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2.05 Ga Isotopic Age for Transvaal MVT Deposits: Evidence for Large-Scale Hydrothermal Circulation Around the Bushveld Igneous Complex, South Africa

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ABSTRACT
The dimensions of hydrothermal fluid circulation associated with emplacement of the Bushveld Igneous Complex (BIC) are documented with new ages for Paleoproterozoic mineral deposits in wallrocks (Transvaal Supergroup) surrounding the BIC. A fluorite-rich MVT deposit in the Zeerust district is dated at 2.05 Ga (Sm-Nd isochron age), and is shown to have a Nd isotopic composition identical to coeval F-rich Lebowa Granite from late in the BIC intrusive sequence.
Hydrothermal illite from the Zn-Pb MVT Bushy Park deposit is dated at 2.05 Ga (K-Ar age), linking widespread MVT deposits of the Kaapvaal craton to basinal brine circulation associated with emplacement of the 2.055 Ga BIC. These data, in combination with gold vein and paleoplacer ages, suggest that a regional Bushveld-age hydrothermal system included basinal, magmatic, and metamorphic fluids that circulated as much as 500 km outward from the present margins of the BIC. This hydrothermal system is among the largest documented and appears to be scaled to the dimensions and heat flow budget of the BIC.

Key words: Bushveld Complex; MVT deposits; Isotopic Ages; Hydrothermal; Paleoproterozoic

Introduction

Hydrothermal systems developed around igneous intrusions are an important agent of chemical exchange in the upper continental crust. Systems of this type around felsic intrusions are well documented (Taylor 1997). Mafic intrusions, with their increased dimensions and higher temperatures (Cawthorn and Walraven 1998), might be expected to produce more complex fluid flow in the surrounding crust. Hydrothermal effects associated with the largest igneous complex in the world, the ca. 2.055 Ga Bushveld Igneous Complex (BIC), have recently been hypothesized to extend >> 100 kilometers outward from the margins of the BIC (Rasmussen et al. 2007; Gutzmer et al. 2007). Products of such extensive hydrothermal systems include mineral deposits, which are widespread around the periphery of the BIC. Here we report isotopic ages that link two important groups of hydrothermal mineral deposits in the Paleoproterozoic Transvaal Supergroup to the emplacement of the BIC. These data expand the
evidence for large-scale hydrothermal activity and multi-component fluid flow around the BIC ca. 2.05 Ga, with distal effects up to 500 km beyond the margins of the BIC being documented.

**Previous Evidence for Bushveld-Related Hydrothermal Effects**

The Bushveld Igneous Complex (BIC) was emplaced largely into the upper part of the Transvaal Supergroup, an unusually well preserved sedimentary shelf sequence of Late Archean–Early Proterozoic age (2.65–2.06 Ga; Beukes 1987; Eriksson and Altermann 1998). The Transvaal Supergroup is exposed today in the Transvaal, Kanye and Griqualand West, erosional remnants of a sedimentary basin that originally extended across the entire Kaapvaal craton (fig. 1A). Emplacement of the BIC took place over a short span of time beginning with eruption of volcanic rocks of the Rooiberg Group at 2061±2 Ma (U-Pb zircon; Walraven 1997), followed by the mafic/ultramafic Rustenburg Layered Suite (RLS) at 2054±1 Ma (U-Pb zircon; Scoates and Friedman 2008) and finally by granites of the Lebowa Granite Suite and related phases (here called Bushveld granites) at 2054±2 Ga (Pb-Pb zircon; Walraven and Hattingh 1993).

Early work on hydrothermal effects in or immediately adjacent to the BIC by Schiffries and Skinner (1987) and Schiffries and Rye (1990) demonstrated that rocks of the RLS in the eastern lobe of the Complex (V, fig. 1B) contain veins that formed at temperatures of 350 to 700°C from saline fluids derived largely from the surrounding Transvaal Supergroup. The RLS in the western lobe of the complex (R; fig. 1B) shows similar evidence for invasion by Transvaal-derived fluids (Buick et al. 2001), as does the Platreef in the northern limb of the Complex (P; fig. 1B) (Pronost et al. 2008; Roelofse and Ashwal 2008) and the Uitkomst Complex, a satellite intrusion east of the Bushveld Complex (Sarkar et al. 2008). An Ar-Ar (biotite) cooling age of 2042±3 Ma (Nomade et al. 2004) from chromitite in the RLS was reassessed recently by Scoates and Friedman (2008), yielding an alteration age of ca. 2054 Ma.
within error of the age of the Bushveld intrusion. Slightly farther outward from the intrusion, Schweitzer and Hatton (1995) described thermal and hydrothermal effects that extended as much as 1.4 km from the contact of the RLS around all parts of the BIC, and Reimold et al. (2007) reported Ar-Ar ages of Transvaal Supergroup rocks along the immediate southern margin of the Complex (T; fig. 1B), interpreted by Alexandre et al. (2006) to reflect Bushveld-related thermal effects.

In addition to these features, which are associated with mafic/ultramafic rocks of the RLS, numerous Sn, F, base and precious metal deposits are found in and adjacent to the Bushveld granites (Robb et al. 2000; Bailie and Robb 2004). These include the Zaaiplaats, Union and Rooiberg Sn (ZP, U, R; fig. 1B), Buffalo and Zwartkloof F (B, ZL; fig. 1B), Vergenoeg Fe-F (VG; fig. 1B) and Spoedwell Cu deposits (S; fig. 1B), all of which are thought to have been deposited largely from fluids of magmatic origin (Robb et al. 2000; Borrok et al. 1998; Goff et al. 2004; Kinnaird et al. 2004).

The widespread distribution and pervasive nature of proximal hydrothermal anomalies around the BIC suggest that distal effects of the same age should also be present, although fewer examples are known and most of these are subtle. For instance, in the Witwatersrand basin as much as 150 km south of the Complex (fig. 2), Rasmussen et al. (2007) reported U-Pb ages of 2.06 Ga to 2.03 Ga for monazite and xenotime which were interpreted by them to be related to distal hydrothermal effects from emplacement of the BIC. Farther to the southwest, in the Griqualand West basin (fig. 1a; fig. 2), Whitelaw et al. (2005) reported a Rb-Sr age of 2014±38 Ma on clinohore from secondary chloride and associated wallrocks from the Katlani and Kalkdam Pb-Zn occurrences (fig. 2), compatible with Bushveld-age hydrothermal activity. Finally, paleomagnetic data from the Transvaal Supergroup in the Griqualand West region (De
Kock et al. 2009) record a distinct Paleoproterozoic overprint that is in agreement with 2.05 Ga re-setting of Rb-Sr isotope systematics in whole-rock samples of Neoarchean (2.65-2.70 Ga) shales across the entire Kaapvaal Craton (Schneiderhan et al. submitted).

**Hydrothermal Mineral Deposits Related to Emplacement of the Bushveld Igneous Complex**

Additional evidence of distal fluid flow associated with the BIC is provided by widespread occurrences of hydrothermal mineral deposits of Paleoproterozoic age in sedimentary rocks of the Kaapvaal craton. These occurrences are largely of two main types: Mississippi Valley-type (MVT), which are found at a wide range of distances from the complex, and vein-type deposits, which are relatively close to the complex (fig. 2).

*Mississippi Valley-type (MVT) Deposits*

MVT deposits in the Kaapvaal craton are hosted largely by carbonate rocks of the Transvaal Supergroup (fig. 1; fig.2) and can be divided into two groups. The first group contains sphalerite, galena and hydrothermal carbonate typical of many MVT deposits around the world (including type-locality MVT), though these deposits are also locally enriched in other elements nearest the BIC. For instance, MVT deposits in the Transvaal basin around the BIC contain chalcopyrite at Leeuwenkloof and Carletonville, siderite and pyrite at Leeuwbosch, magnetite at Hendrina, and manganese oxides with silver at Genadendal and adjacent deposits (Martini 1976; 1986; Clay 1986; Bear 1986; Philpott and Ainslie 1986; Ryan 1986; fig. 2). In contrast, Pering, Bushy Park and numerous smaller MVT deposits in the Griqualand West basin, which is farther west and south of the BIC (fig. 2), have a conventional MVT mineral assemblage consisting largely of sphalerite, galena and hydrothermal carbonate (Martini 1990; Martini et al. 1995; Kruger et al. 2001; Schäfer 2002; Schäfer et. al. 2004; Gutzmer 2006; Huizenga et al. 2006a).
The second group of MVT deposits, which is found only in the Zeerust district (fig. 2), consists largely of fluorite and hydrothermal carbonate with very little galena and sphalerite (Martini 1976; 1986; Ryan 1986; Bear 1986; Roberts et al. 1993; Martini et al. 1995; Poetter 2001). Although the Transvaal basin MVT deposits have a surprisingly wide range of compositions, a genetic relation among them is suggested by similar common lead isotope compositions for Carletonville, Leeuwenkloof, Leeuwbosch and Zeerust (Duane et al. 1991). Fluid inclusion and stable isotope analyses indicate that both groups of MVT deposits formed from fluids consisting largely of basinal brines, but with different admixtures of meteoric and magmatic fluids. In the MVT deposits containing largely lead and zinc, fluid inclusions indicate that mineralization was formed from basinal brines with admixtures of meteoric water as well as CO₂ and CH₄ derived from reaction between the brine and wallrocks, (Schäfer 2002; Kesler and Reich 2006; Huizenga et al. 2006a,b). Mineralization is estimated to have taken place at temperatures of 200 to 240°C and pressures of about 0.8 to 1.5 kb in the upper crust. Fluid inclusions from the fluorite-bearing Zeerust MVT deposits contain generally similar basinal brines, but with evidence also for local or sporadic introduction of much higher temperature fluids of probable magmatic origin (Poetter 2001; Kesler et al. 2007).

Gold and Lead-Zinc-Silver Vein Deposits

Quartz-gold veins of the Sabie-Pilgrim’s Rest and related districts are found along the east side of the BIC (Harley and Charlesworth 1994; Boer et al. 1995) and similar veins of the Witwatersberg district (Killick and Scheepers 2005) are located on the west side. The small Mamre-Slaaihoek deposits farther to the south of Sabie-Pilgrim’s Rest are close to the 2.055 Ga Uitkomst satellite intrusion (Sarkar et al. 2008). Most of these vein deposits are hosted in the lower part of the Transvaal Supergroup where the majority of the MVT deposits occur (fig. 2).
Fluid inclusion and stable isotope data suggest that the vein deposits were formed from saline fluids with variable enrichment in CO$_2$ at temperatures of 300 to 350°C and supra-lithostatic pressures of 2.2 to 2.5 kb (Boer et al., 1995). The data are consistent with either a magmatic or metamorphic source for the fluids and exclude involvement of significant amounts of meteoric water (Boer et al., 1995).

**Ages of the Hydrothermal Mineral Deposits**

Geologic relations and isotopic age determinations show that the gold veins are essentially coeval with the ~2.05 Ga BIC (Boer et al. 1995), but similar constraints on the age of the MVT deposits have not been available. Establishing the age of the Transvaal MVT deposits is important to test their temporal relation to the BIC, but is complicated by the scarcity of suitable mineral phases for isotopic age determinations. Although Rb-Sr isotopic analyses of sphalerite have yielded reliable ages for other MVT deposits (Christensen et al. 1995; Schneider et al. 2007; Heiljen et al. 2003; Leach et al. 2001), Rb-Sr chronology of Bushy Park sphalerite has not yet been successful (Kesler et al. 2003). Both Zeerust and Bushy Park MVT deposits contain fluorite and illite, which are amenable to isotopic age measurements by Sm-Nd and K-Ar age dating, respectively. At Bushy Park, illite is a trace constituent that is intergrown locally with coarse-grained sphalerite (Schäfer 2002; Gutzmer et al. 2007), and at Zeerust, fluorite is the most abundant hydrothermal mineral and represents the main stage of mineralization (Martini 1976, 1986; Ryan 1986).

**Results**

Isotopic ages for Transvaal MVT mineralization were determined for fluorite at Zeerust by Sm-Nd geochronology (Chesley et al. 1991) and for illite at Bushy Park by K-Ar dating. At Bushy Park, hand-picked, millimeter-sized monomineralic aggregates of illite yielded K-Ar ages
of 2038±40 Ma and 2059±41 Ma (Table 1). At Zeerust, Sm-Nd isotopic data on four hand-picked fluorite separates (Table 2) generated a 2046±42 Ma isochron (MSWD=2.0) with initial 
^{143}\text{Nd}/^{144}\text{Nd}_i = 0.509734±0.000059 (\varepsilon_{\text{Nd}} = -4.9; \text{fig. 3}). These ages for Bushy Park and Zeerust are identical within error to the full range of ages obtained for magmatic phases of the BIC (~2.06-2.05 Ga), though not precise enough to directly link the MVT deposits to a specific intrusive phase. The ages reported here for Bushy Park and Zeerust are also similar to that of the Vredefort impact event (2.023 Ga; Kamo et al. 1996) and the Limpopo tectonothermal event (2.03 Ga; Kramers et al. 2006) of the Kaapvaal craton region. A genetic association with the latter two events is deemed unlikely, however, because of the short duration of the Vredefort event (Gutzmer et al. 2007), and because of the apparent limit of the effects of the Limpopo tectonothermal event (Kramers et al. 2006). Instead, the Kaapvaal MVT deposits have a much closer spatial association with the BIC, and a mineralogy much more likely to be related to a regional 2.05 Ga hydrothermal event driven by emplacement of the BIC.

Implications for Hydrothermal Circulation around the Bushveld Complex

Our data linking MVT deposits to the BIC, combined with previous data linking gold deposits to the BIC, shows that the Bushveld hydrothermal system consisted of several different fluid types. A close genetic link between Zeerust MVT fluorite and Bushveld-related F-rich magmatic systems is supported by the similarity of Nd isotopic compositions [$\varepsilon_{\text{Nd}}(2.055 \text{ Ga})$] for the Lebowa Granite suite and Zeerust fluorite (fig. 3, inset). Whole rock Sm-Nd data for the Lebowa Granite Suite at Dennilton (Hill et al. 1997) plot along the same isochron as the Zeerust Sm-Nd fluorite separates. Combined, the two sets of data define an isochron age (2050±66 Ma) that is identical to the Zeerust isochron age (2046±42 Ma), and with the same initial ratio 
($^{143}\text{Nd}/^{144}\text{Nd}_i = 0.509722±0.000071; \varepsilon_{\text{Nd}} = -5.1; \text{fig. 3})$ within error. Recognition of the isotopic
link between fluorine-rich systems of the Zeerust MVT, and F-rich granites of the BIC, establishes that hydrothermal fluids at Zeerust resulted from the invasion of Transvaal basinal brines by F-rich high temperature magmatic fluids (Kesler et al., 2006) of the BIC. At Zeerust, this invasion is further reflected by zones of F-bearing tremolite and talc surrounding the MVT deposits (Martini 1976), consistent with their location within the outer greenschist contact metamorphic aureole of the BIC (Engelbrecht 1990).

From the above discussion, we can infer that a direct link exists between hydrothermal fluids forming the Sn-F type deposits directly associated with the Bushveld granites, and F-bearing MVT deposits of the Transvaal Supergroup (Zeerust). A second hydrothermal fluid type represented by Transvaal Group-hosted MVT deposits (other than Zeerust-type) shows a subtle spatial zonation outward from the BIC, with unusual enrichments in Fe and Mn within Transvaal basin deposits (fig. 2). The presence of these geochemical anomalies does not require a direct magmatic fluid contribution and could instead imply a leached component from the RLS, or enclosing sedimentary rocks, by circulating basinal brines (Martini, 1990). Migration of Transvaal basinal brines was localized by several paleoaquifers, including volcanic rocks of the Ventersdorp Group, which underlies the Transvaal Supergroup (Duane et al. 1991; Kruger et al. 2001; Gutzmer et al. 2007). More distal fluid pathways (also associated with the RLS) probably account for the Bushveld-like ages observed in Witwatersrand Basin rocks (Rasmussen et al. 2007).

The third hydrothermal fluid type is represented by the gold vein deposits, which are most easily explained by mixing of Transvaal basinal brines with carbonic fluids produced by metamorphic devolatilization of BIC wallrocks (Boer et al., 1995). The deposits are just outside the maximum original extent of the Bushveld Complex, where metamorphic fluids would have
been most abundant, and the supra-lithostatic conditions of the mineralizing fluids are consistent with a metamorphic origin (Boer et al. 1995).

It is likely that all three fluid systems were active simultaneously for at least part of the full duration of hydrothermal activity ca. 2.05 Ga, but may have overlapped in only a few locations. As shown in Figure 4, BIC-related hydrothermal activity was focused in the lower part of the Transvaal Supergroup at 2.05 Ga, with rocks proximal to the complex hosting overpressured fluids of largely (contact) metamorphic origin. These deposited gold, while fluids in more distal regions formed MVT deposits with or without direct contributions of magmatic F and Sn from Bushveld granites. Farther outward in regions most distal to the BIC, hot basinal fluids reset paleomagnetic, Rb-Sr and K-Ar systematics in the Transvaal Supergroup, and deposited monazite, xenotime and other low-temperature phosphates as far away as the Witwatersrand basin sequence more than 500 km from the BIC contact aureole.

ACKNOWLEDGMENTS

We would like to acknowledge the roles of Markus Schäfer, Lynette Greyling, Phil Poetter and Craig McClung for their respective contributions during the investigation of the carbonate-hosted Zn-Pb-F deposits of the Transvaal Supergroup. Sm-Nd isotopic work was carried out in the Radiogenic Isotope Geochemistry Laboratory (RIGL) at the University of Michigan (J. Blum, director), and the KECK trace element lab with assistance from M. Johnson and T. Huston, respectively.

REFERENCES CITED

Alexandre, P.; Andreoli, M.A.G.; Jamison, A.; and Gibson, R.L. 2006. \(^{40}\)Ar/\(^{39}\)Ar age constraints on low-grade metamorphism and cleavage development in the Transvaal Supergroup


de Kock, M.O; Evans, D.A.D; Kirschvink, J.L; Beukes, N.J.; Rose, E.; and Hilburn, I. 2009. Paleomagnetism of a Neoarchean-Paleoproterozoic carbonate ramp and carbonate platform succession (Transvaal Supergroup) from surface outcrop and drill core, Griqualand West region, South Africa. Precambrian Research 169:80-99.


Nomade, S.; Renne, P.R.; and Merkle R.K.W. 2004. $^{40}\text{Ar}/^{39}\text{Ar}$ age constraints on ore deposition and cooling of the Bushveld Complex, South Africa. Journal of the Geological Society 161:411-420


Figure 1. A) Location of the Neoarchean-Paleoproterozoic Transvaal and Griqualand West structural basins that preserve part of the Transvaal Supergroup on the Kaapvaal craton in southern Africa. B) Geologic map of the Bushveld Complex and immediately adjacent wallrocks in the Transvaal Basin (modified from Martini et al., 1995; Eriksson et al., 2001), showing the location of areas within the Complex that exhibit evidence of proximal hydrothermal effects including the layered series (V), Burgersfort bulge (BB) and Uitkomst (U) in the east, Rustenburg Layered Suite (R) in the west and Platreef (P) in the north. Also shown are areas of metamorphic effects in proximal wallrocks along the southern margin of the complex (T), as well as mineral deposits hosted by and thought to be associated with Bushveld granites, including Zaaiplaats, Union and Rooiberg Sn (ZP, U, R, Figure 1B), Buffalo and Zwartkloof F (B, ZL, Figure 1B), Vergenoeg Fe-F (VG, Figure 1B) and Spoedwell (S) Cu deposits. Locations are discussed in the text.

Figure 2. Distribution and relative positions of exposed and covered rocks of the Bushveld Complex, Transvaal Supergroup (exposed in the Transvaal, Griqualand West and Kanye basins – see fig. 1a), and Witwatersrand basin showing location of possible distal hydrothermal effects of the Bushveld Complex, including MVT and related deposits (crosses, G = Genadendal, L = Leeuwbosch, H = Hendrina), gold and lead-zinc vein systems (triangles), and U-Pb ages of monazite and xenotime in Witwatersrand rocks (circles). Isotopic ages for Bushy Park and Zeerust from this report and for Witwatersrand samples from Rasmussen et al. (2007).

Figure 3. Main Diagram) Sm-Nd isochron for fluorite separates from the Witkop and Doornhoek deposits in the Zeerust district. Samples plotted on the main isochron include coarse and fine-grained fluorite from both stratiform and breccia units at Zeerust. Data were inputted as 2-sigma values to generate a Model 1 solution (95% confidence interval) using Isoplot Ex3 (Ludwig 2005). The 2-sigma solution yields an age of 2046±42 Ma with MSWD = 2.0, and initial $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.509734±0.000059 (epsilon Nd = -4.9). Inset lower right) Comparison of $\varepsilon_{\text{Nd}}^{2.055}$ values for hydrothermal fluorite from the
Zeerust data (isochron value), with averages for rocks of the Bushveld Complex and the Vergenoeg F-bearing deposit (from data of Buchanan et al. 1999, Maier et al. 2000, Hill et al. 1996, Goff et al. 2004, and Twist and Harmer 1987). Calculated \( \varepsilon_{\text{Nd}} = 10^4 \left[ \frac{^{143}\text{Nd}/^{144}\text{Nd}_{(\text{SAMPLE})}}{^{143}\text{Nd}/^{144}\text{Nd}_{(\text{CHUR})}} - 1 \right] \) assuming modern \( ^{143}\text{Nd}/^{144}\text{Nd}_{(\text{CHUR})} = 0.512638 \) (Bulk Earth) and \( ^{147}\text{Sm}/^{144}\text{Nd}_{(\text{CHUR})} = 0.1966 \) (Jacobsen and Wasserburg, 1980), where \( t = 2.055 \) Ga. Inset upper left) Portion of the Sm-Nd isochron combining all of our Zeerust fluorite data with data for Lebowa F-rich granites from the Bushveld Complex (Hill et al. 1996; Dennilton area only; \( n = 9 \)). The 2-sigma solution yields an Sm-Nd isochron age of 2050±66 Ma with MSWD = 17, and initial \( ^{143}\text{Nd}/^{144}\text{Nd}_i = 0.509722±0.000071 \) (epsilon Nd = -5.1). The two Zeerust data points shown are open squares; Lebowa data points (Dennilton area) are solid symbols.

Figure 4. Schematic distribution of mineral deposits and inferred fluid flow related to the Bushveld hydrothermal system. Fluids closest to the intrusion, largely of metamorphic origin with minor amounts of metals probably leached from the Rustenberg Layered Suite, generated the quartz-gold veins in the Transvaal Supergroup. Outward from these, basinal fluids formed MVT deposits in the Transvaal Supergroup with locally significant contributions of F and heat from the Lebowa (Bushveld) Granites in areas close to the intrusion and minor contributions of Fe, Mn and possibly Cu leached from the Rustenberg Layered Suite. Farthest from the intrusion, basinal fluids deposited phosphate minerals in the Witwatersrand Supergroup and reset paleomagnetic and Rb-Sr isotope systematics as much as 500 km from present contacts. Vertical exaggeration is 10:1 (approximate width of cross section is 1000 km).
Table 1. K-Ar\[^1\] dating of fine grained illite from the Bushy Park MVT deposit.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>K</th>
<th>Rad. $^{40}$Ar [mol/g]</th>
<th>Rad. $^{40}$Ar [%]</th>
<th>Age [Ma]</th>
<th>Error [Ma]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP271-118.2; white friable muscovite/illite</td>
<td>8.38</td>
<td>5.5884E-08</td>
<td>99.53</td>
<td>2059.2</td>
<td>40.77</td>
</tr>
<tr>
<td>BP379-243.2; muscovite/illite only</td>
<td>7.75</td>
<td>5.0780E-08</td>
<td>99.54</td>
<td>2037.6</td>
<td>40.38</td>
</tr>
</tbody>
</table>

\[^1\] The K-Ar dating technique follows standard methods described in detail by Faure (1986). During the course of the study, the international standards HD-B1 and LP6 (Odin et al. 1982) were measured. The error for Ar analyses is below 1.00 % and the $^{40}$Ar/$^{36}$Ar value for airshots averaged 294.54 ± 0.21 (n =2). The K-Ar ages were calculated using $^{40}$K abundance and decay constants recommended by Steiger and Jäger (1977).
Table 2. Sm-Nd isotopic data for Zeerust fluorite used in age interpretation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. (g)</th>
<th>147Sm/144Nd</th>
<th>2-sigma</th>
<th>143Nd/144Nd</th>
<th>2-sigma</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 – WT-PK-F - Witkop</td>
<td>0.4497</td>
<td>0.3080</td>
<td>0.0017</td>
<td>0.513867</td>
<td>0.000010</td>
</tr>
<tr>
<td>4 – PD-2-(P)</td>
<td>0.1087</td>
<td>0.1893</td>
<td>0.0008</td>
<td>0.512304</td>
<td>0.000010</td>
</tr>
<tr>
<td>5 – PD-2-(W)</td>
<td>0.2752</td>
<td>0.1598</td>
<td>0.0005</td>
<td>0.511874</td>
<td>0.000010</td>
</tr>
<tr>
<td>7 – DDH31-268</td>
<td>0.1064</td>
<td>0.2651</td>
<td>0.0005</td>
<td>0.513311</td>
<td>0.000009</td>
</tr>
</tbody>
</table>

1 Sm/Nd ratios were determined by single collector magnetic sector ICP-MS using a standard-sample-standard bracketing technique (Gleason et al. 2007). Two in-house standards of known Sm/Nd composition (ID-TIMS) gave $^{147}\text{Sm}/^{144}\text{Nd} = 0.1266 \pm 0.0010$ (n=8) relative to a true (ID-TIMS) value of 0.1265; and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1466 \pm 0.0020$ (n=8) relative to a true (ID-TIMS) value of 0.1462 during this run. Sample solutions were a 1:10 dilution of the same aliquot used for Nd isotope chemistry.

2 2-sigma errors are based on the in-run average of 4 analyses. True reproducibility of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios by this method is estimated to be ± 1%.

3 Nd isotopic data were determined by TIMS static mode on a Finnigan 262 equipped with 8 collectors following methods of Gleason et al. (2007). Mass 147 was monitored to insure no Sm interference on mass 144. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ for online mass bias correction using exponential law. Multiple measurements of the La Jolla Nd isotopic standard during the course of this study gave a value of $^{143}\text{Nd}/^{144}\text{Nd} = 0.511852 \pm 9$ (n = 23), making corrections unnecessary. Prior to analysis, Nd was pre-concentrated by digesting cleaned and crushed fluorite samples in a mixture of HClO$_4$ and HCl following methods of Chesley (1991). Nd was then separated from matrix using conventional 2-stage column chemistry (Gleason et al. 2007); Nd blanks were < 100 pg.

4 2-sigma errors reflect TIMS in-run precision based on 15 blocks of data on 10 ratios each (150 ratios).
Exposed  Covered

- Bushveld Complex
- Transvaal Supergroup
- Witwatersrand Basin (Central Rand Group)

**Witwatersrand Ages (m.y.)**

- 2043

++ Mississippi Valley-type deposits

△ Au and Pb-Zn vein deposits

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Ventersdorp Supergroup

Basement Rocks
(including Witwatersrand Supergroup and Dominion Group)

Rooiberg Group
Lebowa Granite Suite
Rustenberg Layered Suite

Postmasburg-Pretoria Group
Ghaap-Chuniespoort Group

Ventersdorp Supergroup
Basement Rocks

MVT-(Pb-Zn) Deposit
MVT-(F) Deposit
Au Deposit
Phosphate Ages

Granite Related Fluid
Basinal Fluids
Metamorphic Fluid
Meteoric Fluids