamination would have been much higher, of the order of 36–41%.

As it appears that the crustal assimilation process took place before emplacement, it seems unlikely that these shallow-level crustal rocks could have been available as contaminants. The Transvaal Supergroup sedimentary rocks are only about 200 Myr older than the Bushveld Complex (e.g. Eriksson & Reczko, 1995) and the maximum thickness of the Transvaal Supergroup is of the order of 10–15 km in the area of the eastern limb according to SACS (1980). The RLS was intruded discordantly within the Transvaal Supergroup (e.g. Cawthorn 1998), which means that the thickness of Transvaal Supergroup rocks beneath the RLS is variable and difficult to estimate. It seems unlikely that a staging magma chamber could have been situated within the Transvaal Supergroup.

Multi-isotope constraints on crustal contamination

Differences in initial Sr-isotope composition led Hamilton (1977) to suggest that each zone of the RLS crystallized from magma of a different isotope composition and it is now generally accepted (e.g. Kruger, 1994; Eales & Cawthorn, 1996) that at least three different magma types were involved; one with LZ–CZ affinity, one from

the Merensky interval to the Pyroxenite Marker, and one from the Pyroxenite Marker to the top of the UZ. The first magma was fairly silica- and magnesium-rich (55.7 and 12.4%, respectively) as suggested by Davies *et al.* (1980) and Sharpe (1981). The second magma, emplaced at the level of the Merensky Unit and called B3 by Sharpe (1981), was a more typical tholeiitic composition (between 51 and 53% SiO₂ and 8.5–9.2% MgO according to the previous two workers). The third magma, intruded at the level of the Pyroxenite Marker, contained 49.3% SiO₂ and 6.1% MgO (Davies & Cawthorn, 1984).

The first combined Sr- and Nd-isotope study of the RLS rocks was by Maier *et al.* (2000). Those workers suggested that the LZ was contaminated with relatively small amounts (10–30%) of material of granitic composition, formed by small degrees of melting (5%) of the typical upper-crust composition proposed by Taylor & McClelland (1985). By contrast, the MZ magma was formed through higher degrees (40–50%) of contamination with the depleted restite formed as a result of the first partial melting event. Maier *et al.* (2000) envisaged that the CZ magma would be intermediate between LZ and MZ magmas. At the level in the crust proposed by them for the staging chamber (about 35 km), residues of partial melting would be granulites (Patiño Douce & Beard, 1995), which ought to have lower Nd and higher Sr contents than their partial melts. The conclusions of Maier *et al.* (2000) are qualitatively consistent with the major element compositions of the proposed parental magmas in that the LZ magma had high silica together with high MgO. The MZ magma had lower silica and lower MgO content, which is consistent with higher degrees of contamination (hence lower MgO) by material having lower silica (i.e. restite). The modelling of Maier *et al.* (2000) shows that in terms of Sr- and Nd-isotopes, the lower portion of the crust exposed at Vredefort is also a suitable contaminant with about 15% contamination by a partial melt indicated for the LZ magmas and 35–40% contamination by the restite indicated for the MZ magmas. However, Maier *et al.* (2000) rejected Vredefort lower crust as a potential contaminant in favour of generic upper crust (of Taylor & McClelland, 1985) on the basis of trace element arguments. However, given that major uncertainty exists over the radiogenic isotope and trace element composition of the parental mantle-derived magma for all magma types, arguments against contamination by material similar to Vredefort lower crust cannot be regarded as well founded.

The estimates of Maier *et al.* (2000) for the required degree of contamination by Vredefort rocks to generate the MZ magmas (about 33–40%, their fig. 7c) and the estimates based on simple mass-balance models for oxygen isotopes discussed above (38%) agree well. There is, however, less agreement for the LZ. Our data for the LZ suggest a range in $\delta^{18}\text{O}$ values of 6.2–7.6‰ for the

LZ magma(s) (Fig. 6c). As discussed above, a partial melt of the Vredefort rocks would be unlikely to have a $\delta^{18}\text{O}$ value higher than 10.15‰. Simple mass-balance mixing models assuming a mantle-derived magma of 5.7‰ and a contaminant of 10.15‰ suggest that amounts of contamination from 11 to 43% could generate the range in $\delta^{18}\text{O}$ values, with 29% contamination to generate the average LZ value of 7.0‰. This is much higher than the 15% contamination proposed for the LZ magma by Maier *et al.* (2000).

The UZ was not considered by Maier *et al.* (2000) but it appears to have crystallized from a tholeiitic magma, which had a slightly lower initial Sr-isotope ratio (0.7073) than the preceding MZ (0.7085; Kruger, 1994). However, the magma that was added at the level of the Pyroxenite Marker and then mixed with residual MZ magma had an initial Sr-isotope ratio of 0.706 (Cawthorn *et al.*, 1991). The initial Sr-isotope ratio of the UZ magma is higher than expected for mantle-derived magmas. In the UZ, Sr-isotope ratio does not vary systematically with stratigraphic height, which again suggests that crustal contamination took place before emplacement. As discussed above, $\delta^{18}\text{O}$ values estimated for bulk rocks between the Pyroxenite Horizon and the base of the UZ are on average about 0.2‰ lower than those for the rocks above and below, but apart from this, there is no indication that the UZ and MZ rocks have significantly different $\delta^{18}\text{O}$ values.

The lack of systematic change in $\delta^{18}\text{O}$ value with stratigraphic height in the RLS coupled with the apparent lack of variation in $\delta^{18}\text{O}$ of the middle to lower crust of the Kaapvaal Craton, as suggested by the Vredefort Dome data of La Grange (2004), requires that the amount of contamination was roughly similar in the UZ, MZ and LZ. The initial UZ magma had a lower MgO content than the MZ magma, which would be consistent either with a more felsic contaminant (i.e. the most easily melted fraction) or a greater amount of fractional crystallization at depth. The lower initial Sr-isotope ratio could then be explained either by a lower Sr content or lower Sr-isotope ratio at 2050 Ma of the UZ contaminant compared with the MZ contaminant. These features are consistent with the contaminant of the UZ magma being a partial melt, in the same manner as the contaminant to the LZ. This in turn requires that the staging magma chamber be situated at a different level in the lower to middle crust that was unaffected by the earlier partial melting event. Sharpe (1985) and Maier *et al.* (2001) suggested that the MZ intruded the RLS magma chamber during the later stages of crystallization of the upper CZ. In this model, the UZ represents displaced, less dense, residual magma, which eventually crystallized above the MZ, despite being older. If this model were to be true, it would obviate the need for a second staging chamber.

Four samples from the Marginal Zone of the Bushveld have $\delta^{18}\text{O}$ values that lie at the high end of the entire dataset, averaging 7.6 and 6.8‰ for pyroxene and plagioclase, respectively. Such values suggest crystallization from a magma having higher $\delta^{18}\text{O}$ than all other samples from the RLS except those of the Platreef in contact with the country rock (Harris & Chaumba, 2001). This may be related to contamination of the Marginal Zone magma by local country rocks of the Transvaal Super-group, perhaps by the partial melts described by Johnson *et al.* (2003).

Origin of RLS magmas

It was suggested above that the RLS magmas were contaminated by lower to middle crust because of a lack of availability of upper-crustal material in a sub-RLS staging chamber. However, a mechanism that could account for the presence of upper-crustal material deep within the crust is the meteorite impact hypothesis, first proposed for the Bushveld by Hamilton (1970) and subsequently supported by Rhodes (1975). It has recently been suggested by Jones *et al.* (2002) that impact-induced melting may be more important than hitherto realized in the formation of large igneous provinces, of which the Bushveld Complex is an example. Jones *et al.* envisaged that such a situation would result in mantle melts mixing with melts from the sub-crater materials in a similar manner to that suggested above for formation of RLS magmas. The lack of physical evidence for impact, in the form of a crater, was explained by Jones *et al.* (2002) by auto-oblation by the subsequent volcanism.

Despite the fact that impact is an attractive mechanism for explaining pre-emplacment assimilation of upper crust by RLS magmas, the absence of convincing evidence for shock deformation of pre-Bushveld rocks (e.g. Buchanan & Reimold, 1998) strongly suggests that the Bushveld Complex did not form as a result of impact. The high silica content (55.7%) of the LZ magma combined with its high MgO (12.44%) has led some researchers to suggest that the early RLS magmas were boninites (Sharpe & Hulbert, 1985; Hatton & Sharpe, 1989) and therefore formed in a subduction-related environment. As discussed above, such an origin cannot explain the high $\delta^{18}\text{O}$ values of the RLS magmas, and we believe that their composition can equally well be explained by extensive crustal contamination. The high degree of assimilation proposed here, and by Maier *et al.* (2000), clearly required considerable heat, which suggests that the original mantle-derived magma was high-MgO picritic or possibly komatiitic in composition (e.g. Barnes, 1989). Numerous workers have attributed Bushveld magmatism to the influence of a mantle plume (e.g. Sharpe *et al.*, 1986; Hatton, 1995), and in common with Maier *et al.* (2000) we believe it provides a reasonable

explanation of the composition and extent of the RLS magmas. In this situation, extensive crustal assimilation could be expected only where the crust is already hot, that is, at the deep levels in the crust we have proposed.

Magma influx at the Pyroxenite Horizon?

Although there are no sudden changes in bulk-rock $\delta^{18}\text{O}$ values, the marked decrease in $\Delta_{\text{plagioclase-pyroxene}}$ at the level of the Pyroxenite Horizon (Fig. 4) requires explanation. Given that this stratigraphic level may be close to the interval that marks the influx of the new magma parental to the UZ, it seems reasonable to suppose that influx of magma might be the cause of the change in $\Delta_{\text{plagioclase-pyroxene}}$. The influx of new magma to form the UZ at the level of the Pyroxenite Marker in the eastern and western limbs has previously been suggested on the basis of a reversal in mineral compositions and a sudden decrease in initial Sr-isotope ratio (e.g. von Gruenewaldt, 1973; Sharpe, 1985; Cawthorn *et al.*, 1991). Although its MgO was not especially high (6.1%, Davies & Cawthorn, 1984) the more primitive mineral compositions (in terms of Mg-number) suggest that it was hotter than the magma already in the chamber. The relationship between the Pyroxenite Marker in the eastern and western limbs and the Pyroxenite Horizon in the northern limb is unclear. Ashwal *et al.* (2004) suggested that the level of the Pyroxenite Horizon represents a magmatic transgression of Upper Zone magmas over Main Zone cumulates.

There are four possible causes for change in $\Delta_{\text{plagioclase-pyroxene}}$ at the Pyroxenite Horizon that could be related to an influx of magma:

- (1) crystallization from a hotter magma;
- (2) change in pyroxene type from primary orthopyroxene to pigeonite;
- (3) change in volatile content of the recharge magma;
- (4) change in cooling rate.

In theory, $\Delta_{\text{plagioclase-pyroxene}}$ depends on the temperature of the magma from which the minerals crystallize, but the difference in $\Delta_{\text{plagioclase-pyroxene}}$ for plagioclase of composition An_{60} between 1150 and 1000°C is only 0.15‰ (Chiba *et al.*, 1989). A change from An_{70} to An_{60} (which is not observed) would only increase this difference by 0.07‰. Therefore on both petrographic grounds (the absence of mineral reversals) and consideration of fractionation factors, the shift in $\Delta_{\text{plagioclase-pyroxene}}$ cannot be due to the intrusion of hotter magma at that level of the northern limb.

At the level of the Pyroxenite Horizon, the pyroxene assemblage changes from primary orthopyroxene and calcic clinopyroxene to primary pigeonite and calcic clinopyroxene. Hence, a change in the $\Delta_{\text{plagioclase-pyroxene}}$ may occur coincident with this phase change if pigeonite fractionates oxygen isotopes in a similar manner to calcic clinopyroxene. However, the theoretical fractionations of

Zheng (1993) suggest that the difference in $\delta^{18}\text{O}$ between ortho- and clinopyroxene is of the order of 0.26‰ at 555°C and 0.09‰ at 1150°C. Hence, this difference is not large enough to explain the observed decrease in $\Delta_{\text{plagioclase-pyroxene}}$ across this boundary.

Mechanisms (3) and (4) are related to changes in the temperature of mineral closure to oxygen diffusion (e.g. Giletti, 1986). As discussed above, oxygen can continue to diffuse and equilibrate isotopically between minerals after crystallization down to a theoretical minimum temperature of about 550°C, at which $\Delta_{\text{plagioclase-pyroxene}}$ is much larger (1.74‰ for An_{60}) than at magmatic temperatures. Two parameters that could influence the final closure temperature are volatile content and rate of cooling. Any new magma injected into the Bushveld magma chamber ought to have been less volatile-rich than the existing magma in the chamber. This is because volatiles would have been excluded from the anhydrous crystallizing phases and would have become concentrated in the residual magma as the proportion crystallized increased. The presence of volatiles is known to increase the rate of diffusion of oxygen in minerals (e.g. Cole & Chakraborty, 2001). Alternatively, the decrease in $\Delta_{\text{plagioclase-pyroxene}}$ could represent a sudden increase in the rate of cooling. Of the two mechanisms, the latter is more consistent with the seemingly abrupt change in $\Delta_{\text{plagioclase-pyroxene}}$ and there is no supporting petrographic evidence (e.g. hydrous minerals, or higher H_2O^+ in the samples immediately below the Pyroxenite Horizon) for the former. Hence the Pyroxenite Horizon could represent an influx of magma that initially cooled fairly rapidly in contact with the surrounding, colder cumulates, before inflation of the chamber and intrusion of the main body of UZ magma. There is some petrographic support for this as the rocks within the stratigraphic interval in question are generally finer grained than the rest of the Bellevue core (Ashwal *et al.*, 2004).

CONCLUSIONS

(1) The original RLS magma(s) had $\delta^{18}\text{O}$ values that are on average 1.4‰ higher than the 5.7‰ expected in an uncontaminated mantle-derived magma. The RLS rocks have higher $\delta^{18}\text{O}$ values than other layered mafic to ultramafic intrusions such as Stillwater, Kiglapait and the Great Dyke for which mineral $\delta^{18}\text{O}$ values are available. Crustal contamination is the most likely cause of high $\delta^{18}\text{O}$ values, as previously suggested.

(2) Hydrogen-isotope data suggest that water contained within RLS minerals is of magmatic origin and is not an alteration phenomenon.

(3) There is no evidence for any systematic change in magma $\delta^{18}\text{O}$ value, either in the 2500 m section through the northern limb that was studied in detail, nor in the

Rustenburg Layered Suite as a whole. The intruding magmas must have been already contaminated and well mixed, which suggests a 'staging' magma chamber in the middle to lower crust. It is unlikely that the exposed country rocks around the Bushveld were available as contaminants at the required depth in the crust.

(4) The lower to middle crust in the region has consistent $\delta^{18}\text{O}$ values of around 9.2–9.6‰ over a considerable depth range (>10 km). Considerable degrees of contamination (36–41%) are required to raise $\delta^{18}\text{O}$ from a typical mantle value of 5.7‰ to the observed values of about 7.1‰.

(5) Previously published models using a combination of Sr- and Nd-isotope data have indicated that the LZ was contaminated by 10–30% of a partial melt of the crust, whereas the MZ was contaminated by much greater quantities (40–50%) of the residue of partial melting. Although consistent with the large amounts of contamination required, the O-isotope data require that the amounts of contamination to form both the LZ and MZ magmas are similar. Previous models relating the extent of shifts in radiogenic isotope data to changes in concentration of the element in question in the contaminant caused by partial melting can explain the paradox of changing radiogenic isotope composition with stratigraphic height with the lack of change in $\delta^{18}\text{O}$ value of the various magmas.

(6) The value of $\Delta_{\text{plagioclase-pyroxene}}$ is significantly lower between the level of the Pyroxenite Horizon and the MZ–UZ contact in the northern limb. This can best be explained by a higher closure temperature to oxygen diffusion in these rocks, which is most likely to be a response to the input of new magma intruded at this level. The most plausible explanation is that the initial magma cooled more rapidly against the pre-existing rocks before further inflation of the magma chamber and formation of the UZ.

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REFERENCES

- Ashwal, L. D., Webb, S. J. & Knoper, M. W. (2004). Magmatic stratigraphy in the Bushveld Northern Lobe: continuous geophysical and mineralogical data from the 2950 m Bellevue drillcore. *South African Journal of Geology* (in press).
- Baker, J. A., Macpherson, C. G., Menzies, M. A., Thirlwall, M. F., Al-Kadasi, M. & Matthey, D. P. (2000). Resolving crustal and mantle contributions to continental flood volcanism, Yemen; constraints from mineral oxygen isotope data. *Journal of Petrology* **41**, 1805–1820.
- Barker, F., Friedman, I., Hunter, D. R. & Gleason, J. D. (1976). Oxygen isotopes of some trondjemites, siliceous gneisses, and associated mafic rocks. *Precambrian Research* **3**, 547–557.
- Barnes, S. J. (1989). Are Bushveld U-type parent magmas boninites or contaminated komatiites? *Contributions to Mineralogy and Petrology* **101**, 447–456.
- Barnes, S. J., Maier, W. D. & Ashwal, L. D. (2004) Platinum-group element distribution in the Main Zone and Upper Zone of the Bushveld Complex, South Africa. *Chemical Geology* **208**, 293–317.
- Bell, D. R. & Rossman, G. R. (1992). Water in Earth's mantle: the role of nominally anhydrous minerals. *Science* **255**, 1391–1397.
- Buchanan, D. L., Nolan, J., Suddaby, P., Rouse, J. E., Viljoen, M. J. & Davenport, J. W. J. (1981). The genesis of sulphide mineralisation in a portion of the Potgietersrus limb of the Bushveld Complex. *Economic Geology* **76**, 568–579.
- Buchanan, P. C. & Reimold, W. U. (1998). Studies of the Rooiberg Group, Bushveld Complex, South Africa: no evidence for an impact origin. *Earth and Planetary Science Letters* **155**, 149–165.
- Buick, I. S., Maas, R. & Gibson, R. L. (2001). Precise U–Pb titanite age constraints on the emplacement of the Bushveld Complex, South Africa. *Journal of the Geological Society, London* **158**, 3–6.
- Cameron, E. N. (1978). The lower zone of the eastern Bushveld Complex in the Olifants River Trough. *Journal of Petrology* **19**, 437–462.
- Cawthorn, R. G. (1996). Models for incompatible trace-element abundances in cumulus minerals and their application to plagioclase and pyroxene compositions in the Bushveld Complex. *Contributions to Mineralogy and Petrology* **123**, 109–115.
- Cawthorn, R. G. (1998). Geometrical relations between the Transvaal Supergroup, the Rooiberg Group, and the mafic rocks of the Bushveld Complex. *South African Journal of Geology* **101**, 275–279.
- Cawthorn, R. G., Davies, G., Clubely-Armstrong, A. & McCarthy, T. S. (1981). Sills associated with the Bushveld Complex, South Africa: an estimate of the parental magma composition. *Lithos* **14**, 1–15.
- Cawthorn, R. G., Meyer, S. P. & Kruger, F. J. (1991). Major addition of magma at the Pyroxenite Marker in the western Bushveld Complex, South Africa. *Journal of Petrology* **32**, 739–763.
- Chaumba, J. B. & Wilson, A. H. (1997). An oxygen isotope study of the Lower Mafic Succession of the Darwendale Subchamber of the Great Dyke, Zimbabwe. *Chemical Geology* **135**, 293–305.
- Chiba, H., Chacko, T., Clayton, R. N. & Goldsmith, J. R. (1989). Oxygen isotope fractionations involving diopside, forsterite, magnetite, and calcite: applications to geothermometry. *Geochimica et Cosmochimica Acta* **53**, 2985–2995.
- Cole, D. R. & Chakraborty, S. (2001). Rates and mechanisms of isotopic exchange. *Reviews in Mineralogy* **43**, 83–223.
- Coplen, T. B. (1993). Normalization of oxygen and hydrogen isotope data. *Chemical Geology (Isotope Geosciences Section)* **72**, 293–297.
- Coplen, T. B., Kendall, C. & Hoppé, J. (1983). Comparison of stable isotope reference samples. *Nature* **302**, 236–238.
- Davies, G. & Cawthorn, R. G. (1984). Mineralogical data on multiple intrusion in the Rustenburg Layered Suite of the Bushveld Complex. *Mineralogical Magazine* **48**, 469–480.
- Davies, G., Cawthorn, R. G., Barton, J. M. & Morton, M. (1980). Parental magma to the Bushveld Complex. *Nature* **287**, 33–35.
- DePaolo, D. J. (1981). Trace element and isotopic effects of combined wall rock assimilation and fractional crystallisation. *Earth and Planetary Science Letters* **53**, 189–202.
- Dunn, T. (1986). An investigation of the oxygen isotope geochemistry of the Stillwater Complex. *Journal of Petrology* **27**, 987–997.
- Eales, H. V. & Cawthorn, R. G. (1996). The Bushveld Complex. In: Cawthorn, R. G. (ed.) *Layered Intrusions*. Amsterdam: Elsevier, pp. 181–229.
- Eiler, J. M. (2001). Oxygen isotope variations of basaltic lavas and upper mantle rocks. *Reviews in Mineralogy* **43**, 319–364.
- Eiler, J. M., Crawford, A., Elliott, T., Farley, K. A., Valley, J. W. & Stolper, E. M. (2000). Oxygen isotope geochemistry of oceanic-arc lavas. *Journal of Petrology* **41**, 229–256.
- Eriksson, P. G. & Reczko, B. F. F. (1995). The sedimentary and tectonic setting of the Transvaal Supergroup floor rocks to the Bushveld Complex. *Journal of African Earth Sciences* **21**, 487–504.
- Faure, K. & Harris, C. (1991). Oxygen and carbon isotope geochemistry of the 3.2 Ga Kaap Valley tonalite, Barberton greenstone belt, South Africa. *Precambrian Research* **52**, 301–319.
- Gerbe, M. C. & Thouret, J. C. (2004) Role of magma mixing in the petrogenesis of tephra erupted during the 1990–98 explosive activity of Nevado Sabancaya, southern Peru. *Bulletin of Volcanology* **66**, 541–561.
- Giletti, B. J. (1986). Diffusion effects on oxygen isotope temperatures of slowly cooled igneous and metamorphic rocks. *Earth and Planetary Science Letters* **77**, 218–229.
- Gregory, R. T. & Criss, R. E. (1986). Isotopic exchange in open and closed systems. In: Valley, J. W., Taylor, H. P., Jr & O'Neil, J. R. (eds) *Stable Isotopes in High Temperature Geological Processes*. Mineralogical Society of America, *Reviews in Mineralogy* **16**, 91–127.
- Gregory, R. T., Criss, R. E. & Taylor, H. P., Jr (1989). Oxygen isotope exchange kinetics of mineral pairs in closed and open systems: applications to problems of hydrothermal alteration of igneous rocks and Precambrian iron formations. *Chemical Geology* **75**, 1–42.
- Hamilton, J. (1977). Strontium isotope and trace element studies on the Great Dyke and Bushveld mafic phase and their relation to early Proterozoic magma genesis in southern Africa. *Journal of Petrology* **18**, 24–52.
- Hamilton, W. (1970). Bushveld complex—product of impacts? *Geological Society of South Africa, Special Publications* **1**, 367–379.
- Harmer, R. E. & Sharpe, M. R. (1985). Field relations and strontium isotope systematics of the marginal rocks of the eastern Bushveld Complex. *Economic Geology* **80**, 813–837.
- Harris, C. & Chaumba, J. B. (2001). Crustal contamination and fluid–rock interaction during the formation of the Platreef, northern limb of the Bushveld Complex, South Africa. *Journal of Petrology* **42**, 1321–1347.
- Harris, C. & Erlank, A. J. (1992). The production of large-volume low- $\delta^{18}\text{O}$ rhyolites during the rifting of Africa and Antarctica: the Lebombo Monocline, southern Africa. *Geochimica et Cosmochimica Acta* **56**, 3561–3570.
- Harris, C., Smith, H. S. & le Roex, A. P. (2000). Oxygen isotope composition of phenocrysts from Tristan da Cunha and Gough

- Island lavas: variation with fractional crystallization and evidence for assimilation. *Contributions to Mineralogy and Petrology* **138**, 164–175.
- Hart, R. J., Andreoli, M. A. G., Tredoux, M. & de Wit, M. J. (1990). Geochemistry across an exposed section of Archaean crust at Vredefort: with implications for mid-crustal discontinuities. *Chemical Geology* **82**, 21–50.
- Hatton, C. J. (1995). Mantle plume origin for the Bushveld and Ventersdorp magmatic provinces. *Journal of African Earth Sciences* **21**, 571–577.
- Hatton, C. J. & Sharpe, M. R. (1989). Significance and origin of boninite-like rocks associated with the Bushveld Complex. In: Crawford, A. J. (ed.) *Boninites and Related Rocks*. London: Unwin Hyman, pp. 174–208.
- Ito, E., White, W. M. & Gopel, C. (1987). The O, Sr, Nd, and Pb isotope geochemistry of MORB. *Chemical Geology* **62**, 157–176.
- Johnson, T. E., Gibson, R. L., Brown, M., Buick, I. S. & Cartwright, I. (2003). Partial melting of metapelitic rocks beneath the Bushveld Complex, South Africa. *Journal of Petrology* **44**, 789–813.
- Jones, A. P., Price, G. D., Price, N. J., DeCarli, P. S. & Clegg, R. A. (2002). Impact induced melting and the development of large igneous provinces. *Earth and Planetary Science Letters* **202**, 551–561.
- Kalamarides, R. I. (1984). Kiglapait geochemistry VI: Oxygen isotopes. *Geochimica et Cosmochimica Acta* **48**, 1827–1836.
- Knoper, M. W. & von Gruenewaldt, G. (1992). Main Zone parental magma composition in the northern Bushveld Complex, Potgietersrus: evidence from REE content of plagioclase (abstract). In: *Geological Society of South Africa, 24th Geocongress, Bloemfontein*. Johannesburg: Geological Society of South Africa, p. 237.
- Kruger, F. J. (1994). The Sr-isotope stratigraphy of the Western Bushveld Complex. *South African Journal of Geology* **97**, 393–398.
- Kruger, F. J. & Marsh, J. S. (1982). The significance of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Merensky cycle of the Bushveld Complex. *Nature* **298**, 53–55.
- Kyser, T. K., O'Neil, J. R. & Carmichael, I. S. E. (1981). Oxygen isotope thermometry of basic lavas and mantle nodules. *Contributions to Mineralogy and Petrology* **77**, 11–23.
- La Grange, M. (2004). A detailed petrographic and oxygen isotope study of metamorphic rocks and Archaean basement complex gneisses from the Vredefort Dome, South Africa. M.Sc. thesis, University of Cape Town, 120 pp.
- La Grange, M. S., Stevens, G. & Harris, C. (2000). Metamorphism of Witwatersrand rocks in the collar of the Vredefort structure: a petrographic and O isotope study. *Journal of African Earth Sciences* **31**, 39–40.
- Lana, C., Gibson, R. L., Kisters, A. F. M. & Reimold, W. U. (2003). Archaean crustal structure of the Kaapvaal craton, South Africa—evidence from the Vredefort dome. *Earth and Planetary Science Letters* **206**, 133–144.
- Lee, C. A. (1996). A review of mineralization in the Bushveld Complex and some other layered intrusions. In: Cawthorn, R. G. (ed.) *Layered Intrusions*. Amsterdam: Elsevier, pp. 103–145.
- Lee, C. A. & Tredoux, M. (1986). Platinum-group element abundances in the Lower and the Lower Critical Zones of the Bushveld Complex. *Economic Geology* **81**, 1087–1095.
- Maier, W. D., Arndt, N. T. & Curl, E. A. (2000). Progressive crustal contamination of the Bushveld Complex: evidence from Nd isotopic analyses of the cumulate rocks. *Contributions to Mineralogy and Petrology* **140**, 316–327.
- Mathez, E. A., Agrinier, P. & Hutchinson, R. (1994). Hydrogen isotope composition of the Merensky Reef and related rocks, Atok Section, Bushveld Complex. *Economic Geology* **89**, 791–802.
- Mattey, D., Lowry, D. & Macpherson, C. (1994). Oxygen isotope composition of mantle peridotites. *Earth and Planetary Science Letters* **128**, 231–241.
- Nicholson, D. M. & Mathez, E. A. (1991). Petrogenesis of the Merensky Reef in the Rustenburg section of the Bushveld Complex. *Contributions to Mineralogy and Petrology* **107**, 293–309.
- Patiño Douce, A. E. & Beard, J. S. (1995). Dehydration melting of biotite gneiss and quartz amphibolite from 3 to 15 kbar. *Journal of Petrology* **36**, 707–738.
- Prevec, S. A., Ashwal, L. D. & Mkaza, M. S. (2004). Sm–Nd isotopic evidence for mineral disequilibrium from the Merensky pegmatoid, Bushveld Complex, South Africa. Goldschmidt Conference 2004, Copenhagen, June 2004. *Geochimica et Cosmochimica Acta* **68**(11S), A637.
- Reid, D. L., Cawthorn, R. G., Kruger, F. J. & Tredoux, M. (1993). Isotope and trace-element patterns below the Merensky Reef, Bushveld Complex, South Africa: evidence for fluids? *Chemical Geology (Isotope Geosciences Section)* **106**, 171–186.
- Rhodes, R. C. (1975). New evidence for impact origin of the Bushveld Complex, South Africa. *Geology* **3**, 549–554.
- SACS (South African Committee on Stratigraphy) (1980). *Stratigraphy of South Africa. Geological Survey of South Africa, Handbook* **8**, 690 pp.
- Schiffries, C. M. & Rye, D. M. (1989). Stable isotopic systematics of the Bushveld Complex: I. Constraints of magmatic processes in layered intrusions. *American Journal of Science* **289**, 841–873.
- Schiffries, C. M. & Rye, D. M. (1990). Stable isotope systematics of the Bushveld Complex: II. Constraints on hydrothermal processes in layered intrusions. *American Journal of Science* **290**, 209–245.
- Sharpe, M. R. (1981). The chronology of magma influxes to the eastern compartment of the Bushveld Complex as exemplified by its marginal border groups. *Journal of the Geological Society, London* **138**, 307–326.
- Sharpe, M. R. (1985). Strontium isotope evidence for preserved density stratification in the Main Zone of the Bushveld Complex, South Africa. *Nature* **316**, 119–126.
- Sharpe, M. R. & Hulbert, L. J. (1985). Ultramafic sills beneath the eastern Bushveld Complex: mobilized suspensions of early Lower Zone cumulates in a parental magma with boninitic affinities. *Economic Geology* **80**, 849–871.
- Sharpe, M. R., Evensen, N. M. & Naldrett, A. J. (1986). Sm/Nd and Rb/Sr evidence for liquid mixing, magma generation and contamination in the Eastern Bushveld Complex. In: *Geological Society of South Africa, Geocongress 1986, Abstract Volume*. Johannesburg: Geological Society of South Africa, pp. 621–624.
- Stevens, G., Gibson, R. L. & Droop, G. T. R. (1997). Mid-crustal granulite facies metamorphism in the central Kaapvaal Craton: the Bushveld Complex connection. *Precambrian Research* **82**, 113–132.
- Suzuoki, T. & Epstein, S. (1976). Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochimica et Cosmochimica Acta* **40**, 1229–1240.
- Tankard, A. J., Jackson, M. P. A., Eriksson, K. A., Hobday, D. K., Hunter, D. R. & Minter, W. E. L. (1982). *Crustal Evolution of South Africa—3.8 Billion Years of Earth History*. New York: Springer, pp. 175–199.
- Taylor, B. E. (1986). Magmatic volatiles: isotopic variation of C, H, and S. In: Valley, J. W., Taylor, H. P., Jr & O'Neil, J. R. (eds) *Stable Isotopes in High Temperature Geological Processes*. Mineralogical Society of America, *Reviews in Mineralogy* **16**, 185–225.
- Taylor, H. P., Jr (1968). The oxygen isotope geochemistry of igneous rocks. *Contributions to Mineralogy and Petrology* **19**, 1–71.
- Taylor, H. P., Jr (1987). Comparison of hydrothermal systems in layered gabbros and granites, and the origin of low- ^{18}O magmas. In: Mysen, B. O. (ed.) *Magmatic Processes: Physicochemical Principles*. Geological Society Special Publications **1**, 337–357.
- Taylor, H. P., Jr & Forester, R. W. (1979). An oxygen and hydrogen isotope study of the Skaergaard intrusion and its country rocks: a

- description of a 55-M.y. old fossil hydrothermal system. *Journal of Petrology* **20**, 355–419.
- Taylor, S. R. & McClelland, S. M. (1985). *The Continental Crust: its Composition and Evolution*. Oxford: Blackwell, 312 pp.
- Teigler, B. & Eales, H.V. (1996). The Lower and Critical Zones of the western limb of the Bushveld Complex as intersected by the Nooitgedacht boreholes. *Bulletin of the Geological Society of South Africa* **111**, 126 pp.
- Uken, R. & Watkeys, M. K. (1997). Diapirism initiated by the Bushveld Complex, South Africa. *Geology* **25**, 723–726.
- Valigy, A. M. (1998). The lower part of the Rustenburg Layered Suite in the eastern limb of the Bushveld Complex around Clapham 118KT. B.Sc.(hons) thesis, University of the Witwatersrand, Johannesburg, 36 pp.
- Vennemann, T. W. & O'Neil, J. R. (1993). A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent. *Chemical Geology (Isotope Geosciences Section)* **103**, 227–234.
- Vennemann, T. W. & Smith, H. S. (1990). The rate and temperature of reaction of ClF_3 with silicate minerals, and their relevance to oxygen isotope analysis. *Chemical Geology* **86**, 83–88.
- Vennemann, T. W. & Smith, H. S. (1992). Stable isotope profile across the orthoamphibole isograd in the Southern Marginal Zone of the Limpopo Belt, South Africa. *Precambrian Research* **55**, 365–397.
- Von Gruenewaldt, G. (1973). The Main and Upper Zones of the Bushveld Complex in the Roossenekal area, eastern Transvaal. *Transactions of the Geological Society of South Africa* **76**, 207–227.
- Wager, L. R. & Brown, G. M. (1968). *Layered Igneous Rocks*. San Francisco, CA: W. H. Freeman, 588 pp.
- Willmore, C. C., Boudreau, A. E., Spivack, A. & Kruger, F. J. (2002). Halogens of Bushveld Complex, South Africa: $\delta^{37}\text{Cl}$ and Cl/F evidence for hydration melting of the source region in a back-arc setting. *Chemical Geology* **182**, 503–511.
- Zheng, Y.-F. (1993). Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochimica et Cosmochimica Acta* **57**, 1079–1091.