Compositional and textural peculiarities of gold-rich alloys from the Merensky Reef

Roland Merkle, Wiebke Grote and Peter Gräser
Bushveld Intelligence Center, Department of Geology, University of Pretoria, Pretoria 0002, South Africa.

ABSTRACT
Gold-rich alloys with variable amounts of Pd from the Merensky Reef, Bushveld Complex, are characterized by a range of finely dispersed inclusions. The small sizes of these inclusions (median of 1.85 μm) make fully quantitative analyses virtually impossible. Tentative interpretation of semi-quantitative microprobe analyses demonstrates the presence of atokite, kotulskite, laurite, moncheite, niggliite, paolovite, rustenburgite, sobolevskite, and sperrylite. Some inclusions appear to represent unnamed minerals.

Textures and assemblages imply that these gold grains and their inclusions formed from fluids through occasional remobilisation and co-precipitation.

Introduction
The Merensky Reef of the Bushveld Complex is not only a major source of platinum-group elements (PGE), it also contains gold which is recovered as a by-product. Very little information about the concentrations and distribution of gold in the Merensky Reef is available, but the recommended value for Au in SARM-7, an international standard for PGE which was prepared from Merensky Reef (Steele et al., 1975), is 310 ± 0.015 ppb for the 95% confidence interval, and an average value for Au in the Merensky Reef was reported to be 220 ppb (Vermaak, 1976). Regional variation in gold concentration is linked to variations in ΣPGE+Au grade (Viljoen, 1994; 1999) and to variable proportions of Au (1.5 to 6.6% of ΣPGE+Au) in different types of Merensky Reef (Leeb-Du Toit, 1986; Viljoen and Hieber, 1986; Farquhar, 1986; Mossom, 1986; Viljoen et al., 1986a; 1986b).

Even in single boreholes through the Merensky Reef (ignoring differences in rock types) with an average Au-content of 460 ppb (Von Gruenewaldt et al., 1990) and 570 ppb (Barnes and Maier, 2002) respectively, individual samples were found to vary between <50 and >2000 ppb (Barnes and Maier, 2002; Wilson and Chunnett, 2000). Tin contents in the Merensky Reef are assumed to be about 2 ppm (Vermaak, 1976), while silver may reach 1.4 ppm in individual samples (Barnes and Maier, 2002) with a large scale average of 0.54 ppm (Vermaak, 1976). Gold shows positive correlations with Ag, Pt, and Pd, but the number of reported analyses is too small to allow a rigorous evaluation of variations between the different rock types that make up the Merensky Reef (i.e. the economically mineable PGE ore, irrespective of the rock type). It is reasonable to assume that different rock types of the Merensky Reef are petrologically and genetically different (Cawthorn and Maier, 2002) with a large scale average of 0.54 ppm silver may reach 1.4 ppm in individual samples (Barnes et al., 2006).

MINERALOGICAL DESCRIPTIONS
Mineralogical descriptions mention the occurrence of metallic gold and electrum (Mihalik et al., 1975; Schwellnus et al., 1976; Brynard et al., 1976; Vermaak and Hendriks, 1976; Kingston and El-Dosuky, 1982; Mostert et al., 1982; Franklin and Merkle, 1999) in the Merensky Reef. For simplicity, all these grains will be referred to as metallic gold in this communication, irrespective of the Au/Ag ratio. Most of these grains are very small. Volume proportions of metallic gold amongst PGE and Au-containing minerals range typically from traces to 4.1% (Brynard et al., 1976; Vermaak and Hendriks, 1976; Kinloch, 1982), although in individual boreholes the proportion of Au-Ag alloys may exceed 40% (Kinloch, 1982).

Large metallic gold grains of up to 500 μm in length and up to 100 μm in thickness can be found in Merensky Reef concentrate. A microscopic investigation of such grains from Rustenburg Platinum Mine (Kingston and El-Dosuky, 1982) revealed that many of them contain variable amounts of tiny inclusions which were identified to be atokite and mertieite II. Such inclusions are not restricted to Rustenburg Platinum Mine and can be observed in coarse metallic gold from around the Bushveld Complex and have even been observed in detrital gold from the eastern Bushveld drainage system (Oberthür et al., 2004).

The information presented here is based on observations of ~250 gold grains handpicked from production concentrate, with the main emphasis on the composition of the metallic gold, associations and types of inclusions, and micro-textures. Because such concentrates are dependent on the mining operation at a specific time, they are representative for a large volume of Merensky Reef. They can, however, not be taken to be representative for the Merensky Reef per se. The concentrate was put at our disposal under the condition that its source may not be revealed.

Analytical Conditions
Electron microprobe analyses were performed with a JEOL 733 electron microprobe and attached ISIS energy dispersive system with an accelerating potential of 20kV and a beam current of 2 x 10^-8 A. We decided on this
The non-linear determination in mixtures of Au and Ag (Reid et al., 1988), or Pt and Pd (Merkle and Verryn, 1991) are just two. Correction procedures (mainly absorption and fluorescence) in electron microprobe analysis assume that the analyzed material is homogeneous and all elements are evenly distributed throughout the excitation volume from which X-rays are produced (Reed, 1975). Analyses (i.e., excitation areas) that represent two or more distinct phases inevitably lead to incorrect results.

Attempts to produce metallic standards with complex matrices failed because heterogeneities on μm-scale could not be overcome. Suitable standards close to the unknown, which are required to achieve very good quality results in complex matrices (Cabri, 1980), were therefore not available. We had to resort to a large range of metals, alloys, and synthetic PGM in attempts to approach the matrix in question. Consequently, many analyses are too low and in some cases, element ratios appear to be represented inaccurately. Even if totals of the microprobe analyses approach totals of 100%, we consider this to be coincidence and the analyses are considered to be only semi-quantitative. We therefore refrain from any interpretation of small variations of composition or stoichiometry, but consider the analyses perfectly acceptable for the tentative identification of the phases.

**Figure 1.** Frequency distribution of Au content in gold-rich alloys.

**Figure 2.** Compositional variation of gold-rich alloy from Merensky Reef concentrate. Literature data from Kingston & El-Dosuky (1982) and Schwellnus et al., (1976).
Figure 3. Backscatter electron images of gold-rich alloy from Merensky Reef concentrate. Dark inclusions of PGM (with lower average density than gold) define distinct zones.

Observations

The metallic gold host

Our study confirms the compositions of the gold-rich alloys reported previously (Schwellnus et al., 1976; Kingston and El-Dosuky, 1982). The gold analyses in our study were performed in areas of the gold grains which did not contain visible inclusions. It appears that a small proportion of these grains are very pure gold with ~86 to 92 atomic % Au, while the majority contains substantial amounts of Ag with ~74 to 44 atomic % Au (Figure 1). Many of the more Ag-rich alloys contain up to ~ 9 atomic % Pd (~6 weight % Pd) in solid solution (Figure 2).

The inclusions

Not all gold grains contain visible inclusions. However, it is not clear whether the lack of inclusions is a function of the grain exposure. Most grains have areas that are free of inclusions, with the highest density of inclusions in specific zones or rims of the gold grains (Figure 3).

Most of the inclusions in the gold-rich alloys are round to lenticular with the largest axis commonly below 2 μm, with a median of 1.85 μm for 430 inclusions (Figure 4). It is sometimes possible to microscopically distinguish more than one type of inclusion in a particular gold-rich alloy grain, but the small grain sizes make an identification impossible. Therefore, these inclusions can only be distinguished and identified based on their element combinations.

Figure 4. Size distribution of 430 inclusions in gold-rich alloy. Arithmetic mean 2.11 micron; median 1.85 micron.
Quantitative microprobe analyses are hampered by interference from the surrounding gold-rich alloys. Although many analyses resulted in totals close to 100 weight % (Table 1) and imply element proportions close to expected stoichiometries, the high proportions of Au and Ag render these analyses only semi-quantitative.

### Table 1. Selected analyses in wt.-% of inclusions in gold-rich alloys to demonstrate the mixed character of analyses of atokite ((Pd,Pt),Sn) and paolovite ((Pd,Pt)Sn)

<table>
<thead>
<tr>
<th>Pd</th>
<th>Pt</th>
<th>Sn</th>
<th>Au</th>
<th>Ag</th>
<th>Total</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.76</td>
<td>13.22</td>
<td>39.30</td>
<td>9.16</td>
<td>100.44</td>
<td>atokite</td>
<td></td>
</tr>
<tr>
<td>31.64</td>
<td>10.25</td>
<td>46.95</td>
<td>12.00</td>
<td>100.84</td>
<td>atokite</td>
<td></td>
</tr>
<tr>
<td>54.05</td>
<td>18.93</td>
<td>19.69</td>
<td>7.67</td>
<td>100.34</td>
<td>atokite</td>
<td></td>
</tr>
<tr>
<td>42.18</td>
<td>14.07</td>
<td>35.77</td>
<td>8.69</td>
<td>100.71</td>
<td>atokite</td>
<td></td>
</tr>
<tr>
<td>33.26</td>
<td>12.06</td>
<td>40.56</td>
<td>12.51</td>
<td>98.39</td>
<td>atokite</td>
<td></td>
</tr>
<tr>
<td>39.84</td>
<td>13.98</td>
<td>36.52</td>
<td>9.18</td>
<td>99.52</td>
<td>atokite</td>
<td></td>
</tr>
<tr>
<td>45.52</td>
<td>23.26</td>
<td>25.05</td>
<td>7.28</td>
<td>101.11</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>63.04</td>
<td>2.48</td>
<td>35.16</td>
<td>3.18</td>
<td>103.86</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>55.75</td>
<td>3.77</td>
<td>30.81</td>
<td>9.17</td>
<td>100.75</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>59.07</td>
<td>1.81</td>
<td>32.99</td>
<td>6.71</td>
<td>100.58</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>60.58</td>
<td>2.25</td>
<td>34.77</td>
<td>2.02</td>
<td>99.62</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>23.64</td>
<td>11.59</td>
<td>40.76</td>
<td>24.03</td>
<td>100.02</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>42.93</td>
<td>19.84</td>
<td>31.14</td>
<td>8.14</td>
<td>102.05</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>40.05</td>
<td>20.44</td>
<td>32.29</td>
<td>9.18</td>
<td>101.96</td>
<td>paolovite</td>
<td></td>
</tr>
<tr>
<td>45.55</td>
<td>22.54</td>
<td>27.90</td>
<td>5.08</td>
<td>100.87</td>
<td>paolovite</td>
<td></td>
</tr>
</tbody>
</table>

Based on their element combinations and proportions, a wide range of inclusions were recognized (Table 2). The most common inclusions contain Pd or Pt and Sn. Our observations imply that in the Merensky Reef, Pd-rich inclusions vastly outnumber the Pt-rich inclusions. Niggliite, (Pt,Pd)Sn, is a rare mineral, while paolovite ((Pd,Pt)Sn with variable but low Pt content) and atokite ((Pd,Pt)Sn without detectable Pt) are the most common inclusions. Rustenburgite, (Pt,Pd)Sn, inclusions were encountered only rarely, but their composition appears to fall inside the range of Pt/Pd

### Table 2. Platinum-group minerals identified as inclusions in gold-rich alloys *not observed in this study

<table>
<thead>
<tr>
<th>Platinum-group mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>atokite</td>
<td>(Pd,Pt)Sn</td>
</tr>
<tr>
<td>kotulskite</td>
<td>Pd(Te,Bi)</td>
</tr>
<tr>
<td>laurite</td>
<td>Ru$_2$</td>
</tr>
<tr>
<td>mertitite II</td>
<td>Pd$<em>x$Sn$</em>{1-x}$</td>
</tr>
<tr>
<td>moncheite</td>
<td>(P$<em>x$Pd$</em>{1-x}$)(Te,Bi)$_2$</td>
</tr>
<tr>
<td>niggliite</td>
<td>(Pt,Pd)Sn</td>
</tr>
<tr>
<td>paolovite</td>
<td>(Pd,Pt)Sn</td>
</tr>
<tr>
<td>rustenburgite</td>
<td>(Pt,Pd)Sn</td>
</tr>
<tr>
<td>sobolevskite</td>
<td>Pd$_{1-x}$Bi</td>
</tr>
<tr>
<td>sperrylite</td>
<td>PtAs$_2$</td>
</tr>
</tbody>
</table>

Figure 5. Compositional variation of Pt-Pd-Sn phases. Rustenburgite, (Pt,Pd)Sn, attached to gold (open circle) shows compositional overlap with rustenburgite inclusions in gold (stars).
Figure 6. Distinction between paolovite, (Pd,Pt)\textsubscript{2}Sn, and atokite / rustenburgite, (Pd,Pt)\textsubscript{3}Sn, despite interference from gold-rich alloy.

Figure 7. (Pt + Pd) / (Te + Bi) ratios of some inclusions.
Figure 8. Analyses of kotulskite, Pd(Te,Bi), should plot on the line of 50 at % Pd.

Figure 9. Analyses representing sperrylite, laurite, and mixed analyses between the two.
Figure 10. Projection of six analyses of unnamed PtSnS.

Not all analyzed inclusions could be allocated to known PGM. Even if severe analytical problems are assumed, some grains appear to represent unnamed minerals. We observed three grains consisting of Pd, Sn, and As, but were not able to obtain acceptable analyses. The analysis with the highest total of 93.5 weight % calculates to $\text{Pd}_3\text{Sn}_2\text{As}$.

Several grains of a phase containing only Pt, Sn, and S were encountered (Figure 10). Although all analyses have low totals and are considered semi-quantitative, there is little doubt that the composition of this phase is PtSnS.

We did not observe any inclusions containing Sb and can therefore not confirm the presence of inclusions which may be considered to be mertieite II ($\text{Pd}_3\text{Sb}_3$).

Discussion

Mineralogy

There are clearly similarities between the compositions of the gold found in our study and the analyses reported previously from the Merensky Reef. Gold from Atoke appears to contain small amounts of Pt instead of Pd (Schwellnus et al., 1976), while none of our analyses of inclusion-free gold contained platinum in detectable amounts. We are inclined to believe that tiny inclusions of Pt-containing minerals may be responsible and that the reported Pt is not present as a solid solution in gold.

Palladian gold has been reported from many localities. Judging from the available literature it seems...
Gold-rich alloys are rarely reported, the observation of $\%$ undeniably has Pd in solid solution and contains (Stumpfl and Tarkian, 1976; Ballhaus and Stumpfl, 1986; the PGE were remobilized, if not introduced, by fluids (J.H.D. Schorscher, personal communication, 2004). The gold from the Merensky Reef, with a considerable lower Pd-content of up to about 6 weight $\%$, undeniably has Pd in solid solution and contains particulate Pd-rich phases as inclusions.

Although inclusions of platinum-group minerals in gold-rich alloys are rarely reported, the observation of such a case in the alluvium of the Durance River, France (Johan et al., 1990), where the gold contains $\approx$ 2 $\mu$m-sized inclusions enriched in Ni, Pt and Sn and up to $\approx$ 3 weight $\%$ of Sn, shows that the Merensky Reef is not unique and that a systematic search for such inclusions might reveal more examples.

Unfortunately, the gold grains in this study are isolated from their original setting and it is therefore not possible to relate the dominance of specific minerals observed as inclusions (i.e., platinum group minerals containing Bi, Te, Sn, and As) in a gold grain to the proportions of platinum-group minerals in the mineral assemblage in a given locality (Kinloch, 1982).

The unnamed Pt-Sn-S phase is occasionally encountered in very small grains in the UG-2, the Platreef, and the Merensky Reef (Kinloch, 1982; Louwrens, 1996), but normally grain sizes are too small to obtain quantitative information about the proportions of the elements. The only quantitative analyses in the available literature (Barkov et al., 2001) show very little variation in the composition compared to our analyses. Whether this is purely an analytical artefact remains unresolved.

**Genesis**

The “hydrothermal” concept for the formation of the Merensky Reef has been advocated by some scientists, i.e., that the Merensky Reef is a mineralization in which the PGE were remobilized, if not introduced, by fluids (Stumpfl and Tarkian, 1976; Ballhaus and Stumpfl, 1986; Barnes and Campbell, 1988). Evidence for the hydrothermal modification of platinum group minerals in the Merensky Reef has been presented (Merkle and Verryn, 2003). The formation of metallic gold grains of the sizes which form the bulk of this investigation is very unlikely if only magmatic processes are considered.

The tenor of 2 to 3 weight $\%$ base metal sulphides (Merkle and McKenzie, 2002) in the Merensky Reef is thought to have accumulated under magmatic conditions as a sulphide melt (Naldrett et al., 1986; Barnes and Campbell, 1988; Cawthorn and Boerst, 2006; Wilson and Chunnell, 2006). The partition coefficient of Au into such sulphide melts (i.e., the ratio of the concentration in the sulphide melt divided by the concentration in the silicate melt under equilibrium conditions) has been estimated to be up to 1800 (Peach et al., 1990; Stone et al., 1990), depending on intrinsic conditions like oxygen fugacity, cation ratios in the sulphide melt, or metal/sulphur ratio of the sulphide melt (Crockett et al., 1992; 1997; Fleet et al., 1999). Such high partition coefficients suggest that the element in question is homogeneously distributed throughout the sulphide melt.

Gold is alloyed with variable amounts of silver, copper, and other minor components (like Pd) in a metallic phase of very high density, whereas most of the PGE form compounds (with sulphur, tellurium, and other ligands) of lower density. A variable proportion of Pd is present as solid solution in base metal sulphides (Paktunc et al., 1990; Cabri, 1992; Ballhaus and Ryan, 1995) and except for selected localities, Pt-Fe alloys are rare (Kinloch, 1982), i.e., the volume proportion of metallic gold should be considerably lower than the weight proportion (1.5 to 6.6% of $\Sigma$PGE+Au) suggests. It is also to be expected that the bulk of the low gold concentration in the sulphide melt would result in small, finely dispersed grains on cooling. Reports of higher proportions of metallic gold in Merensky Reef (Kinloch, 1982) therefore imply remobilisation and concentration of metallic gold. Large grains of up to 500 $\mu$m length as studied here are therefore considered to have formed by hydrothermal remobilisation from magmatic sulphides and the co-precipitation of the gold and its inclusions.

Individual grains contain distinct zones in which the dusting of PGM occurs. In our opinion these zones represent growth zones of the gold. Our observations imply that in the coarse gold from the Merensky Reef, Pd-rich inclusions vastly outnumber the presence of Pt-rich inclusions.

If these inclusions of PGM represent exsolutions, this would imply that the high temperature alloy contained a higher amount of Pd in solid solution, which exceeded solubility on cooling, while the concentration of Pt was lower and was more efficiently exsolved. It also would imply that the Sn, Bi, and Te in the PGE in the PGE had to be dissolved in the gold as well. We were not successful in our attempts to locate phase diagrams which would allow us to quantify the maximum solubility of Sn, Bi, and Te in gold as a function of temperature under hydrothermal conditions. However, phase diagrams of binary systems relevant to our study show that there is an extended solid solution between Au and Pd, Pt, or Sn at elevated temperatures, by far exceeding the values observed in the gold grains under investigation (Massalski, 1990), although solubility might be reduced at low temperature. There is no indication that the solubility of Pt in gold is so distinctly lower than of Pd at the concentration levels in this gold that it could cause the observed dominance of Pd-rich PGM. This implies that the element content of the inclusions are unlikely to have been in solid solution and unmixed on cooling. The finely dispersed PGM in gold-rich alloys are
therefore considered to be physical inclusions, not exsolutions, and the additional presence of Sn, Bi, Te, and As in the fluid must be seen as the reason for the presence of particular PGM.

The palladium dominance must therefore be a function of the composition of the hydrothermal fluid from which the gold precipitated.

In the aqueous geochemistry of Pt and Pd are small but distinct enough to cause a smaller stability field of PdS (vysotskit¢) compared to PtS (cooperite), depending on temperature, pH, chlorine activity, and oxygen fugacity (Wood et al., 1992; Gammons et al., 1992). It is therefore possible to preferentially leach Pd from (Pd,Pt,Ni)S (braggite). This is the reason why braggite, the most likely primary PGM forming from the sulphide melt, may lose Pd preferentially through interaction with hydrothermal fluids (Merkel and Verryn, 2003). Examples for such Pd-depleted braggite are known, amongst others, from the Merensky Reef (Schwellnus et al., 1976; Cabri, 1992, 398, 1978; Kingston and El-Dosuky, 1982; Mostert et al., 1982) and Lukkulaisvaara (Barkov et al., 1995).

The precipitation of PGM and inclusion in the gold grains would have to happen below the upper thermal stability limits of the inclusions. Unfortunately, the upper thermal stability limits for all the minerals found as inclusions are rather high. Kotulskite has a minimum stability temperature of 720°C (Elliot, 1965; Shunk, 1969), while atokite, moncheite, nigglite, and rustenburgite were synthesized at 1000°C (Shelton et al., 1981; Kim, 1990). Laurite and sperrylite can be found as primary inclusions in chrome needles, which imply even higher stability temperatures. All the phases that occur as inclusions in gold, and for which thermal stability could be obtained, are stable at temperatures which are to the high end of temperatures expected for any hydrothermal activity that may have redeposited gold.

Summary and Conclusions

We conclude that the assemblage of inclusions in the large gold-rich alloys of the Merensky Reef reflects the variability of compositions and intrinsic conditions of hydrothermal fluids, which occasionally remobilised and precipitated Au and Ag in the Merensky Reef into large grains. The rarity of these large gold-rich alloy grains implies that the bulk of the low Au concentration is finely dispersed in small grains. Inclusions of PGM are interpreted to be co-precipitates from the same hydrothermal fluids. It is at present not possible to quantify the conditions under which these gold grains were precipitated.

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