Osmium isotopes and crustal sources for platinum-group mineralization in the Bushveld Complex, South Africa

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ABSTRACT

The Bushveld Complex in South Africa is the largest layered mafic intrusion in the world and a major producer of platinum-group elements (PGEs). Economic mineralization is found in the Merensky Reef and the UG2 and UG1 chromitites and includes osmium-bearing laurite (Ru, Ir, Os)S_2. The laurite-bearing samples have $^{187}Os/^{186}Os$ ratios of 1.28–1.60, which are more radiogenic than predicted for mantle-derived, 2.0 Ga Os (~0.9) and indicate a system-wide assimilation of crustal Os. The UG1 chromitite is stratigraphically the lowest and the least radiogenic (1.28), whereas the Merensky Reef is the highest and most radiogenic (1.41–1.60; Hart and Kinloch, 1989). Radiogenic Os from crustal assimilation in mantle-derived magmas or from hydrothermal fluids can account for these high isotopic ratios. Assimilation models require that Os, and by inference other PGEs, are carried in Al-rich tholeiitic (A) magmas rather than high-Mg ultramafic (U) magmas. Pyritic black shales in contact with the intrusion may be high in radiogenic Os, and less than 1% shale assimilation in an A magma can explain the observed ratios. Late-stage hydrothermal fluids driven by the heat of the intrusion could also have carried Os and other PGEs from adjacent rocks into specific layers of the Bushveld. The Os-isotope data add to mounting evidence that PGEs in layered mafic intrusions may be derived from crustal sources and can no longer be considered as solely a product of mantle-derived magmatic processes.

GEOLOGIC SETTING OF THE BUSHVELD COMPLEX

The Bushveld Igneous Complex in South Africa, the largest layered mafic intrusion in the world, is several hundred times larger than the Stillwater, Muskox, or Skaergaard complexes and accounts for about 40% of world platinum-group element (PGE) production (Willemse, 1969; Loebenstein, 1984). The complex includes three major rock units: the andesitic to rhyolitic Rooiberg Felsites (>2.0 Ga), the ultramafic to mafic Rustenburg Layered Suite (2.05 Ga), and the Bushveld granites (2.0–1.7 Ga; Fig. 1). The Rustenburg Layered Suite intrudes the 2.2–2.1 Ga pelitic and calcareous sedimentary Transvaal Sequence and is exposed in three areas known as the western lobe, the eastern lobe, and the northern limb (Fig. 1). These areas, though widely separated, appear to have shared a common magma source, because radiometric ages, chemistry, and layering sequences are similar (von Gruenewaldt et al., 1985; Hatton and von Gruenewaldt, 1987; Sharpe, 1985).
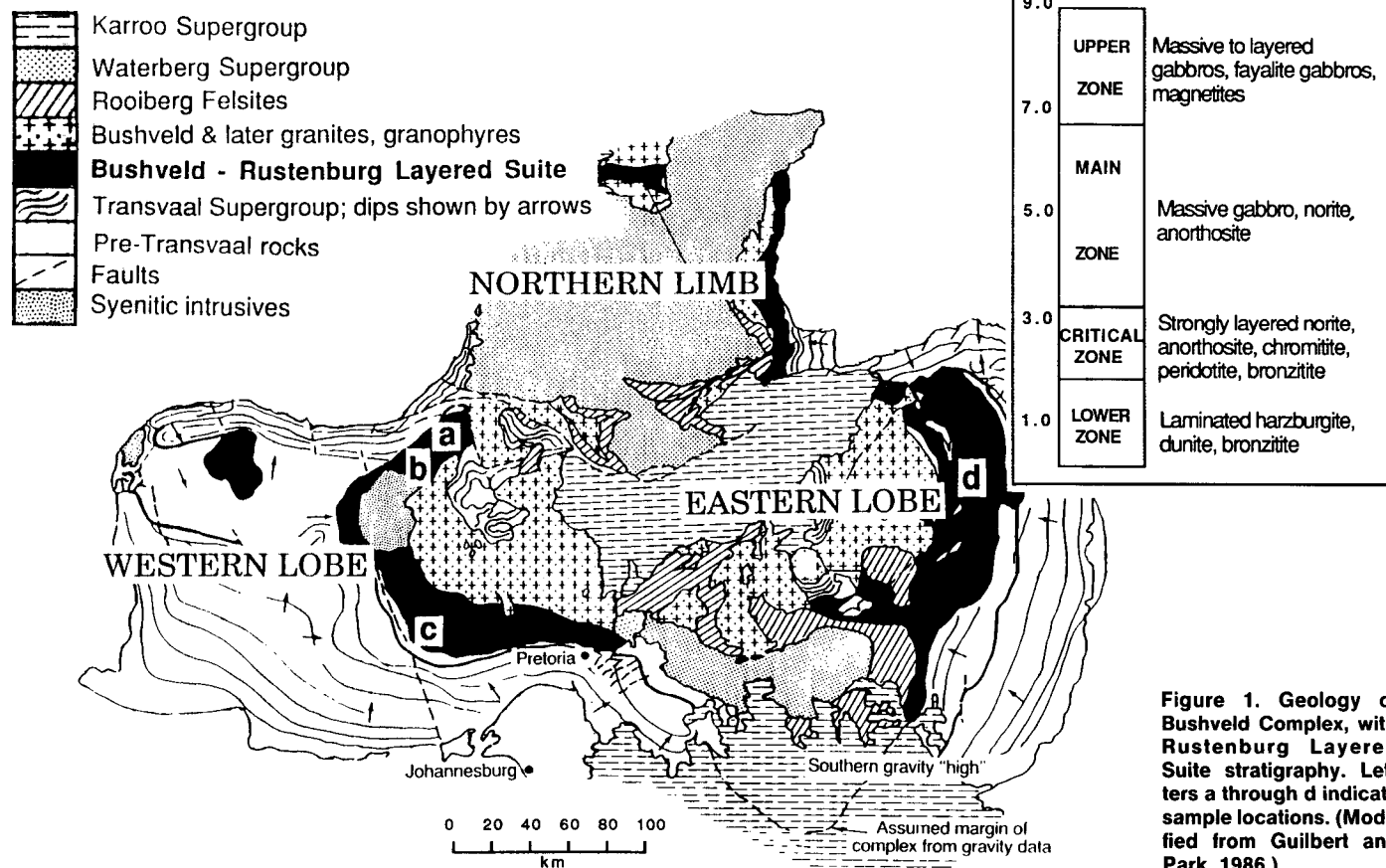

Figure 1. Geology of Bushveld Complex, with Rustenburg Layered Suite stratigraphy. Letters a through d indicate sample locations. (Modified from Guilbert and Park, 1986.)

The Rustenburg Layered Suite is divided into the lower, critical, main, and upper zones and varies in thickness from 7 to 9 km (Schiffries and Skinner, 1987; Fig. 1). The layering is remarkably continuous and can be traced for kilometres in outcrop and correlated in exposures over 300 km apart (Figs. 1, 2). Roughly 20 chromitite layers up to 2 m thick are found in the critical zone, and in the eastern and western lobes the uppermost of these layers contain economic levels of PGEs (Schiffries and Skinner, 1987; Kinloch, 1982). The PGEs are present as sulfides, tellurides, and alloys associated with the upper group or UG1 and UG2 chromitites and the Merensky Reef (Fig. 2).

PGE MINERALIZATION AND Os-ISOTOPE SYSTEMATICS

Ideas concerning the origin of PGE mineralization are diverse. Many favor a magmatic origin involving immiscibility of sulfide, oxide, and silicate melts and crystal settling (von Gruenewaldt et al., 1990; Naldrett and von Gruenewaldt, 1988) or late-stage magmatic fluids that carry PGEs upward from the base of the cumulate-magma pile to precipitate at sulfur-bearing chromitite layers (Ballhaus and Stumpfl, 1986; Boudreau et al., 1986; Ballhaus et al., 1988). These theories are dependent on geochemical and petrologic modeling which suggests that the Bushveld formed by mixing of two magmas: an early, high-Mg ultramafic (U) magma and a later, Al-rich tholeiitic (A) magma that had more radiogenic Sr (Sharpe, 1985; Irvine and Sharpe, 1986). Sr isotopes suggest that influx of the more radiogenic A magma started in the critical zone just below the UG1 chromitite (Eales et al., 1990), continued through to the end of the critical zone (Kruger and Marsh, 1982; Lee and Butcher, 1990), and dominated in the main zone (Sharpe, 1985). Increases in the Sr-isotope ratio of the Bushveld magma coincide with the mineralized UG1 and UG2 chromitites and Merensky Reef, leading to speculation that the PGEs were carried in the A magma (Sharpe, 1985; Irvine and Sharpe, 1986). These speculations

about PGE mineralization are unresolved because previous studies examined silicate minerals and not the actual PGE minerals.

Postmagmatic hydrothermal activity may also play a part in PGE mineralization. Mineralogical and field studies document the presence of veinlets filled with hydrothermal minerals and fluid inclusions (Schiffries and Skinner, 1987; Boudreau et al., 1986; Schiffries and Rye, 1989, 1990), "potholes" and other types of Merensky Reef mineralization that require widespread volatile activity (Kinloch and Peyerl, 1990), and "dunite pipes," which have remobilized PGEs and hydrothermally altered PGE chromitites (Schiffries, 1982).

Os isotopes are particularly appropriate for studying the source of PGE mineralization because Os is one of the six PGEs and is present in laurite (Ru, Ir, Os)S_2, the principal Os-bearing mineral in the Bushveld (Kinloch, 1982). ^{187}Re decays to ^{187}Os, and because of the large Re/Os fractionation between crust and mantle, any crustal source should have a significantly higher ^{187}Os/^{186}Os ratio than the mantle does. Neither hydrothermal nor magmatic processes should fractionate Os isotopes, and if minerals with very low Re/Os ratios are analyzed, then the ^{187}Os/^{186}Os ratio of the Os-bearing mineral should reflect that of the Os source at the time of the mineralization. For large volumes of mafic to ultramafic magma such as the Rustenburg Layered Suite, a ^{187}Os/^{186}Os ratio similar to that of the mantle at the time of formation is expected (0.9 for 2.0 Ga). High Re/Os crustal materials such as granites, basalts, and clastic sedimentary rocks have high ^{187}Os/^{186}Os ratios (Ravizza and Turekian, 1987; Walker et al., 1989). Hence the ^{187}Os/^{186}Os ratio of Os-bearing minerals is a sensitive monitor of crustal contamination, whether from assimilation of crust or from hydrothermal fluids.

Os ISOTOPES IN THE BUSHVELD COMPLEX

In this study we analyzed laurite-bearing samples from the UG1 and UG2 chromitites and the Merensky Reef in the eastern and western lobes of the Bushveld Igneous Complex. Methods are described in Appendix 1. Sample locations are indicated by letters a through d in Figures 1–3.

The analyzed ^{187}Os/^{186}Os ratios range from 1.28 to 1.60 and are significantly more radiogenic than predicted for mantle-derived Os (Table 1). For the Merensky Reef, our value is similar to ratios obtained by Hart and Kinloch (1989). That study showed a lateral isotopic homogeneity of laurite samples regardless of location (Fig. 3). An exception are two erlichmanite grains (OsS$_2$) with ratios of ~0.95, indicating a mantle derivation. Our results show that the Bushveld is more heterogeneous when the UG1 and UG2 chromitites and Merensky Reef from both eastern and
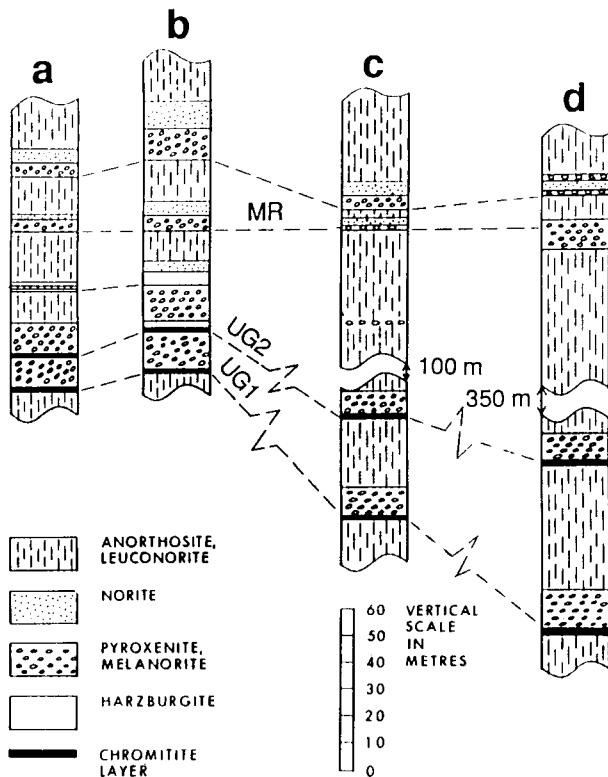

Figure 2. Stratigraphic sections of Rustenburg Layered Suite showing location of Merensky Reef (MR) and UG2 and UG1 chromitites. Letters a–d correspond to locations shown in Figure 1. (Modified from Naldrett, 1989.)
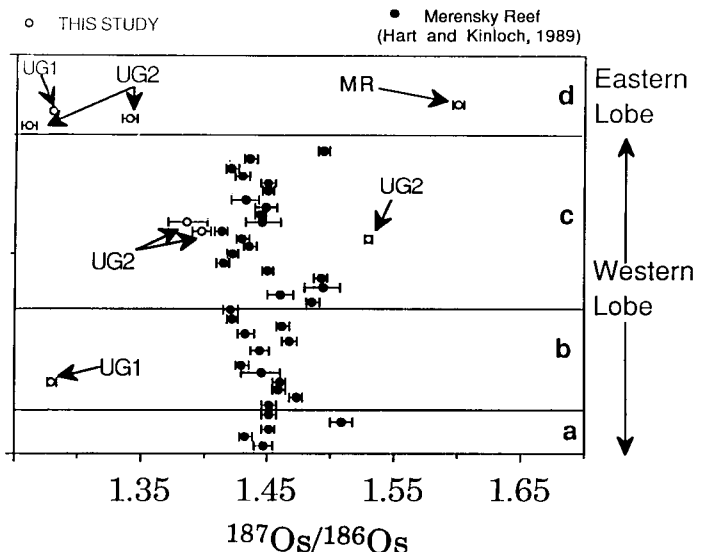

Figure 3. ^{187}Os/^{186}Os ratios for laurites from locations a through d. Data from this study and from Hart and Kinloch (1989).

western lobes are considered. For example, there is an increase in the $^{187}Os/^{186}Os$ ratio of laurite with height in the intrusion. The Os from the UG1 chromitite, which is stratigraphically the lowest, is the least radiogenic. The Merensky Reef is the highest and the most radiogenic (Fig. 4). In both lobes, similar values occur at the UG1 chromitite, but lower ratios were maintained in the eastern lobe until formation of the Merensky Reef (Fig. 4). Variable amounts or sources of radiogenic Os may explain the differences observed vertically and between lobes. The data suggest that the eastern and western lobes recorded different magmatic or hydrothermal histories with respect to Os, in spite of their lithologic similarities.

The high $^{187}Os/^{186}Os$ ratios in both the eastern and western lobes of the Bushveld require either system-wide incorporation of radiogenic Os or aging of a magma by more than 30 m.y. (Allègre and Luck, 1980). Aging of the magma is unreasonable on the basis of thermal considerations (Hart and Kinloch, 1989), so crustal Os must have been added to the Bushveld. Assimilation of crustal material by the Bushveld magmas is suggested by Sr isotopes (Sharpe, 1985). The gabbroic-anorthositic rocks (A magmas) that overlie the ultramafic rocks of the lower and critical zones (U magmas) have more radiogenic Sr ratios (Fig. 4), and an increase in the $^{87}Sr/^{86}Sr$ ratio is recorded in the upper critical zone, where the UG1 and UG2 chromitites and Merensky Reef are (Sharpe, 1985; Kruger and Marsh, 1982; Eales et al., 1990; Lee and Butcher, 1990). The most likely contaminants that would satisfy both the Sr and Os data are either lower-crustal rocks or country rocks in contact with the Bushveld intrusion.

CRUSTAL CONTAMINATION IN THE BUSHVELD—A MAGMATIC OR HYDROTHERMAL PROCESS?

Contact metamorphic assemblages for the Rustenburg Layered Suite indicate its emplacement at depths of 10–15 km and at 700–800 °C (Sharpe and Hulbert, 1985). Feeder magmas that supplied the Bushveld Complex may have resided deeper than this and thus may have assimilated lower crust. A 3.0 Ga granulite with 0.37 ppb Re and 0.16 ppb Os added to a tholeiitic A magma (0.84 ppb Re, 0.03 ppb Os; Morgan and Lovering, 1967) can produce $^{187}Os/^{186}Os$ ratios of ~1.5 with only 10% assimilation. Unreasonably high amounts (>70%) are required to raise the $^{187}Os/^{186}Os$ ratio of a U magma (0.5 ppb Re; 1.0 ppb Os; Walker et al., 1989). Similar results are obtained for a granitic crust contaminant (Allègre and Luck, 1980; Hart and Kinloch, 1989). Thus, if lower-crust assimilation is called upon to explain PGE mineralization in the Bushveld Complex, then the tholeiitic A magma must have been the carrier of Os, and by inference other PGEs, to explain the observed $^{187}Os/^{186}Os$ ratios. Similar conclusions have been reached for PGE mineralization in the Stillwater Complex on the basis of Os isotopes (Lambert et al., 1989; Martin, 1989).

Nearly 60% of the country rock in contact with the Bushveld Complex is shale, including pyritic black shale (Button, 1976). If this shale has high Os concentrations similar to black shale elsewhere (0.9 ppb Os; 56 ppb Re; Ravizza and Turekian, 1987), assimilation of only 8% shale in

a U magma can produce $^{187}Os/^{186}Os$ ratios of ~1.5. However, to produce the same ratio in an A magma, less than 1% is required.

An alternative proposal is that a hydrothermal process accounts for radiogenic Os in the Bushveld (Hart and Kinloch, 1989). Given the small amount of shale assimilation required to produce high $^{187}Os/^{186}Os$ ratios, the possibility that hydrothermal fluids carried radiogenic Os from the country rocks into the Bushveld Complex is easy to envisage. Transvaal shales have been metamorphosed at temperatures of ~500 °C up to 40 km from the Bushveld intrusive contact (Button, 1976; Engelbrecht, 1976), and crosscutting vein networks within the Bushveld document enhanced permeability and contain hydrothermal minerals (Schiffries and Skinner, 1987). Sufficient heat and permeability were present so that hydrothermal fluids could move significant amounts of crustal Os from sedimentary rocks and produce the radiogenic $^{187}Os/^{186}Os$ ratios observed in the Bushveld ores.

GENESIS OF PGE DEPOSITS

We have assumed that all PGEs in the Bushveld Complex can be traced through the chemical behavior of Os. This may not be entirely true, as the various PGEs are concentrated differently in proximity to potholes and dunite pipes where volatile activity is documented (Kinloch and Peyerl, 1990). However, the chromitite layers in the Bushveld enriched in the other PGEs are also enriched in Os, which suggests similar chemical behavior (Teigler, 1990). Nevertheless, some PGEs in the Bushveld must come from mantle sources, as supported by mantle $^{187}Os/^{186}Os$ ratios in erlichmanite, PGE minerals included in chromite, and close association of PGEs with mafic rock types (Hart and Kinloch, 1989; Kinloch, 1982). The Os-isotope data presented here are intriguing, however, as they indicate that the mantle is not the *only* source for PGEs in these deposits. Rather, some of the PGEs were obtained from the crust and concentrated in the layered intrusion by assimilation or hydrothermal processes. Given the size of the Bushveld and the magnitude of thermal energy expended during its formation, both processes were likely effective to some degree.

These implications are significant in the realm of ore-deposit genesis. The concept of crustal source and hydrothermal transport for base and

TABLE 1. $^{187}Os/^{186}Os$ RATIOS OF LAURITE-BEARING CHROMITITES UG1, UG2 AND MERENSKY REEF

Sample	Location*	$^{187}Os/^{186}Os$	2σ
12UG15	b--UG1	1.280	0.004
UG2-46	c--UG2	1.530	0.003
UG2-7	c--UG2	1.397	0.007
UG2-8	c--UG2	1.386	0.016
11BV7613	d--UG1	1.280	0.001
9BV7615B	d--UG2	1.340	0.006
10BV7616	d--UG2	1.260	0.006
15MRSRT	d--MR	1.600	0.004

*Locations b,c, and d shown in Figure 1.
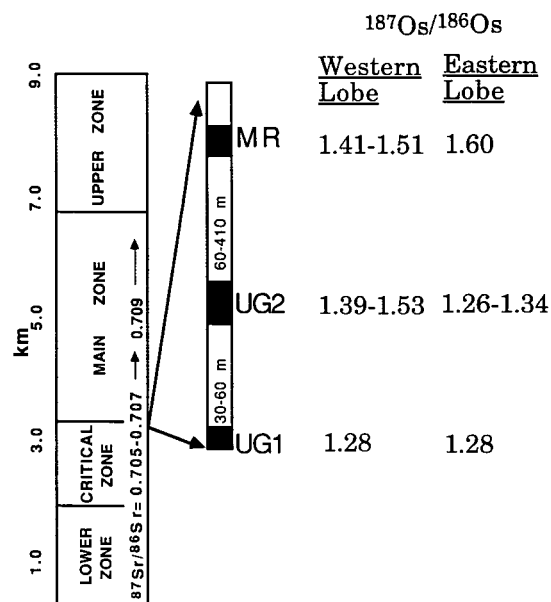
Figure 4. Stratigraphic trends in $^{187}Os/^{186}Os$ and $^{87}Sr/^{86}Sr$ ratios for Bushveld Complex. Expanded section of upper critical zone shows UG1 and UG2 chromitites and Merensky Reef (MR). Data from this study, Hart and Kinloch (1989), Sharpe (1985), Eales et al. (1990), Lee and Butcher (1990), and Kruger and Marsh (1982).

precious metals associated with felsic intrusions is not new (Knight, 1957), though new evidence now supports it (e.g., Titley, 1985; Bouse et al., 1990). In contrast, platinum-group mineralization in layered mafic intrusions has long been represented as mantle-derived, truly "magmatic" ore deposition (Willemse, 1969; Naldrett, 1989). The Os-isotope data presented here and for layered mafic intrusions elsewhere (Martin, 1989; Lambert et al., 1989) are mounting evidence that crustal involvement and hydrothermal processes must be seriously considered in the genesis of platinum-group mineral deposits as well.

APPENDIX 1. METHODS OF ANALYSIS

Os was extracted from the samples by crushing 1–5 g of sample in an agate mortar and adding concentrated, doubly distilled $16N$ HNO_3 to the powder in a still similar to the one described by Walker (1988). The solution was heated to 115 °C to produce OsO_4, which was trapped as $OsCl_6$ in a 3:1 mixture of doubly distilled $10N$ HCl and ethanol. Isotopic ratios were determined from this solution on a VG inductively coupled plasma mass spectrometer (ICP-MS; Ruiz and McCandless, 1990; McCandless and Ruiz, 1990). To confirm that laurite was successfully dissolved, we distilled and analyzed three splits from a sample of UG2 in which detailed studies by scanning electron microscope showed laurite to be the only Os-bearing mineral. Excellent signals were obtained on the ICP-MS. Residues were combined, redistilled, and reanalyzed; no measurable Os was detected. We are therefore confident that laurite was dissolved during the distillation process. Reproducibility of the data based on multiple runs of standards and samples is within 1%, which is adequate for this study.

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