

Platinum group mineralization in the Bushveld Complex: A combined QEM-SEM and LA-ICPMS study

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Introduction

For decades, the Bushveld Complex has been considered an ideal example of platinum group element (PGE) mineralization directly related to igneous processes (von Gruenewaldt *et al.*, 1990). There is now ample evidence that both deuteric and hydrothermal fluids have left their mark in the Bushveld, and controversy has risen over their role in PGE mineralization (Naldrett and von Gruenewaldt, 1988; Ballhaus and Stumpfl, 1986; Stumpfl, 1986, 1993; Boudreau *et al.*, 1986; Schiffries and Skinner, 1987; Ballhaus *et al.*, 1988; Nicholson and Mathez, 1991; Hart and Kinloch, 1989; McCandless and Ruiz, 1991). Each of these processes affects the silicate, oxide, sulphide, and/or PGE phases present in the rocks, and can best be evaluated by *in situ* Os isotope analysis of the actual PGE phases in their proper textural setting. The geochemical significance of Os is that it is one of the PGE, and the isotopic ratio $^{187}\text{Os}/^{188}\text{Os}$ can be used to trace the source of Os, and by inference, the other PGE. In the past this approach has been hindered by the difficulty of quantitatively determining the relative abundances of PGE, which are extremely rare in even the most mineralized rocks, and a need for instrumentation that can measure Os isotope ratios *in situ* in samples with low Os concentrations. We have overcome these difficulties by combining QEM-SEM and LA-ICPMS studies of samples from the Bushveld that are affected by igneous, deuteric, and hydrothermal processes.

Methods

QEM-SEM is quantitative evaluation of materials using scanning electron microscopy, developed by the CSIRO, Australia, to rapidly assess the occurrence chemistry and textural associations of minerals in rocks. QEM-SEM systematically searches through a sample, locates, identifies and acquires the energy dispersive spectra of minerals containing the elements of interest, and produces a

chemical map of each occurrence and its associated phases. This is rapidly accomplished using programmable hardware and operates without operator supervision. It is statistically accurate and rapid and is currently the industry standard for PGE beneficiation studies. In our study, 30 mm blocks of 1 mm rock fragments were examined for all phases containing PGE, and in particular for phases containing osmium. Osmium-bearing minerals were analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a Finnigan MAT Sola ICPMS equipped with a laser operating in the UV region. The instrumentation consists of a Nd:YAG Q-switched laser with frequency quadrupling hardware that allows the original infrared laser to operate in the UV part of the spectrum. The laser operates at a repetition rate of 2 Hz and 2 mJ power per shot, with a beam diameter of 20 microns. More importantly, matrix effects on the laser/sample coupling seem to be minimized when the laser is operated in the UV. The instrument is capable of measuring $^{187}\text{Os}/^{188}\text{Os}$ ratios to within 3% precision in samples with Os in the parts per million range. Sample splits were also taken prior to QEM-SEM and LA-ICPMS analysis and measured for Os isotopes by solution ICPMS.

Results

Stratiform (i.e. magmatic) layers in the Bushveld formed during crystallization, and are free from any obvious post-layering effects. Averaged bulk analyses of stratiform UG1, UG2, and Merensky Reef from both the eastern and western lobes show a similar increase in $^{187}\text{Os}/^{188}\text{Os}$ from $\sim 0.154 \pm 0.001$ (UG1) to 0.166 ± 0.008 (UG2) and 0.191 ± 0.002 (Merensky Reef). Potholes and iron-rich ultramafic pipes (IRUP) are late magmatic/early deuteric features that erode or cross-cut the stratiform layers. Near potholes, Merensky Reef silicates and oxides are significantly altered, PGE minerals change from sulphides to Ti-Be phases, and $^{187}\text{Os}/^{188}\text{Os}$

increases to 0.199 ± 0.005 . Near IRUP features, Merensky Reef PGE are Sb phases and alloys and $^{187}\text{Os}/^{188}\text{Os} = 0.206 \pm 0.004$. PGE sulphides in the UG2 are also converted to alloys near IRUP pipes, but the $^{187}\text{Os}/^{188}\text{Os}$ ratio is unaffected (0.164 vs 0.167 ± 0.003). Hydrothermal alteration overprints these earlier events and converts silicates to hydrous phases, and base metal sulphides (BMS) alter from primary pentlandite + chalcopyrite to millerite + pyrite + chalcocite + bornite. Bulk $^{187}\text{Os}/^{188}\text{Os}$ ratios are lower in hydrothermally altered Merensky Reef (0.178 ± 0.005) and UG2 (0.156 ± 0.005). Individual phases analyzed by laser ablation ICP-MS have $^{187}\text{Os}/^{188}\text{Os}$ ratios that vary from mantle values to 0.35 ± 0.03 , indicating that PGE redistribution is not homogeneous during the hydrothermal stage, and highly radiogenic Os from country rocks may be introduced at this time. LA-ICPMS analysis indicates that gross isotopic disequilibrium is present in Merensky Reef altered by fluids that migrated along post-magmatic faults, where PGE phases have $^{187}\text{Os}/^{188}\text{Os}$ ratios of $\sim 0.38 \pm 0.03$ in contrast to a bulk isotopic signature of 0.178 ± 0.003 .

Preliminary results suggest that in stratiform samples, system-wide, similar increases in $^{187}\text{Os}/^{188}\text{Os}$ support the introduction of crustal Os by a tholeiitic magma that first appears in the upper critical zone where the bulk of PGE mineralization occurs. Later deuteric and post-magmatic processes seem to have remobilized PGE, in their immediate vicinity, with possible minor additions of extremely radiogenic Os from

adjacent country rocks. QEM-SEM and LA-ICPMS analysis of additional *in situ* phase will elucidate the relative importance of these post magmatic processes to the bulk of PGE mineralization in the Bushveld.

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