

Re-Os and S isotope evidence for the origin of Platreef mineralization (Bushveld Complex)

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Abstract

The Bushveld Complex contains the largest platinum-group element (PGE) deposits of the world that are represented by persistent stratiform reefs highly enriched with PGE with respect to underlying and overlying rocks. New Re-Os isotope and elemental LA MC-ICPMS data on platinum-group minerals (PGM) from the mineralized reefs are presented with implications to correlation between the different segments of the Bushveld Complex and a role of superimposed processes at the reef formation. We analyzed laurite (RuS₂), hollingworthite (RhAsS), sperrylite (PtAs₂) and Pt-Fe alloys from the Merensky Reef, Pseudoreef and the PGE reef of the Platreef. The measured ¹⁸⁷Os/¹⁸⁸Os value for Platreef laurite is 0.1751 ± 0.0004 whereas the ratios for sperrylite and hollingworthite range to slightly higher values (0.1713–0.1818 and 0.1744–0.1835 respectively). The observed textures of the analyzed PGM, such as Pt-Fe symplectites in base metal sulfides (BMS), laurite inclusions in chromite and sperrylite rims around sulfide-silicate aggregates, are interpreted as features of primary magmatic crystallization whereas hollingworthite overgrowths and exsolutions in sperrylite are likely to have originated from later solid state transformation or metasomatic processes.

The Platreef is a composite sill-like body in the northern limb correlative to the Critical Zone in terms of stratigraphic position, whole-rock geochemistry and isotope characteristics. The pristine magmatic character of sulfides and PGM in the stratiform reefs at the top of the Platreef strongly resembles the style of Merensky Reef mineralization. However, the basal part of the Platreef pyroxenitic sequence is variably contaminated and mineralized with a significant hydrothermal overprint. Sulfides from underlying Lower Zone peridotite yield δ³⁴S values varying from +9‰ to +14.2‰ that are much higher than the values for the overlying Platreef and are a consequence of sulfur assimilation from sedimentary sulfates. The same homogeneous mantle-like S isotope compositions in the high-grade PGE reef of the Platreef and the Merensky Reef can be explained by enhanced S isotope exchange through the orthomagmatic process of sulfide upgrading. The similar values and the limited variations of the initial Os isotopic ratios of all PGMs in both reefs also support their magmatic crystallization and origin from a common source.

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1. INTRODUCTION

Enormous reserves of chromium and platinum-group elements (PGE) in the Bushveld Complex together with high-Mg compositions of the earlier cumulates undeniably indicate the mantle as a source of Bushveld melts (Naldrett, 2011). Nevertheless, radiogenic isotope systems of mantle-incompatible elements and O isotopic signatures reveal a significant crustal contribution or require an unusual composition of a sub-continental mantle lithospheric source (Davies et al., 1980; Maier et al., 2000; Prevec et al., 2005; Harris et al., 2005; Richardson and Shirey, 2008). An involvement of crustal material is least expected to be seen in Re-Os isotope characteristics of Bushveld platinum-group minerals (PGM) as Os is highly compatible and much less abundant in the crust (Pearson and Shirey, 1999). However, it has been clearly established and confirmed in several isotope studies that platinum-group minerals (PGM) from Bushveld mineralized reefs have elevated Os/Os values compared to cogenetic barren silicate rocks and chromitites, as well as with respect to the contemporaneous mantle (Hart and Kinloch, 1989; McCandless and Ruiz, 1991; Schoenberg et al., 1999; McCandless et al., 1999; Reisberg et al., 2011; Coggon et al., 2012). This radiogenic homogenous Os isotope composition of platinum mineralization, nearly homogeneous within each ore-bearing level was interpreted to indicate either a metasomatised nature of the Proterozoic mantle or contamination with lower crustal components, which both potentially could give rise to radiogenic sulfides.

Studies on podiform chromitites testify that the Os isotope system is able to retain the primitive mantle characteristics during complex superimposed processes. PGM assemblages in podiform chromitite commonly include a wide range of primary magmatic Os-bearing minerals and carry few BMS (i.e. Malitch, 2004; Distler et al., 2008; González-Jiménez et al., 2012). Laurite (RuS_2), erlichmanite (OsS_2) and Os alloys are mostly used for isotope studies of podiform chromitites and regularly yield very similar ranges of Os/Os values in both primary chromite and later sulfide associations. In layered intrusions Os-bearing alloys and sulfides are exceptionally rare and small, whereas laurite is more common and can be observed in both sulfide-poor chromitites and sulfide-rich platinum reefs (Kingston and El-Dosuky, 1982; Kinloch and Peyerl, 1990; Maier et al., 1999). Laurite is considered to be one of the earliest magmatic minerals, and it may crystallize directly from silicate melt before it achieves saturation in sulfide (Brenan and Andrews, 2001; Bockrath et al., 2004). The osmium budget in the Bushveld platinum reefs is also governed by the presence of other important Os carriers, such as sperrylite (PtAs_2), minerals of the platarsite-hollingworthite-irarsite series (PtAsS-RhAsS-IrAsS), Pt alloys and Os solid solution in pyrrhotite. Interpretation of their origin is not straightforward as they can form as a result of various processes from orthomagmatic to hydrothermal, pneumatolytic and to deuteric. Experimental studies show that sperrylite crystallizes and is stable over a wide temperature range, from $<1150^\circ\text{C}$ coexisting with sulfide melt (Helmy et al., 2013), down to 150°C precipitating from hydrother-

mal solutions (Evstigneeva and Tarkian, 1996). The natural occurrences of sperrylite illustrate well the wide range of conditions deduced from the experiments. Disseminated sperrylite in Sudbury ores are assigned to orthomagmatic process (Dare et al., 2010), whereas the coarse metacrystals among Norilsk massive sulfides and in Sudbury metasomatic-hydrothermal quartz-rich footwall veins undoubtedly originate from the circulation of post-magmatic (Farrow and Watkinson, 1992; Sluzhenikin and Mokhov, 2015) or metamorphic fluid (Spiridonov et al., 2015). In the Bushveld Complex sperrylite is common in magmatic ores (Cawthorn et al., 2002) but it is also famous from contact-metamorphic and metasomatic assemblages of the Platreef at Tweefontein (Nex, 2005). Another Os carrier, Pt alloys, including isoferroplatinum, are found to form early from S-undersaturated silicate melts and then captured as mineral inclusions in the later chromite in picritic basalt (Park et al., 2012). This is consistent with findings of nano- and micronuggets of these phases during high-temperature experiments on silicate melts (Makovicky, 2002). However, the coarser crystals and nuggets of Pt alloys, which are typical of the Ural-Alaskan complexes and some podiform chromitites, are assumed to be of pneumatolytic origin related to volatile activity in chromititic pods (Pushkarev et al., 2015). The occurrence of Pt alloys and other PGMs in the Waterberg quartz-hematite veins in the Bushveld aureole (McDonald et al., 1995; Distler et al., 2003) and in cross-cutting granophyric granite veins within the Platreef (Hutchinson and Kinnaird, 2005) strongly indicate that both low-temperature fluid and later anatectic felsic melt are able to remobilize platinum metals at a postmagmatic stage.

The Re-Os and Pt-Os isotope isochron ages (Schoenberg et al., 1999; Ruiz et al., 2004; Reisberg et al., 2011; Coggon et al., 2012) for the Bushveld Complex (Fig. 1) are regularly younger than the U-Pb zircon isotope ages (Zeh et al., 2015), which possibly reveals a superimposed hydrothermal process affecting the PGM isotope characteristics. However, this interpretation is not consistent with the robustness of the Os isotope system and is not supported by

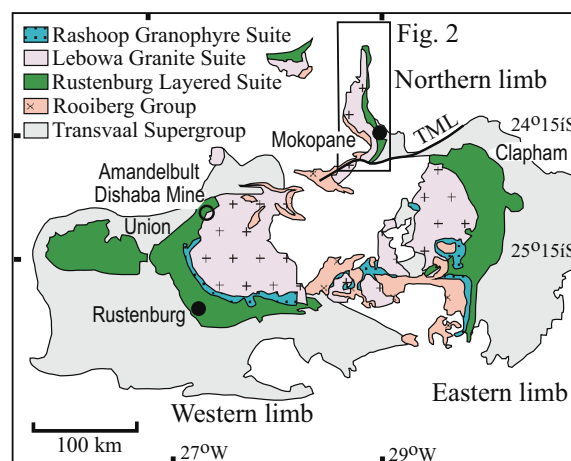


Fig. 1. Schematic geological map of the Bushveld Complex. Simplified after the 1:250,000 geological map by the South African Geological Survey. TML – the Thabazimbi-Murchison Lineament.

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