

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

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“Those who assume hypotheses as first principles of their speculations . . . may indeed form an ingenious romance, but a romance it will still be.” Roger Cotes, preface to Sir Isaac Newton’s Principia Mathematica, second edition, 1713

Colonel Smithers: We, here at the Bank of England, Mr. Bond, are the official depository for gold bullion... just as Fort Knox, Kentucky is for the United States. We know, of course, the amounts we each hold, we know the amounts deposited in other banks, and we can estimate what is being held for industrial purposes. This allows our two governments to establish, respectively, the true value of the dollar and the pound. Consequently, we are vitally concerned about unauthorized leakages.

James Bond: I take it you mean smuggling.

Colonel Smithers: Yes. Gold, gentlemen, which can be melted down and recast, is virtually untraceable... making it, unlike diamonds, ideal for smuggling... attracting the biggest and most ingenious criminals.

From: *Goldfinger* (1964)

Declaration

I, Roger David Dixon, hereby state that this work is a result of my original research, and that the results and conclusions contained herein are my own.

.....

17th September 2014

Abstract

The theft of gold from primary deposits, primary producers and legal title holders is a major problem in many countries around the world. The identification of the source of gold and the means by which it was beneficiated are therefore crucial in determining ownership and legality, especially in the South African context, where large quantities of gold are stolen and illicitly mined, with major economic losses, predominantly from the mines in the Witwatersrand Basin.

Gold usually occurs in its metallic form, often alloyed with a limited range of elements which include Ag, Hg and Cu, in addition to a wide range of trace elements. The concentrations and associated elements are typical for specific genetic types of the gold deposits from which they are mined, and this elemental fingerprint can be used for identifying deposits.

Most stolen gold is melted down into small pieces of gold, or consolidated into small bars, which are then traded by criminal syndicates, and finally laundered via refineries. Before it gets to the refinery, however, it is possible to identify (via the elemental distribution) possible sources and processes employed to recover the gold. The processes used to produce illicit gold are discussed, as well as their effects on the gold metal produced, which may have an effect in masking the origin of the gold.

The legislation in South Africa regarding the mining and possession of precious metals is discussed, as well as the establishment of the South African Gold Database as a means for combatting the theft of gold from the major goldmining companies in South Africa and the reason for the type of sample selected to be representative of the gold produced at each mine – unrefined d'ore gold.

The different analytical techniques utilised for the analysis of gold grains, and their development and improvement of the past few decades are then discussed. It is important that a method to analyse stolen gold be fairly straight-forward and repeatable, so the different types of instrumentation with their strengths and weaknesses are discussed. It is shown that the best method for the analysis of all types of gold material, from a comparison point of view and not for absolute analysis, is laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS). The development of this technique and its applications for gold are evaluated.

The composition of the d'ore samples across the Witwatersrand Basin was analysed in order to determine compositional trends in the extracted gold between mines and goldfields, focussing on three goldfields in particular – Free State, Klerksdorp and West Wits. It is shown that there are two major groups of gold samples, spatially defined, within these three goldfields, which are clearly distinguished on the basis of Pb isotopic systematics and Ni content. It is also shown that the different goldfields can be distinguished on the basis of the d'ore composition, and that to a lesser extent discrimination between individual gold mines in the West Wits and Free State goldfields is possible.

Illicit gold recovered from the vicinity of the Driefontein mine was analysed and compared to the samples in the database in order to determine whether the use of d'ore gold samples, produced with the carbon-in-pulp method, would be sufficient to identify illicit gold recovered using mercury amalgamation. It is shown that depending on the elements used, such identification can be made. In addition it is shown that, due to differences in beneficiation methods and the stage within the beneficiation process, the specific type of material processed to extract the gold can be identified. This has important intelligence benefits when investigating the theft and the place from where the material was stolen.

The identification of two different types of gold mineralisation within the Witwatersrand Basin, and the use of the database to identify stolen gold from the basin, showed the applicability of the methodology. A second scenario was therefore examined, dealing with gold from two different genetic sources from northern South America, in which illicit gold bars were compared to artisanally recovered gold from two countries, and gold samples from the suspected source as a control. It is shown that in this second case, the two ore deposits could be very clearly distinguished, and even though the artisanal gold was recovered by amalgamation, a clear identification could be made with the control sample. The discrimination made here was much more distinct than that made within the Witwatersrand basin, and this is considered to be due to a single source of gold compared to possible multiple sources, as is the case in the Witwatersrand Basin.

Each mine within the Witwatersrand basin extracts gold from one or more reefs, so the variation within and between reefs at the Driefontein mine was studied, using gold prills as samples. The identified variation is discussed in terms of depositional and post-depositional processes, and it is shown that there appear to be two populations of gold within the Ventersdorp Contact Reef (VCR), *i.e.* one alluvial and the other hydrothermal. For the

Carbon Leader Reef (CLR), however, the prill compositions differ from those from the VCR, and show that the gold mineralisation in this reef could have arisen from another, different process or combination of processes.

Individual gold grains from different reefs were then analysed, in order to determine to what degree the d'ore and prill results correlate with the gold grain compositions. Four distinct populations were found, each linked to a specific and different mineralisation process. Within the Vaal Reef, alluvial gold of epithermal vein gold from a granite-greenstone terrane was identified, as well as a second population of gold with an anomalous composition (containing U and Pb) which was interpreted as being of a remobilised origin, being formed during the first stages of diagenesis, and a third population of gold typical of low temperature hydrothermal mineralisation. Gold-bearing carbon from the CLR was also analysed, which revealed gold mineralisation attributed to precipitation of colloidal organometallic compounds. The uranium mineralisation associated with the CLR is shown to be co-eval with the gold on microbial mats, and this mineralisation was the source of the Au (and U and Pb) which was remobilised in an initial post-depositional event. The two populations identified within the VCR are confirmed as being of hydrothermal and alluvial origins.

The variation within the Witwatersrand Basin, due to differences between source areas of original detrital material and hydrothermal events post-deposition, provide sufficient discrimination to enable the identification of the origin of seized illicit gold. In addition, the use of LA-ICP-MS enables the discrimination of different gold materials of natural origin to a level not seen before, with trace element resolution at micron scales, resulting in a much better and more precise identification of genetic processes.

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1 Introduction

1.1 The illicit gold trade – an international problem

Illegal trade in stolen precious metals and diamonds is very profitable due to their high values and established identities as global currencies. With high poverty levels, especially in the less developed countries, which coincidentally have substantial gold reserves, the theft and illegal mining of gold is rife. The ultimate beneficiaries of this illegal trade are often well-organised syndicates also involved in a variety of other illegal activities, such as drug and firearm trafficking, with wide-reaching contacts and set-off areas. These organisations present a global threat, and could best be monitored and opposed on an international level.

Established money laundering systems using gold have been found in many European countries, such as Switzerland and Italy, and from there across the world (including the USA, and South- and Central America). Reportedly, Uruguay became the leading gold supplier to the USA during 1989 (George, 2007) even though the country had no gold industry, as a scheme for covering up narcotics profits. International terrorist groups also regularly use gold as a bargaining tool. Prior to and during the US attack on Afghanistan, al-Qaeda moved large funds out of that country by smuggling gold, diamonds and other precious stones across the borders, and then to Dubai, from where the funds were spread across the world, including the USA (Farah, 2002). Due to the general absence of formal banking systems in the Middle East, North Africa and Asia, the informal Hawala system is often used to refund gold deliveries, where money is transferred across large distances by e-mail or telephone calls, and all records are destroyed afterward. These and many other routes exist whereby illegal funds can be legitimised, using precious metals and precious stones, often themselves having been obtained by illegal means.

The illegal mining of gold in the Democratic Republic of the Congo (DRC) generates profits which are reportedly used to buy arms and fund the civil war (Donovan, 2014). In the DRC, criminals rely on the state's inability to control its territory and borders. It is reported that around 70 per cent of the gold currently being mined in the DRC has been exported illegally (White, 2005), reaching up to 95 per cent in the eastern DRC (BSR, 2010). A large volume of illicitly mined gold is smuggled into Uganda where it is bought by traders who, by completing the requisite customs and export forms, export it legally and in the process

launder it (Bariyo *et al.*, 2013). Although Uganda has relatively little domestic gold production, it was still able to export US \$60 million in gold in 2002. A large proportion of this gold is known to have reached South Africa (Haken, 2011).

Approximately 171,300 tons of gold has been mined from historical times up till now, of which an estimated 15% has been lost, used up by industry, or is otherwise unaccounted for (Müller & Frimmel, 2010; George, 2013). The balance consists of about 32,000 tons held by central banks, and the rest is in private hands in various forms (World Gold Council, 2013). Total world reserves of gold are very variable, depending on the gold price, costs of extraction, etc. At present, it is estimated that economically recoverable known reserves are 52,000 tons (George, 2013).

In 2007, South Africa was the largest gold-producing nation (George, 2013) but the changing economic situation has caused several South African gold mines to reduce gold production, even though overall world production is rising. The world gold production and estimated reserves for 2011 are given in Table 1.1, with the top eight producers shown. Globally, gold mining has increased dramatically, and many smaller producers are located in Africa and South America, from where a large amount of artisanal gold is produced.

Table 1.1 World mine production and reserve base in 2011, in tons (from George, 2013).

Country	Production	Reserve
United States	234	3000
Australia	258	7400
Canada	97	920
China	362	1900
Indonesia	96	3000
Peru	164	2200
Russia	200	5000
South Africa	181	6000
Other countries	1068	22580
World total (rounded)	2660	52000

The illicit gold trade is worth more than US \$2.3 billion annually. Major producers of illicit gold are Peru (40% of its gold production is illegal), Russia, Mali, Brazil, Uzbekistan, Papua New Guinea and Argentina. The rise in the price of gold has spurred on the illicit trade, as policing the artisanal producers is often impossible or very difficult in the terrains where the deposits are found (Haken, 2011). Most of the profits go to the middlemen, who in many cases are syndicates, and the country of origin benefits little from this illegal trade. As a result of the extent of the illicit mining in Peru, and its damage to the economy, illegal mining has been criminalised and the Peruvian government is making a major effort to curb these activities, after years of inaction (Andean Air Mail & Peruvian Times, 2012).

1.2 Gold theft in South Africa

Gold production annually lost to theft in South Africa comprises a significant portion of the total production value. Loss estimates made during studies conducted on the topic by the Institute of Security Studies proposed that in 2001 approximately 35 tons of gold may have been stolen on average per annum over the period 1994-1998 (Gastrow, 2001). The estimated value then would have been in the region of R1.84 billion per annum. On 1998 production figures, 35 tons would have constituted approximately 7.5 % of total production. The report suggests that this figure could possibly have been as much as 50 to 60 tons. A subsequent report for 2007 confirmed the findings in the initial research report (Coetzee & Horn, 2007). If the 7.5 % were used as a rule of thumb on 2008 gold production figures, 514 000 ounces may have been lost to criminal activity at a market value of R3.7 billion per annum.

In South Africa, such a large loss of income to the mining industry simultaneously results in a loss of national income to the state from revenue, as well as a loss of available jobs to mineworkers as a result of increased production costs. The domino effect of job losses leading to a variety of economical and social problems have crippling effects on entire communities in this country in particular, due to the extremely high rate of unemployment (one worker is estimated to support an average of about 10 people who are dependent on this income (Stoddard, 2013)). This problem has echoes in a number of other countries (Haken, 2011).

The thriving illicit gold market in South Africa is also a market for illicit gold from other parts of Africa, including the so-called “blood gold”, mined in war-torn regions in order to fund paramilitary activities (Bariyo *et al.*, 2013). The circulation of illicit gold is controlled

by large criminal syndicates, which are heavily involved in other criminal activities within South Africa (Coetzee & Horn, 2007). Shipments of gold from other countries can readily be assimilated into the illicit gold circuit, and illicit gold from South Africa can also be transferred to refineries in Europe.

In South Africa there exists a legal requirement to relate recovered stolen gold (i.e. natural (alluvial, etc.), stolen from mine, smelter or illegally processed in a backyard) to source, and also to identify the process by which it was beneficiated in order to confirm or refute its origin (Precious Metals Act, 2005; Smith, 2008).

In 2012 the Rand Refinery, the largest gold refiner in the world, processed over 440 tons of gold from d'ore, almost twice the legal production recorded for South Africa. The balance of the gold refined was mainly from South American and African sources, and submitted by a variety of parties (Rand Refinery, 2012).

Section 1502 of America's Dodd-Frank Wall Street Reform and Consumer Protection Act requires companies buying minerals, including gold, to submit an annual report describing their measures to ensure their material is "conflict-free" (Dodd-Frank, 2010). The World Gold Council is now implementing procedures that require certification of origin of all gold which is traded (World Gold Council, 2011). These actions place the onus on each gold producer to certify the origin of its gold in that it originates from legal and licit sources. A means to cross-check these statements of origin would be to have a database of known gold samples and a methodology to compare those samples with the gold being traded.

The Kimberley Process has been developed to "identify" blood diamonds (United Nations, 2000), but cannot always be implemented successfully. On the opposite end of the spectrum, it is a relatively simple process to implement for "coltan", or columbite – tantalite (e.g. Savu-Krohn *et al.*, 2011; Gäbler *et al.*, 2011), much of which derives from the war-torn areas of Africa (Lublinski *et al.*, 2010). Similarly, due to its nature, it is much easier and practicable to fingerprint gold. Fast identification of illicit precious metals using certified and internationally accepted methods utilising universal databases, and identification of the original producers, would promote worldwide cooperation and trust. It should ultimately be possible to prevent illegally obtained precious metals from re-entering the legal economic systems, and therefore drastically reducing the profits to the smugglers.

1.3 Legal and forensic requirements

There is a legal requirement in South Africa to relate recovered stolen gold to source, in order to confirm or refute its origin (Precious Metals Act, 2005; Smith, 2008). This requirement is needed as part of a criminal case, to prove guilt relating to the possession of unwrought stolen gold, as well as determining the legal owner of the gold in order to return it to them.

In a study looking at the burden of proof during litigation in South African courts of law, de la Rey (2007) assessed the differences between “beyond reasonable doubt”, required for criminal cases, and “balance of probability” required for civil cases. In South African case law, probabilities must be based on proven facts (*S v Abrahams*, 1979) and proof is delivered by means of deductions derived from these facts (Schmidt & Rademeyer, 2006), with the difference between a criminal matter being that the deduction must be the only reasonable deduction, and the deduction in a civil case must be the most probable one. Nowhere in South African nor English law is absolute proof necessary.

Analysis of suspected stolen gold for court purposes can be done by a single competent person: “Section 208 of the [Criminal Procedure] Act stipulates that an accused may be convicted on the evidence of a single and competent witness. This does not displace an important principle in our law that the evidence of a single witness must be approached with caution. Before the court can place any reliance thereon, the evidence of a single witness must be clear and satisfactory in every material respect. In other words, the evidence must not only be credible, but must also be reliable.” (*S v Janse van Rensburg and Another*, 2008).

Forensic science is the application of the laws of physics and chemistry to interrogate evidence. In other words, the processes surrounding the piece of evidence which give rise to its appearance and composition, which are properties which can be determined by analysis. In the examination of a piece of suspected stolen gold, traditional forensic concepts involved would be identification (classification), association (linking) and reconstruction (understanding the sequence of events). Inman & Rudin (2002) showed that this traditional approach failed, and that the concept of “divisible matter” had to be incorporated, to take into consideration the “origin, change and subsequent relationship of physico-chemical traits in the evidence and reference samples”.

In light of the above discussion, it can be seen that for physical evidence that was once part of a whole, and in this case we are considering pieces of gold, or gold-bearing material, which

originated from a specific location or mine, it is necessary to be able to demonstrate a shared origin or source by comparison of the evidence to material from the putative source. This implies that a collection of samples must be available for comparison which would comprise a database. Saks & Koehler (2005) state that “data should be collected on the frequency with which ... attribute variations occur in different populations. In addition to their case-specific benefits, these data may also facilitate the development of ... computer-aided pattern recognition programs...”. It is not necessary to prove uniqueness for forming forensic conclusions, nor is it possible in the case of a piece of gold coming from a particular source. As Page *et al.* (2011) state: “The question of whether a particular forensic assay is accurate is far more important than that of uniqueness”.

For acceptance in court, therefore, the origin or source of a piece of gold or gold-bearing material must be able to be shown as being the only probable one i.e. does the gold come from the alleged source or from elsewhere, and has this gold been illegally processed or not. The return of recovered stolen material would go to the most probable owner (balance of probability). There is a wide range of materials which consist of or contain gold, both natural and manufactured, and thus the information required must be as comprehensive and inclusive as possible, in order for a sound conclusion to be made on the basis of expert and informed scientific judgment (Stoney, 1991).

The use of a database for such purposes can enable the elimination of sources, but unless the number of potential sources is limited and known, it is not possible to make a categorical identification (Broeders, 2003). Due to the nature of gold deposits and manufacturing processes, however, it should be possible in many cases to constrain the number of potential sources and thus arrive at a most probable or only probable source, meeting the legal requirements.

1.4 Aim of the study

The Witwatersrand goldfields are the main source of gold mined in South Africa in South Africa, and also the area which suffers the most from gold theft. This study was started to provide a means for determining whether suspected stolen gold and its legal owners could be identified, and whether such gold came from the Witwatersrand deposits or from elsewhere. In order to do this it was deemed necessary to have a database of gold compositions against which the suspect material could be compared.

Initially it was intended to focus on the composition of native gold grains from the various reefs and goldfields of the Witwatersrand Basin, and to compare these with gold compositions from extant gold deposits on the periphery, mainly Archaean greenstone deposits, in order to elucidate the source of the gold and interpret the various post-depositional processes that might have affected the gold composition.

“An important source of clues to the origin of the gold in the Witwatersrand Basin is the suite of metals associated with mineralisation. This is because the co-transport and deposition of metals such as gold, arsenic, antimony, mercury and silver invariably reduces the number of possible ore-forming processes to those consistent with mineral phases containing those metals. An accurate description of the gold deposition must account for the fact that precipitation and adsorption reactions involving gold are invariably tied to the solubility of arsenic (Arehart *et al.*, 1993; Simon *et al.*, 1999). Models of deposition must also be consistent with observed paragenetic sequencing of minerals... Finally, models must account for differences in gold composition within and between deposits.” (Bagby & Berger, 1985).

However, due to limitations in collecting individual gold grains on a representative basis from around the Witwatersrand Basin, and in order to relate to the problem of stolen gold, it was decided to approach the problem from the end product, and work backwards until the origin was identified in a targeted manner. The aim of this study, therefore, is three-fold:

- To develop a method for the identification of the source of a seized piece of illicit gold. This includes both the geographic and genetic origin of the gold by means of a simple analytical process, to determine whether it is natural or processed gold, and if processed, the method used. The combination of these different factors can then be used to determine the provenance of the gold and its legal status.
- To practically apply the method to identify the source of a seized piece of illicit gold that is presumed to have originated from a mine, or mines, within the Witwatersrand Basin, thereby enabling the return of the seized gold to its lawful owners. In order to achieve this, it is necessary to be able to identify from which gold field within the Witwatersrand Basin the gold originated, and to determine the reason for this discrimination between goldfields, if any.

- To identify the genetic origin of the gold mineralisation within the Witwatersrand Basin, based on the geochemical behaviour and distribution of the trace elements detected in the gold samples investigated during the course of this study.

2 Gold compositions and provenance

2.1 Variation in gold and gold deposits

There has been the formation of gold deposits for over 3 billion years, episodically during the Middle Archaean until the Precambrian, and then continuously through the Phanerozoic. The association of granitoids with a variety of compositions with orogenic events shows that many gold deposits owed their formation to the related thermal events (Groves *et al.*, 1998). Placer gold deposits, which are commonly associated with orogenic deposits, together with other gold sources, comprise economic Phanerozoic orogenic-gold deposits which contain an estimated one billion ounces gold. Precambrian gold deposits contain half as much, excluding the Witwatersrand deposits, which comprise the world's largest gold deposit. (Goldfarb *et al.*, 2001). Greenstone belts host major goldfields in a number of Archaean cratons around the world (De Wit & Thiar, 2005). Globally, extensive gold deposition occurred at around 2 Ga, as the occurrence of sedimentary gold deposits increased. For almost 1 billion years of Earth history (~1.6 Ga - 570 Ma) there are few significant vein gold deposits. From around 570 Ma, the initial phase of Gondwana formation, orogenic gold-vein formation started which has continued till the present day (see Goldfarb *et al.*, 2001, for a review).

The fluids active during much primary gold deposit formation are thought to be from magmatic-hydrothermal fluids, with deposition triggered due to sudden decompression. This is particularly evident in the more recent volcanogenic deposits such as at Ladolam (Simmons & Brown, 2006). Associated elements with the gold include Ag, As, B, Cu, Hg, K, Mn, Mo, Na, Pb, Sn, Sb, Te, Tl, V and Zn. Repeated episodes can give rise to widespread deposits, such as in Peru (Winter, 2008; Teal & Benavides, 2010). Combinations of some or all of these elements are found in gold from all types and ages of deposits and may be used to fingerprint the gold composition from a specific deposit.

Naturally occurring gold is a mineral usually consisting of an alloy of Au, Ag, Hg and Cu in solid solution, often containing several trace elements in mineral inclusions, lattice impurities, at grain boundaries, or in surface coatings. The presence and abundance of the various elements constitute an elemental "profile". Gold occurs in a large variety of deposits and has characteristic profiles (also referred to as "fingerprints" or "signatures") for each of them (Antweiler & Campbell, 1977). These profiles can be used to determine the origin of

gold grains which have been liberated from their specific deposit, such as in prospecting for lode gold (Knight *et al.*, 1999; Mortensen *et al.*, 2005).

In primary gold deposits, such as vein and lode gold, the gold composition will be fairly well-constrained and distinctive of that deposit (e.g. Mortensen *et al.*, 2005). However, for a complicated sedimentary deposit such as that of the Witwatersrand Basin, the original composition of detrital placer gold from primary deposits, which may be a mixture of different genetic types, may be modified by later hydrothermal overprinting (e.g. Frimmel & Gartz, 1997). This is further complicated by the fact that a number of reefs in a vertical succession are mined at one particular operation, and a characteristic profile of gold from such a source may not be immediately apparent. This requires comprehensive spatial and temporal databases to be created to define a particular profile to discriminate between different mines within the larger basin.

The physical characteristics of individual gold grains are obviously important when comparing suspected stolen gold with a control sample - morphology, inclusions, wear and transport damage. Morphology, however, is not characteristic of genetic ore types in primary lodes as a wide range of features are seen in each deposit (e.g. Bonev *et al.*, 2002) and cannot be used to profile deposits. It is better to use the geochemistry of the associated mineralogy, as well as included mineralogy, for such purposes.

Hierarchical identification of the regional source of gold can be achieved by considering elements very indicative of associated ore minerals (e.g. Ni and As being derived from associated sulpharsenides such as arsenopyrite (FeAsS) or gersdorffite (NiAsS) such as in the ores from the Barberton Greenstone Belt, or Te and Sb reflecting the Sb-rich nature of the ores in the Murchison Range). Concentrations of platinum-group elements in gold-containing products from the Witwatersrand Basin depend on details during the metallurgical process. Small amounts (3-100 ppb estimated *in situ*) of PGE are concentrated in small (typically 100-150 μm in diameter) nuggets at the same stratigraphic levels as the gold (Feather, 1977). Most of these PGM are not affected by the cyanidation, but can be concentrated by mechanical means during milling, such as behind the liners of the mills. This liner concentrate is typically very rich in gold (up to 10s of %) and contains a substantial amount of PGM as well. If this liner concentrate is introduced directly into the smelting process, unusually high amounts of PGE can be found in the gold. (A description of the typical gold extraction process on the Witwatersrand gold mines is given in Chapter 2.6)

Mineralogical characteristics of many products allow the identification of the type of material as well. X-ray diffraction and microscopic techniques are useful to identify gold ore and concentrate from the greenstone belts, but are much less diagnostic if the matrix is overwhelmingly dominated by quartz. During the processing of the ore during different stages of the beneficiation, the concentrations of some elements are reduced, while others are enriched (or relatively less reduced) together with the gold. Bulk chemical analyses (by XRF) or mineral analyses (by EMP) may be needed to distinguish materials with similar mineralogical matrix or appearance.

A large amount of material has to be characterized in order to increase confidence that the correct source of material can be identified. The identification itself is a hierarchical procedure, in which major elements or ubiquitous minor elements often suffice to identify the genetic type of mineralisation. However, the problem becomes exponentially more complex if it is required to identify the source in a specific district. Adjacent mines may mine the same stratigraphic horizon, but even adjacent mines in the same deposit can be distinguished as sources, if analyses with very high precision and accuracy are available for a large range of elements and isotopes. This separation is facilitated partly due to lateral variations in the ore bodies and partly by differences in the beneficiation processes employed. The combination of all analytical information and the use of multivariate statistics can enable the determination of the source with a high level of confidence.

When gold is illicitly mined or stolen, however, the source is not limited to natural geological occurrences, but to all the stages of beneficiation of the ore, and leading eventually to refined products. The composition of illicit gold can thus be reflective of a single stage in the process from mining the ore to the production of a commercially available alloy, or a mixture of several of these, often mixed with other materials as contaminants or diluents. In addition to knowing the natural range of gold compositions, the manufactured product also has to be considered.

2.2 Principle of gold profiling

Trace element profiling of gold is a technique aimed at the determination of minor and trace components, which then enables the classification of materials from ores to flotation concentrates, smelter products, and materials at different steps in the refining process, and

finally the commercially available products. Understanding the compositional profiles should permit the identification of genetic processes, based on the assumption that differences or changes in the ore-forming processes (e.g. intrinsic conditions of hydrothermal fluids or magmas) will be reflected in the trace element pattern of ore minerals (or associated minerals which inevitably are also introduced into the beneficiation process). Trace element profiles of gold in deposits could therefore be used to understand the sources of mineralisation. In such a scenario, the trace element pattern will differ between genetic ore types, as will the pattern of different mineral species within a specific ore type.

Single grains of naturally occurring gold have until recently mainly been analysed using the electron microprobe (EMP), which gives major and minor element abundances, but is not sensitive enough for trace elements. This has meant that EMP analyses have been useful in determining whether the gold originates, for instance, from a high-temperature or low-temperature environment based on its Cu content (Hedenquist & Lowenstern, 1994), but would not be able to discriminate between different deposits of a similar genetic origin. Recent developments in the EMP field, however, have resulted in much greater accuracy of the measurements (e.g. Hayward *et al.*, 2005)

More sensitive methods of analysis have been utilised in an attempt to determine the trace element content of gold. These methods either require bulk samples (e.g. INAA) or dissolution of grains (e.g. ICP-MS), with the result that inclusions and heterogeneity can influence the analytical results to show the presence of a large range of trace elements, or are analytical methods which are not readily available (e.g. PIXE, Sy- μ XRF). Sie *et al.* (1996) used PIXE to investigate trace element distribution in gold from alluvial deposits and *in situ* deposits. They found a “*significant uniformity from samples of the same source, while showing significant variation in the trace element content with different provenance*”, which was shown when looking at the following elements: Bi, Cu, Cr, Fe, Hg, In, Mn, Pb, Sb, Sn, Zn.

Inductively-coupled plasma mass spectrometric (ICP-MS) analyses have been used to determine the origin of alluvial gold grains (e.g. Outridge *et al.*, 1998; Chapman *et al.*, 2000; Chapman & Mortensen, 2006). It has been shown that the large variation of trace elements in Au provides each deposit with its own suite of detectable elements, the concentrations of which can vary considerably between deposits (e.g. McCandless *et al.*, 1997; Outridge *et al.*, 1998; Penny, 2001). This trace element signature is influenced by the presence of inclusions

of bedrock material as well as material included by mechanical action during erosion and transport, and is useful in determining the geological source of the gold (Outridge *et al.*, 1998; Chapman *et al.*, 2000; Chapman & Mortensen, 2006; McInnes *et al.*, 2008).

In order to determine the composition of the gold itself, rather than that of its inclusions, trace element analysis needs to be performed on a small volume of material that is inclusion free and is locally homogeneous. The advent of laser ablation coupled with inductively-coupled plasma mass spectrometry (LA-ICP-MS) has made this possible (Watling *et al.*, 1994; Chen *et al.*, 1997). This technique has the advantage over other trace-element analytical techniques in that it is reasonably affordable, and offered by a number of suppliers.

The ability of LA-ICP-MS to determine low levels of trace elements imparts the ability to discriminate between gold which is otherwise similar. Brown *et al.* (2003) showed that using LA-ICP-MS they could discriminate between two banded iron-formation-hosted lodes in the Cleo gold deposit, Western Australia. The gently-dipping Sunrise Shear Zone and high-grade vein-hosted Western Lodes have similar isotopic compositions in ore-related minerals and fluid inclusions in vein quartz. The only differences between the ore zones which could give a strong indication of different genetic origins to the gold deposition was in the trace-element profiles of the gold. Gold from the Sunrise Shear Zone is enriched in Ni, Pb, Sn, Te and Zn, and depleted in As, Bi, Cd, Cu and Sb, compared to gold from the Western Lodes.

A recent comparison of different analytical methods for gold analysis done on gold grains from the Black Reef Formation, above the Witwatersrand reefs (Gauert *et al.*, 2011), looked at the use of EMP, LA-ICP-MS, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and synchrotron micro-X-ray fluorescence (SR- μ XRF). They found that the EMP provided the best quantitative results, but that LA-ICP-MS results are far superior for trace element detection.

The paper also highlighted the problems of small grain size for the gold (<5 to 250 μ m) resulting in partial analyses of adjoining mineral grains, but concluded that the only alternative was separation and analysis of individual grains. This is not necessary, however, if time-resolved analyses are performed. This method enables the discrimination of inclusions within the gold alloy, and the subtraction of these elements from that of the matrix. Many sub-micron mineral inclusions occur within gold grains, including minerals such as monazite

which can add substantial rare earth element signatures to the overall composition, as has been documented by Outridge *et al.* (1998).

2.3 Requirements for identifying gold provenance

How, then, is one to identify a piece of seized, suspected stolen, gold and determine its origin and legal owner? There are a number of requirements which have to be met before such a process can be accomplished:

- The principle that gold from different genetic origins has differing chemical compositions.
- A database of gold samples must be established for the region in question, so as to provide representative compositions for various individual sources (including genetic and beneficiation types).
- A simple analytical procedure must be in place so the method can be used in most well-equipped laboratories, as the theft of gold is not restricted to South Africa, but is a world-wide phenomenon.
- It must be shown that notwithstanding different extractive processes being used, gold from different genetic types can be distinguished.
- It must be shown that gold from different source areas (goldfields) within the Witwatersrand Basin can be distinguished.
- It must be determined whether the gold profile from one shaft in the Witwatersrand Basin can be uniquely characterised, notwithstanding the different reefs which may be contributing to the the gold mined.
- It must be shown that when different extractive processes have been used, gold from the same source can be identified.
- It must be shown that even when diluted to mask the origin of the gold, such as to lower the carat value to be one in line with a jewellery alloy, or when used as a

coating over a substituted bar, information as to the origin of the gold can still be determined.

2.4 Composition of naturally-occurring gold

The Au content in naturally-occurring gold alloys varies from 20% to 100% (Samusikov, 2002). Unless the gold grain is very large and does not contain inclusions of other minerals (which cannot be seen due to the opacity of gold) it is very difficult to get an accurate analysis. Analyses of gold in which a number of grains were pooled together for a bulk analysis are not considered because of the inclusion problem and the variability between individual grains.

There are a number of published gold compositions, obtained by EMP, from many different deposits from around the world. Unfortunately, the EMP technique is only capable of detecting the small number of elements that occur in naturally occurring gold at sufficient concentrations. This limitation means that gold from a number of sources has a similar composition, making it difficult to characterise the gold from a single mineralising event. This is a problem when a population of gold grains has more than one source (Mortensen *et al.*, 2005).

Laser ablation inductively-coupled plasma mass-spectrometry (LA-ICP-MS) analyses of gold show that many elements are present at lower and highly variable levels from different styles of mineralisation, providing a much broader range of analytes for geochemical profiling than EMP methods. However, published LA-ICP-MS data for gold from different deposit types is sparse.

The composition of gold particles has been used to determine the origin of gold deposits, looking at the variation in grain composition on a sample scale (*e.g.* Hayward *et al.*, 2005) or on a regional scale (Knight *et al.*, 1999). Gold derived from different types of deposit (*e.g.* igneous-metamorphic, hypothermal, mesothermal and epithermal) has a composition reflective of the conditions of ore formation. Deposition of gold occurs in a wide temperature range, mostly between 180 °C and 700 °C (Groves *et al.*, 1998). Higher temperature gold has a lower Ag and a high Cu content, with Bi and Pb the most abundant trace elements, while at lower temperatures Ag is high, Cu is low, and Pb is the most abundant trace element (Antweiler & Campbell, 1977).

It has been found that in general, orogenic deposits have gold with containing >90 wt% Au, the balance consisting mainly of Ag and Hg, making these the most diagnostic features of gold in mesothermal systems (Frimmel & Gartz, 1997; Knight *et al.*, 1999; Morrison *et al.*, 1991). The Hg content of gold has been used in other parts of the world to discriminate between gold deposits and their genesis (e.g. Shikazono & Shimizu, 1988; Healy & Petruk, 1990; MacKenzie & Craw, 2005).

2.5 Composition of naturally-occurring gold from the Witwatersrand Basin

South Africa has a large number of gold mines, exploiting a wide range of genetically distinct gold deposits in discrete geological environments (Department of Minerals and Energy, 2006; Robb & Robb, 1998; Ward & Wilson, 1998). However, the majority of the gold mining takes place within the Witwatersrand Basin. In contrast to most other gold deposits in the world, the Witwatersrand Basin is sedimentary, with gold hosted in Archaean alluvial fans (Frimmel, 1997; Goldfarb *et al.*, 2001; Hallbauer & Barton, 1987). Detrital gold reflects the whole hinterland with different fans represent different source areas, with the result that a single gold mine shaft, mining one or more reefs, with each reef containing gold from potentially different sources, may produce gold which may have no distinctive genetic origin in the classic sense of the word.

Previous studies on illicit gold have focussed on linking gold seized from suspected criminals with the gold produced by a specific mine (e.g. Watling *et al.*, 2010). However, depending on which reef has been mined, and from how many mines the gold has been sourced, identifying the origin of illicit gold from within the Witwatersrand Basin poses many challenges.

In addition to the composition of the gold as it occurs in the ore, the beneficiation process used will alter this composition, by subtracting and adding various elements. Further, gold from different mines and different regions are regularly smelted together, mixing the original trace element profiles.

Over the years there have been a number of studies looking at the composition of gold grains in the Witwatersrand Basin, the majority limited to the major elements detectable by EMP: Au, Ag, Hg and Cu. Some of these studies have also looked at the distribution of the same elements within an ore sample, in order to determine the genesis of the gold grains. Saager

(1969a,b) looked at the relationship of Ag and Au in individual gold grains and ore-samples from the Basal Reef in the Free State goldfield. He found that the Ag: Au ratios in gold grains were very constant (at ~ 0.0812), while the Ag: Au ratios in the bulk ore samples from which they had been extracted had much higher values and showed a large variation.

Von Gehlen (1983) came to a similar finding, with EMP analyses of gold grains from localities around the Witwatersrand Basin. He found an homogeneous distribution of Ag and Hg in the gold grains, and concluded that this “*strongly suggests that the Ag and Hg contents in Witwatersrand gold grains represent geochemical 'fingerprints' inherited from their eroded primary sources. Combined analysis for Ag and Hg in Witwatersrand gold grains by electron microprobe can therefore be a valuable tool in establishing the types of primary sources for the gold.*”

Another EMP study by Reid *et al.* (1988) was of gold grains from the Klerksdorp gold field. They found gold compositions in wt% of Au 80–95 (av. 90), Ag 4–18 (av. 8) and Hg 0.5–4 (av. 2). They found that single grains were homogeneous but between gold grains from small samples and average compositions in separate samples, significant differences exist. They stated that “*The data do not fit any simple model of gold compositional control by provenance or by metamorphic homogenisation*”.

This study was followed by Frimmel *et al.* (1993) who looked at the Basal Reef from the Welkom gold field. They found that there was “*homogenisation of the gold on a hand specimen scale*” with Ag at 8.9 wt% and Hg at 1.0 wt% and attributed this to gold mobilisation which was coeval with a fracturing and shearing event after deposition of parts of the Transvaal Supergroup above the Witwatersrand and Ventersdorp Supergroups. The only other element detected was Cu in one sample. This, together with evidence from inclusions in the gold, was taken as evidence for a post-depositional hydrothermal event.

Another EMP study which focused on gold particles from the Ventersdorp Contact Reef in the Klerksdorp and West Wits goldfields (Frimmel & Gartz, 1997) once again found that although there was a wide range in Au (80.9 – 92.9 wt%), Ag (6.0 – 17.6 wt%), and Hg (0.6 – 5.8 wt%), individual gold particles were generally homogeneous. They also found that the mean gold composition of the same reef across different mines could be quite variable. As well as concluding that these results confirmed that the gold occurred in a metamorphosed and hydrothermally altered placer deposit, they stated that “*in spite of a significant post-*

depositional modification of the composition of individual gold particles, the mean gold composition at a given reef locality may be used to distinguish different source areas of the originally detrital particles”.

The homogeneity of the gold grains was shown to be an analytical artefact by Hayward *et al.* (2005) who showed that with higher resolution EMP, gold grains were heterogeneous on the micron scale. However, their study, which revealed the presence of only Au, Ag, Hg and Cu, with traces of Co, As and Te in the gold grains, showed that although the heterogeneity existed both within and between gold grains, the compositions of the gold grains between the various gold fields were distinctly different, and that the compositions of the gold grains within the Carbon Leader Reef showed much greater variation than those in the Ventersdorp Contact Reef, within the same gold field.

2.6 Composition of extracted gold

Gold is not a pure metal in nature, but comprises a number of gold-metal alloys, as well as trace elements in solid solution, which normally would include some of the following: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Se, As, Mo, Ru, Rh, Pd, Ag, Sn, Sb, Re, Os, Te, W, Ir, Pt, Pb and Bi (Outridge *et al.*, 1998; Bendall *et al.*, 2009). Different gold depositional processes and subsequent chemical alteration of the gold due to post-depositional processes, combined with the incorporation of minerals associated with gold during the processing of the gold, lead to gold from specific localities acquiring unique trace element compositions. The trace element composition of the gold can be profiled, and the profile compared to other samples on record, as is done with tracing the origin of ancient gold coins and artefacts (Junk, 2001; Guerra *et al.*, 2007, 2008).

Different ore-bearing layers, which, in the Witwatersrand Basin, formed at different times and reflect changes in the source area of the sediments (Frimmel & Minter, 2002) or ore bodies, such as different vein systems in a mineralised zone in a greenstone belt (Goldfarb *et al.*, 2001), may be mined and blended at any stage of the beneficiation process, and differences exist in the beneficiation procedures, depending on the nature of the ore *e.g.* native gold versus refractory gold in arsenopyrite (Cabri *et al.*, 1989; Afenya, 1991).

For the same type of ore, commercial processes will also differ from illegal processes (*e.g.* amalgamation). It is therefore very challenging to arrive at characteristics that are common to

all intermediate products derived from a specific ore body, and also reflect the characteristics introduced by the beneficiation process. It is also important that such elemental profiles remain identifiable as far as possible along the beneficiation process, which is aimed at reducing all impurities.

2.6.1 Carbon-in-pulp process

Mineral processing and concentration creates a distinctive trace element profile in the processed gold. In the majority of legal gold mining across the world, the carbon-in-pulp (CIP) process is used to extract and concentrate gold from the gold-bearing ores (Pryor, 1965; Adamson, 1972; Bailey, 1987; Young, 1987; Dai *et al.*, 2012). This large-scale process depends on the physical properties of gold, and results in very little chemical modification to the composition of the original, natural gold. In the gold mines of the Witwatersrand Basin, the CIP process is used by the legal, licensed producers.

Once at the processing plant, the raw ore is crushed then milled in a series of roller mills. These mills are lined with wearing plates (the liners) against which the rock is crushed finely to liberate the gold grains. During the milling process, some of these liberated gold and other heavy metallic grains (e.g. platinoid minerals) become lodged in the space behind the liners and form a highly enriched concentrate which is sought after by would-be thieves. After milling, the larger grains of liberated gold are separated out via a gravity feed process, and then the milled ore is subjected to froth flotation. The resultant heavy mineral separate is then processed using the carbon-in-pulp (CIP) method, in which the gold is preferentially dissolved and separated from the accompanying pyrite using cyanide complexing, and then separated from the cyanide leaches by the addition of activated carbon to the leaching tanks (Henley, 1975; Afenya, 1991). The activated carbon adsorbs the Au in solution, as well as other elements which behave similarly, such as Ag, Cu, Co and Ni (Koshima & Onichi, 1986; Laxen *et al.*, 1979). The resultant pulp is then smelted at high temperatures to produce what is colloquially termed “doré” or d’ore bars, gold bars with purity generally between 75 and 99 wt% gold, usually 80 – 90 wt% Au, depending on the type of ore processed.

After the gold concentrate is smelted to produce doré, it is transferred to a refinery, where large-scale electrolytic separation of the doré is undertaken to remove all impurities in the finished product. The resultant gold bullion is normally 99.999 or 99.9999 wt% pure. This pure gold is then alloyed with copper, silver and other refined metals to create the alloys used for jewellery, dentistry and industrial and chemical applications. Small producers also

transfer their doré to the large refineries in order to provide a final product suitable for sale.

2.6.2 Mercury amalgamation

The process whereby stolen gold is processed is significantly different. Gold is either extracted from ores and concentrates by panning and sluicing of alluvial deposits, or the crushing and milling of ore. This is followed by either mercury amalgamation, after which the mercury is boiled off (often by means of a blow torch), or by the use of lead-collection fire assay (Marsden & House, 2006) and subsequent cupellation. The amalgamation route is the most commonly used. This stolen material is then smelted together, and base metals are often added to the gold to achieve commonly used carat gold concentrations. This “illicit gold” often has a high gold content, but has not been electrolytically purified.

Theft of ore directly from the ore faces underground in the gold mines is the most common activity of syndicated gold theft in South Africa. The stolen product consists of raw ore, which runs at relatively low grades. Though the illegal miners are able to mine the most profitable parts of the ore face, the gold content of the stolen ore generally does not exceed 50 grams per ton. This product must then be upgraded significantly to obtain enough gold to be sold. Similarly, gold stolen from the roller mills or from the flotation tanks in the processing plants is of relatively impure quality, and needs further processing before it can be sold or fed back into the legal gold industry.

In order to process such low grade gold sources, mercury amalgamation and low temperature smelting is done on crushed ore. Only gold that has free surfaces is able to be amalgamated, so theft of ore concentrates, which has been milled to liberate gold particles, is also a problem. The ore and concentrates are then crushed in home-made ball mills and then mercury is added, so that the gold and mercury can combine to form an amalgam.

The gold recovery by crushing and then gravity concentrating Witwatersrand ores varies between 27.8 and 73.3 percent, with an average recovery of 43.2 % (Douglas & Moir, 1961). By crushing the stolen ore in a ball mill until fine, and then adding mercury to perform amalgamation (Henley, 1975), sufficient gold can be recovered to make the theft of gold ore from underground economically viable. The relatively enriched gold product obtained by this method is then sold on to middlemen and either smuggled out of the country or sold to holders of a precious metal recovery license, who then launder it by selling it to a refinery as scrap jewellery, effectively legitimising the stolen product.

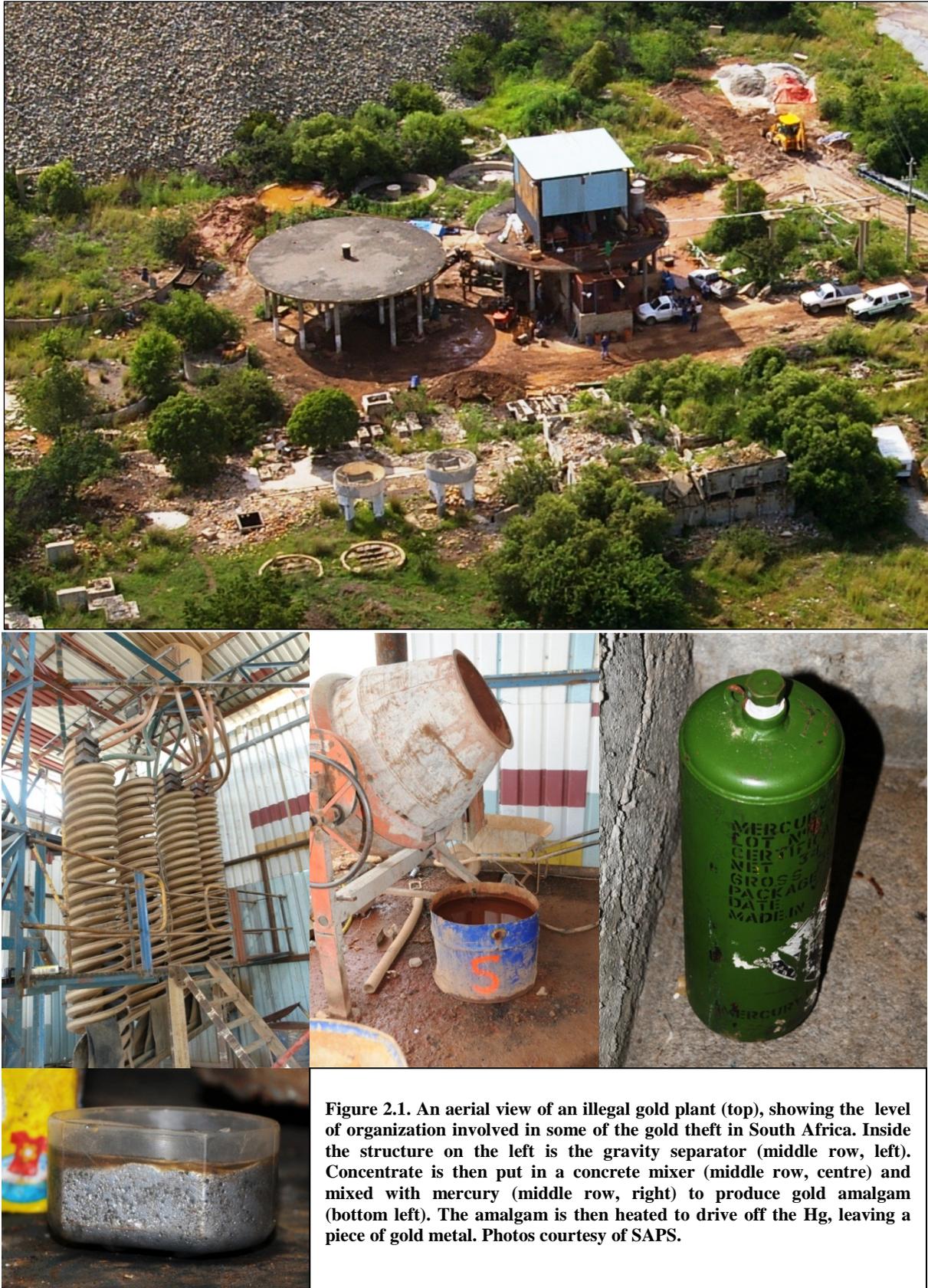


Figure 2.1. An aerial view of an illegal gold plant (top), showing the level of organization involved in some of the gold theft in South Africa. Inside the structure on the left is the gravity separator (middle row, left). Concentrate is then put in a concrete mixer (middle row, centre) and mixed with mercury (middle row, right) to produce gold amalgam (bottom left). The amalgam is then heated to drive off the Hg, leaving a piece of gold metal. Photos courtesy of SAPS.



Figure 2.2. Illegal miners underground, showing the level of organisation and using mine equipment (top left) and one of them with a mortar and pestle in which concentrate is crushed together with mercury to amalgamate the gold particles (top right). The top two photographs were retrieved from a camera belonging to one of the illegal miners. The bottom photograph shows part of the “plant” built in the abandoned mine workings where they recovered the gold concentrate (Photographs courtesy of Willem Els, ISS).

In order to keep costs down, the main emphasis in the forensic profiling process has been to obtain tools to identify illicitly processed gold. It must be pointed out that this is inseparable from the identification of the source of stolen gold and the evaluation of the geological questions of ore genesis and the characterisation of genetic ore types. However, it goes beyond the geological needs because metallurgical products have to be considered as well. Identifying the mine of origin of materials is complicated by many factors (Merkle *et al.*, 2004).

In most primary gold deposits, a particular vein or lode will often have only one depositional process, and therefore the gold will also have a fairly distinctive and homogenous fingerprint. In a multi-lode deposit each lode, if the result of a separate event, will be distinguishable on the basis of its trace elements. The action of processing will reduce the concentration of these traces, but, up to a point, characteristic trace elements will be retained in sufficient quantity to enable identification. At the refinery stage, however, the gold is so mixed and purified that any trace of a distinctive elemental profile is lost.

In a disseminated gold deposit, such as the Witwatersrand Basin, the gold has to be extracted by a variety of techniques which will, by their nature, remove some of the original trace elements from the gold and add other elements from the associated mineral suite. The carbon in pulp extraction (CIP) method (Bailey, 1987), used widely in this ore deposit, concentrates not only gold but also large quantities of nickel (*e.g.* Laxen *et al.*, 1979) giving rise to a distinctly unnatural composition to the mine gold as compared to its original native composition. In this way, discrimination of processed gold versus natural gold is possible.

Sophisticated criminals might try the addition of other elements, either as other metal alloys or as chemical mixtures, to mask the “fingerprint” of the gold source. Often, an attempt is made to present the illegally processed gold as having a legal origin, being derived from melted scrap gold, of an industrial or jewellery origin. Typically, brass and copper are regularly added to the stolen gold in order to bring the gold concentration with the stolen material to approximately 18 carat (75 wt% gold), 12 carat (50 wt%) or 9 carat (36 wt%) levels. Fortunately the large range of elements present in gold and the various isotope ratios of minor and trace elements present a formidable challenge to any such attempt. The material added will also have its own characteristic signature, so the identification of this signature will allow the additive to be subtracted from the bulk and the original profile of the gold reconstructed.

One feature of Witwatersrand gold is that has a relatively low Ag content compared to gold from many other deposits, and in this it is similar to the gold from deposits in greenstone belts. A plot showing the relative abundances of Hg and Ag in native gold is shown in Figure 2.3.

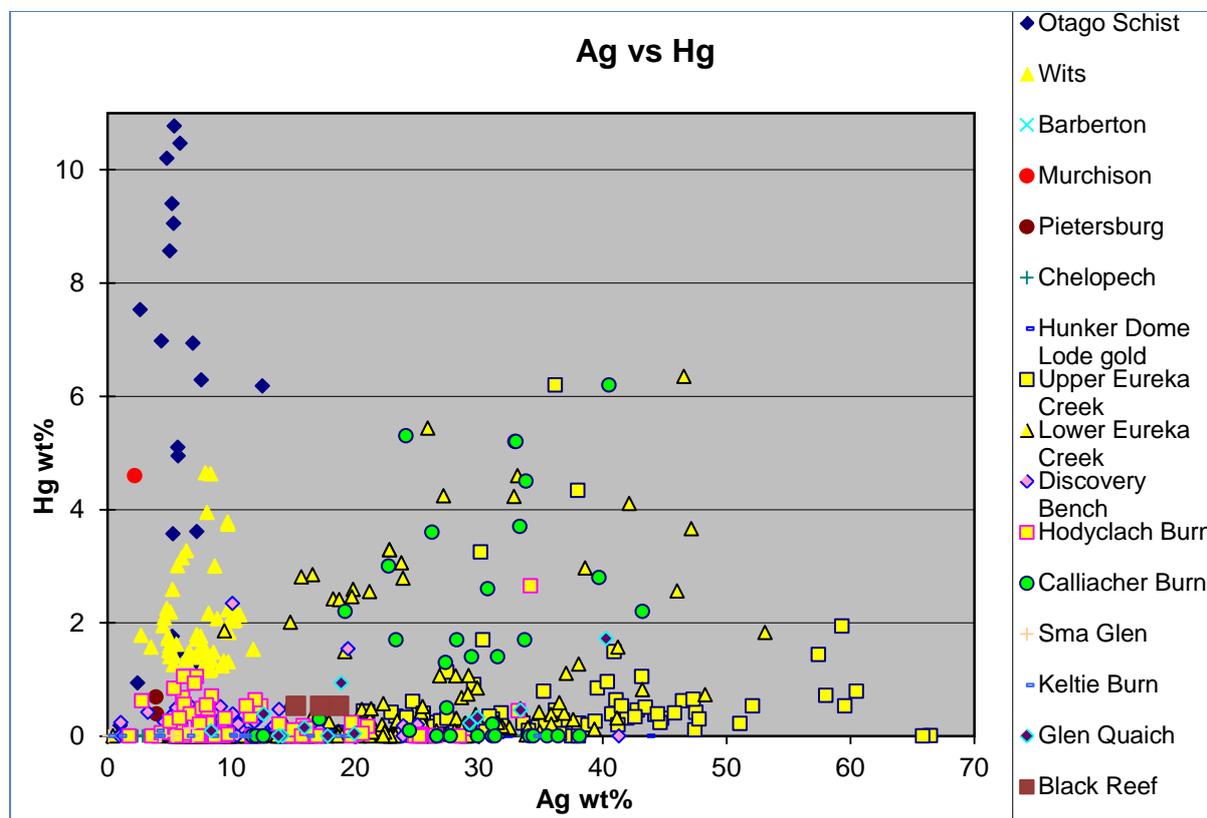


Figure 2.3: Plot of Hg and Ag values of analysed gold grains from the literature. The lode gold from the Yukon and Scotland shows a large variation in both the Hg and Ag, with Ag predominating. Gold grains from greenstone belts (New Zealand and South Africa) and the Witwatersrand Basin have comparatively little variation in their Ag values but a much wider range in Hg values. Note that the few analysed grains from the Black Reef, from above the Witwatersrand deposits, appear to fall in with the lode gold group. The high fineness gold grains plotting near the origin are mainly orogenic gold and higher temperature Cu-bearing gold from volcanogenic terranes. (Data from Kucha *et al.*, 1998; Youngson *et al.*, 2002; Erasmus *et al.*, 1987; Bonev *et al.*, 2002; Chapman & Mortensen, 2006 and Gauert *et al.*, 2011).

3 The South African Gold Database

3.1 The need for a database

South Africa has introduced legislative measures requiring samples of all imported and South African produced unrefined precious metals to be sent to the Forensic Science Laboratory (FSL) of the South African Police Services. The FSL maintains a database of elemental profiles of these samples which will allow the recognition of illegal gold and to ideally trace the gold to its original source. The ultimate aim is not only to return such metals to the mines from which they were stolen, but also to investigate syndicate operations and the movement of precious metal containing materials to refineries all over the world (Dixon *et al.*, 2007; Smith, 2008).

South Africa is a hub for gold trading in Africa, with many legal mining companies bringing gold in to be refined. It is also a mecca for illicit gold traders, many of whom have obtained precious metal recovery licences to process scrap precious metals. These licenses are a poorly regulated way for syndicates and entrepreneurs to launder illicit gold into a form that they can then either export or sell to a refinery in South Africa (Cuvelier, 2011; Haken, 2011).

The Chamber of Mines of South Africa, which includes the major gold and platinum mining companies in South Africa, in collaboration with the South African Police Service, established the National Precious Metals Forum (NPMF) in 1996. The role of the NPMF is to assess the impact of crime (not restricted to precious metals related crime alone) on precious metals producing mines, to identify those crimes that should be prioritised based on their ability to adversely affect the sustainability of mining operations and the production of precious metals, and to devise strategies and initiative operations to counteract these crimes in conjunction with relevant law enforcement agencies domestically and where applicable internationally. The NPMF and its members played a key role in establishing the legislation which led to the precious metals database, as one of its main objectives is to profile South African precious metal containing materials scientifically, in order to identify its their origin once recovered in as a result of crime combating operations.

3.2 The database legislation

South Africa is one of those countries where it is illegal to mine and possess unwrought gold without a government issued license. It is also one of the few to have a well-defined legal structure for the precious metals industry regarding unwrought precious metal (and in particular gold) which regulates its production, possession, purchase, sale, processing, import and export, and the only one to have legislated the requirement for a database (Smith, 2008).

The precious metals legislation has a long history in South Africa (van der Schyff, 2012). Some of the acts covering this include The Precious Minerals Act, 1898 (Act No. 31 of 1898, Cape Colony), the Natal Mines Act, 1899 (Act No. 43 of 1899) and the Precious and Base Metals Act, 1908 (Act No. 35 of 1908, Transvaal). All these remained in force until their repeal by the Mining Rights Act, 1967 (Act No. 20 of 1967) which applied to the whole of South Africa and remained in force until repealed by the Minerals Act, 1991 (Act No. 50 of 1991). This was partially replaced by the Mineral and Petroleum Resources Development Act, 2002 (Act No. 28 of 2002) which in turn saw the Precious Metal Act, 2005 (Act No. 37 of 2005) consolidate all the relevant legislation for precious metals to “*provide for the acquisition, possession, smelting, refining, beneficiation, use and disposal of precious metals; and to provide for matters connected therewith.*”

According to the definitions in the Precious Metal Act, a precious metal is “*the metal gold, any metal of the platinum group and the ores of such metals*” and a precious metal producer is “*any person who holds a permit or right to prospect for or mine precious metals in terms of the Mineral and Petroleum Resources Development Act, 2002 (Act No. 28 of 2002)*”.

The Act legislates for unwrought precious metal which is precious metal that:

- “(i) *is unrefined (including concentrate and matte), or has been refined to a purity less than 99,9% and has not undergone any manufacturing process other than being refined or formed into a bar (but not a minted bar), an ingot, a button, plate, sponge, powder, granules, (excluding granules made from precious metal that has been refined to or beyond 99,9% purity, and carat gold alloys), solution; or*
- “(ii) *is prescribed as any substance, material or product of similar form to any such substance, material or product listed in paragraph (i); or any article or substance containing or consisting of precious metal*”

as stated above.

The Act then makes provision in paragraph 22 for a “*Database for precious metals*”:

- (1) *Any producer or any person who imports precious metal must submit to the Forensic Science Laboratory of the South African Police Service such specimens of any precious metals produced or imported by him or her as may be prescribed.*
- (2) *The Head of the Forensic Science Laboratory or a person designated by him or her must create and maintain a database containing such information in respect of the precious metals contemplated in subsection (1) as may be prescribed.*

In the Regulations of the Act, (Precious Metals Regulations, 2007), the frequency of submission and also the type and form of the samples to be submitted for inclusion in the database were prescribed:

Manner of submission and form of specimens

- (1) *A producer of precious metals must submit specimens of such precious metals to the Forensic Science Laboratory of the South African Police Service every six months: Provided that a new mine must submit its first specimen within the first month of production.*
- (2) *All specimens submitted to the Forensic Science Laboratory must be accompanied by a fully completed Form MLS0087F, which is obtainable from the Forensic Science Laboratory.*
- (4) *A mine with several shafts must submit specimens of the relevant precious metal extracted from each shaft.*
- (5) *Specimens of gold submitted by producing mines must be of raw, unprocessed gold in nugget form or of gold retrieved from concentrate, as well as processed gold (dore metal), whereas specimens of the platinum group of metals must be of furnace matte, converter matte and refinery feed.*
- (6) *Metal specimens must consist of at least 2 grams of the relevant precious metal, while ore or concentrate specimens must be representative and must consist of at least 100 grams of the relevant ore or concentrate.*
- (7) *Specimens submitted for inclusion in the profiling database shall remain part of the database and shall be retained by the Forensic Science Laboratory.*

Unfortunately the geological and beneficiation differences between gold and platinum-group element deposits were not properly understood when drafting these regulations. However, a mechanism was thus created to ensure that every producer of gold in the country was legally obliged to submit specimens to the database at regular intervals.

3.3 The gold database

The Precious Metal Act requires a database of all precious metals. However, the database for gold will be very different to that for the platinum-group elements, due to the nature of the ores and the beneficiation process. In order to apply the database and the analytical methods employed when presenting evidence in a court case, the protocol and methodology must be validated and shown to be fit for purpose.

The protocol and methodology for PGE has been developed and validated internationally, and started with a procedure for such source determination developed in Russia and incorporating a variety of chemical and mineralogical techniques for the identification of Russian products, based on a database of samples collected over time. For court acceptance of the results and expert opinions derived from them, it was essential to have an analytically and forensically validated procedure. For this purpose, the European Network of Forensic Science Institutes (ENFSI) convened an independent Forensic Review Board comprised of experienced forensic scientists, academics and legal experts, including the South African producers (ENFSI, 2008).

One of the results of the review process was the finding that effective interpretation of the results of the procedure within the context of legal casework required specialist knowledge and an understanding of the mining and beneficiation of PGE-bearing materials. This was crucial for the identification of components in a mixture and in situations where the materials did not fully match those in the database because of undocumented variation. There is no reason to suppose that the situation is any different with regard to gold.

Identifying the original source of suspected stolen gold relies on the elemental composition of the gold. Anything from ore to final metal product is stolen and elemental profiling is utilised to identify the source despite different beneficiation procedures utilised by legal and illegal producers.

Elemental profiling has been used in forensic science for a variety of purposes. The trace element profiles of substances such as paint (Deconinck *et al.*, 2006), cannabis (Watling, 1998), glass (Trejos *et al.*, 2003; Harrington *et al.*, 2006), diamonds (Dalpé *et al.*, 2010) and precious metals (Watling *et al.*, 2010) have been used to prove a link between a sample of the material in question and another sample. In many cases, the suspect sample is matched against a database of samples of known provenance in order to determine origin.

There are, however, problems with the application of this type of forensic profiling. Most importantly, a sample of known provenance is needed for comparison. Without such a sample, no meaningful comparisons can be made. For example, if there is no match between an unknown sample and the samples in the database, then one can only conclude that there is no match currently possible. This has been used in the field of gold exploration, where gold nuggets in placer deposits are matched to known deposits, and the non-matching gold samples can indicate further exploration targets (Knight *et al.*, 1999; Mortensen *et al.*, 2005).

This issue is extremely important in the field of gold profiling. The term “gold” describes a group of varied products containing some proportion of Au. These products range from naturally occurring Au and Au-alloys, to Au produced by mines for further refining, to pure refined Au and Au-alloys incorporating refined Au and other metals and used in jewellery and other applications. These Au-bearing products represent small volume, high value products, with little or no obvious indication of provenance, and are thus obvious targets for theft. In the South African situation, identifying the source of stolen gold has not proved as easy as linking an alluvial nugget back to an outcrop.

The aim of the precious metal profiling database is to enable gold of unknown origin to be identified. To this end samples are needed to establish a reference collection which is the physical aspect of the database. The analytical data and production data relating to the sample is the information used in the process of making comparisons with questioned material in order to determine origin.

Ideally, samples would be obtained from all geographically distinct gold mining areas. By this is meant samples from each mine, if an established mine, or samples from an area if an alluvial mining operation (small or large scale). The geographical (GPS) coordinates and a description of the type of mining practised there and the geological description is also

desirable. The samples should also be in two forms. The first is the raw form in which the gold is found at a particular deposit, and the second should be the form in which the miner or mine processes it for sale. For instance, if a mine sells its gold in the form of a bar of bullion, then a sample of that bullion together with a sample of raw mined gold from the same mine should be supplied. If the miner is a single person or small scale operation where the gold is amalgamated into a button for sale, then a sample of that button of gold as well as the raw mined gold must be supplied.

Initial attempts to utilise a gold bullion database of the Witwatersrand Basin (Grigorova *et al.*, 1998) were not always successful, as the methodology used assumed that each mine had a unique profile, and that mixtures of gold from different mines could be resolved on that basis using a purely statistical approach. Results of these investigations were given as percentage probabilities of origin, and as one needs to have a “beyond reasonable doubt” answer (>95%) rather than a “balance of probability” (>50%) to succeed in a criminal prosecution, this was insufficient. The new database required a new approach, and so the critical factors which could make it a success had to be identified, and from the outset it was determined that in addition to having a database of samples, we also needed knowledge of the geological processes influencing the gold deposition, its beneficiation, and also the illicit processing of the gold, in order to successfully identify the origin of the piece of gold in question.

Initially it was thought that the best and quickest way to build up a database would be to concentrate on the unrefined gold bullion produced by each mine, as a representative sample of the gold from that mine, as was done for the previous database (Grigorova *et al.*, 1998). However, instead of having one sample as representative of a mine, it was considered that as ores and mining and beneficiation methods change over time, so too should samples be collected. In April 2002, the first samples were received from Ergo Mining (Pty) Limited. Shortly thereafter AngloGold Ashanti, Gold Fields Limited and Harmony Gold Mining Company Limited started submitting samples. Due to the fact that a large amount of stolen gold was being recycled via so-called “jewellery scrap” it was necessary to obtain samples of jewellery alloys as well, the first being obtained from Rand Refinery in July 2003.

A statistical method of comparing the analyses of a questioned sample to the best match in the database was also developed (Merkle *et al.*, 2004; Merkle & Dixon, 2006). It was found that it was possible to discriminate between the different gold-mining areas within the Wits Basin, on the basis of the bullion composition, and to clearly differentiate between stolen

mine gold and recycled jewellery scrap. However, the gold that is stolen is not processed the same way as the gold that is legally mined, and it was considered necessary to validate the method by analysing gold extracted via lead or mercury collection to confirm whether the bullion samples could be used for the database samples. For this to be done it was necessary to obtain reef and concentrate samples, representative of the material which is normally stolen for processing, and extract the gold via fire assay, for subsequent analysis. The first of these samples were received in July 2003. This proved to be a logistical problem, as the number of samples required for a statistically meaningful validation is large, and the FSL lacked the necessary labour force to process such a large number of samples.

At the beginning of 2006 Gold Fields Limited provided a large number of prills from different reefs within a mine, native gold from those reefs, as well as the resultant concentrate and bullion produced from mining those reefs, for the validation process (approximately 400 prills per reef, for 3 reefs per mine from two mines). This gave the statistically representative samples required, and the validation was thus facilitated. In addition to samples from the Witwatersrand Basin, there are also samples from other South African deposits, as well as from several areas in Africa and a few samples from other areas in the world.

4 Analytical methods

4.1 Requirements for the analytical method

A big aim of this project was to identify a simple analytical procedure which could be employed in most well-equipped laboratories, and not be restricted to a few. This is because the theft of gold is not restricted to South Africa, but is a world-wide phenomenon, and needs to be addressed everywhere.

Because naturally occurring gold, gold products and illicit gold are alloys, they do not have a fixed composition which is easily deciphered. It is rather the trace element contents and the inter-element ratios which give the most information, and for which standards are either difficult or expensive to obtain, and often do not contain the wide range of elements seen in unrefined d'ore gold.

In addition, when looking at naturally-occurring gold grains, or small amounts of illicit gold, the sample size is important – it is necessary to get a comprehensive analysis of the gold, while retaining sufficient material for further analysis or as a reference. It is also necessary to be able to determine the composition of the inclusions in the gold, separate from the composition of the gold itself. The presence of inclusions can give important additional information about associated minerals or the place in the beneficiation process from where the gold-bearing material was obtained.

4.2 Review of analytical methods used for gold

Various methods have been and are used for the analysis of gold, both as a component (Au) in a material, such as an ore or metal, and for the analysis of the associated elements in a gold alloy or compound. This brief review covers a range of different methods, highlighting their applications and their usefulness in profiling gold.

4.2.1 Fire Assay

Fire assay is a high-temperature chemical analysis method for the quantitative determination of specific elements, mainly in ores and metals. It is one of the oldest known methods of quantitative chemical analysis which is still in use (Martín-Torres & Rehren, 2005). The

analysis of gold has traditionally been done by fire assay, followed by acid parting to remove silver, and the Au content then being determined gravimetrically, on the assumption that what was left after parting is gold. In fire assay this normally involves first liberating the precious metals from the ore, and then fusing the concentrated sample with a suitable collector. In the case of gold, lead is commonly the metal of choice due to its affordability. The resultant lead metal, which collects the precious metals, is then cupelled, driving off the lead and other base metals, and the resultant product is a prill consisting mainly of precious metals. It is the dominant procedure worldwide for the determination of the Au content in ores and metal, where the goal is the determination of gold content (*e.g.* Haffty *et al.*, 1977; Hall & Pelchat, 1994; Reddi & Rao, 1999).

The main drawback of this process for quantitative analysis is that it relies on the assumption that after treating the prill with nitric acid to remove silver, the remaining metal is gold. However, other precious metals are often present as well, such as platinum and palladium, and the gravimetric result could lead to an over-estimation of the gold content while ignoring other metals of potential economic interest. In the Witwatersrand Basin fire assay is used as the main grade determining technique during mining, and is a quick and efficient way of determining the variation of gold grade and associated elements for large areas.

4.2.2 X-Ray Fluorescence Spectrometry

XRF is a commonly available technique which is able to determine most elements in gold alloys to the ppm level, depending on the configuration of the instrument. However, certified reference materials are required which have the same matrix as the material to be analysed. For gold, there are few available, they are expensive, and the range and levels of elements present which are certified are limited to those normally found in manufactured gold alloys. Another problem with these standards is that they are not normally available in the correct size and shape for XRF.

The sample size required for XRF is normally standardised, in a disk shape, which means that the gold sample must be shaped to fit the instrument and must have a “reasonable” size. XRF is a surface analytical technique, and the effects of cooling and inhomogeneity can result in analytical results which do not reflect the true composition of the gold sample. The development of handheld XRF instruments has meant that this analytical technique is commonly and reasonably cheaply available, but without proper sample preparation the results are still not representative, only indicative. These instruments are of great utility,

however, if one needs to do a quick assay of a piece of gold (Marucco, 2004). The type of material encountered in mining and criminal activities are often small or irregular in shape, inhomogenous and usually may not be reshaped into a suitable form for analysis, so XRF is of most use in analysing bulk metal.

4.2.3 Electron probe microanalysis

EPMA is designed for the quantitative analysis of small samples, with a surface area of $1 \mu\text{m}^2$ but due to the energy of the electron beam this is not a surface analysis but instead volumetric. If there is an inclusion in the volume being analysed, this will be included in the analytical result. If the material being analysed is homogeneous, then an accurate quantitative analysis to a few hundred ppm can be obtained (Reed, 2005). With field emission EPMA, even lower levels are possible, at much improved resolution at sub-micron scale (Ehrke *et al.*, 2013; Rowe *et al.*, 2010). However, this is a time consuming method, and the determination of a range of trace elements in a single sample makes it impractical for a routine method for a lot of samples, taking into consideration the degree of sample preparation required.

The grain size of naturally occurring gold disseminated in rocks is in the range <5 to $250 \mu\text{m}$ and most published analyses of gold grains in the literature have used this method. With this technique, however, most naturally occurring gold only shows Au, Ag, Cu and Hg present, with occasional traces of elements such as Co, Ni, Fe and Te. For obtaining a trace element profile, this method is not sufficient or has not been developed yet.

4.2.4 Spark ablation optical emission spectrometry

Spark-OES was designed for the analysis of metal alloys in the production environment. It can reach lower levels of detection than XRF, but the area analysed is large and most gold is not homogeneous at this scale. Similar to XRF, standards are a problem unless bulk analysis is all that is required. This is a destructive method of analysis which requires sample preparation, but is a very reliable and robust analytical method (Zhou *et al.*, 2005).

4.2.5 Inductively-coupled plasma optical emission spectrometry

ICP-OES has the advantage over XRF and Spark-OES in that although it has similar capabilities for detecting all elements, it can be used to analyse small amounts of material. Unfortunately, samples need to be dissolved in acid and analysed in solution, which means that the effect of dilution will lower the concentration of a number of elements to below the detection limit. The dissolution process results in a homogeneous solution, so the analysis is a

bulk analysis, if the entire sample can be dissolved. Also, in order to analyse high silver content gold alloys, separate dissolution methods need to be employed, and the analytical results combined. The sample preparation method is thus lengthy and costly, as high purity reagents need to be used in order to ensure that low levels of trace elements in the sample are not compromised by contamination. In spite of its inherent problems, ICP-OES provides a cost-effective way of achieving routine bulk analyses of many types of material.

4.2.6 Inductively-coupled plasma mass spectrometry

ICP-MS requires similar sample preparation to ICP-OES, but due to its greater sensitivity is able to reach lower levels of detection for the same sample. Under ideal conditions, detection limits for some elements reach the part per trillion (*i.e.* 1 gram in 1 million tons of material) level. It has the added benefit of enabling analysis of isotopes, where isotopic ratios may be used to discriminate between gold-bearing materials of different origins. However, due to the small variations in isotopic ratios which are measured, most isotopic discrimination work requires the use of multi-collector ICP-MS. Due to the greater sensitivity of ICP-MS compared to ICP-OES, samples in solution often need to be diluted to a greater extent. For the analysis of low levels of trace elements, this can be a problem.

4.2.7 Laser ablation inductively-coupled plasma mass spectrometry

The use of laser ablation as a sample introduction method removes the problem of dilution, and enables much smaller sample sizes to be analysed. Over the last 20 years, the development of laser technology has progressed and become reliable and popular. Nowadays the use of LA-ICP-MS is widespread within the earth sciences as it not only has the capacity to focus on small areas (down to $1 \mu\text{m}^2$) but can also supply enough sample to enable trace element analyses of the sample. It is now an almost universally accepted method for determining elemental and isotopic compositions (Günther & Hattendorf, 2005; Butler *et al.*, 2011).

The sensitivity of LA-ICP-MS has also improved dramatically over the past two decades, and the ability of this method to analyze a wide range of material types with minimal surface preparation is a great advantage where speed is critical, and where sample size is often restricted. It is important to note, however, that LA-ICP-MS is prone to non-stoichiometric effects within the ICP, which give rise to the effect known as elemental fractionation. This is a matrix-dependent phenomenon which limits the accuracy of quantitative analysis, unless one resorts to matrix-matched calibration standards, which is the exception in most earth

science applications (Günther & Hattendorf, 2005). The strength of LA-ICP-MS is that it can be used to analyse a large number of masses across a range of matrices, as long as inter-element fractionation during analysis is limited (Sylvester, 2008).

The ionisation source and detection systems used in LA-ICP-MS have a major impact on detection capabilities. Quadrupole-based instruments are mainly used, due to their relative cheapness and fast scanning speed required for multi-element and fast transient signal detection (Tanner & Günther, 2009). Interferences formed in the plasma, however, lead to problems in these systems. These problems can be obviated by use of high resolution ICP-MS (HR-ICP-MS) (Gießmann & Greb, 1994), but they are not suitable for recording short duration, variable height, transient signals. Transient, or time-resolved signals allow the distinction between trace elements in the matrix and those in small inclusions (Fryer *et al.*, 1995). The addition of collision and reaction cells to quadrupole instruments has reduced the level of polyatomic interferences (Tanner *et al.*, 2002). Isobaric and doubly-charged interferences cannot be resolved instrumentally and rely on the use of interference corrections.

For multi-element analysis the sequential scanning of the quadrupole ICP-MS can place some restrictions on the number of isotopes which can be measured in one analysis and to some extent on the detection limits achievable. A small laser spot size requires instruments which are able to make use of the entire sample ablated. Most ICP-MS instruments are sequential in that they measure one mass at a time. Therefore, the speed at which a single mass can be measured, and the accuracy of that measurement, are very important for getting as much information as possible out of a single ablation shot.

Time of flight ICP-MS (TOF-ICP-MS) permits essentially simultaneous measurements of isotopes without degrading the detection limit (Leach & Hieftje, 2000). Because TOF-ICP-MS can scan at over 30,000 Hz, as compared with a scanning rate of quadrupole-based systems in the region of 2 Hz for the number of masses, LA-TOF-ICP-MS is theoretically capable of producing exceptionally good results for a small amount of sample. The downside of TOF-ICP-MS is that the linear dynamic range of the detector is too low to determine elements at concentrations from ppb to percent in the same acquisition, which is a problem when analysing materials containing a wide range of elements of interest at highly variable concentrations (Ardelt *et al.*, 2013).

With high rates of measurement, the ability to do time-resolved analyses is another feature which enables the variation in composition to be determined while ablating. The importance of spatial resolution over bulk composition cannot be over-emphasized, as most materials are inhomogeneous and the high spatial resolution of laser ablation is ideally suited for the characterisation of inclusions.

Modern laser ablation systems are capable of ablating at variable spot sizes, down to 1 μm . In practice, when analysing for trace elements, a larger spot size is needed to collect sufficient material. A typical scenario would be ablation along a line scan with a beam diameter of 10 microns, at an ablation rate of 10 Hz, a scan speed of 10 micron per second, and an integration time of 10 milliseconds per mass for 20 masses will give rise to an overall acquisition time of 250 milliseconds. This means that 4 data points are acquired per second, at a spatial interval of 10 microns, resulting in an effective lateral spatial resolution which records the variation in mass abundance of 2.5 microns.

The choice of laser wavelength is important, especially for metals. A variety of wavelengths (*e.g.* 1064 nm, 532 nm, 266 nm, 213 nm (Nd:YAG) and 308 nm, 248 nm, 222 nm, 193 nm (Excimer laser) can be used to ablate a wide variety of solid samples. At the lower wavelengths a much more controlled ablation process and the improved coupling of the laser energy onto the sample surface is achieved, resulting in a more efficient ablation process. Horn *et al.* (2001) showed that for metals, ablation rates were better for 193 nm than for 266 nm and the best signal was obtained for the shorter wavelength in He carrier gas. In addition, for the 266 nm laser, Au had the fastest ablation rates (mm per pulse) compared to other metals (Al and Zn had greater ablation rates, but formed oxide chimneys around the crater, reducing the effectiveness of the ablation with respect to the amount of material liberated for analysis). Horn *et al.* (2001) found that the broad range of ablation rates meant that without internal standardisation the method was not suitable for quantitative analysis.

The propensity for different metals to have different rates of ablation is clearly demonstrated when apparently homogenous gold grains from the Witwatersrand display great heterogeneity, ablating at greatly different rates, due to the change from one gold alloy to another (Merkle *et al.*, 2001).

Horn *et al.* (2001) observed that in the ablation of gold, melting cannot be the primary factor for controlling ablation at 266 nm. Demaske *et al.* (2010) showed that for gold the intense

heating of the gold caused cavitation which, when the absorbed fluence was above the ablation threshold, the coalescence of the voids to a large bubble can lead to detachment of a runaway ablated layer. The more typical ablation effects observed during a line ablation, which has a shallow crater path, can suddenly change to deep excavation which could be a result of changes in composition of the gold, which causes the resonance frequency to be close to the wavelength of the lased light. Au has an electronic transition at 267.60 nm, the $2P_{3/2} - 2S_{1/2}$ Au I line. The lower level of this transition is coupled to the ground state of the neutral atom, which gives rise to resonance broadening (Amador-Hernández *et al.*, 2000). At this wavelength the gold can absorb up to three times as much energy as would be needed to ordinarily ablate it. This results in extreme heating which leads to cavitation and subsequent excavation. This effect has been employed in the laser-induced explosion of absorbing Au nanoparticles in the nanophotothermolysis of cancer (Letfullin *et al.*, 2006)

LA-ICP-MS has been applied successfully to obtain quantitative results for silicate matrices using matrix-matched standards e.g. NIST 600 series glasses (Van Heuzen, 1991; Pearce *et al.*, 1997; Sylvester, 2008) and MPI-DING (Jochum *et al.* 2007). One of the big problems with most published reports of quantitative analyses by LA-ICP-MS is that they utilise only one or two calibration points, with no reference to the homogeneity of the reference materials used.

The inhomogeneity of naturally-occurring minerals means that even if a suitable calibration method is available or developed, quantitative information can be difficult to obtain, and only areas that are deemed optically clear can be analysed with any confidence (Axelsson *et al.*, 2000; Axelsson & Rodushkin, 2001). The presence of inclusions and varying composition of a grain, such as zonation, can result in element fractionation effects during laser ablation, due to differential heating and melting effects.

In metal matrices, inhomogeneous trace element distribution leads to problems in producing good calibrations (Aeschliman *et al.*, 2003; Aeschliman *et al.*, 2004). One of the very few instances where accurate quantitative analysis of steel has been carried out used femtosecond laser ablation in an experimental setup to avoid the effects of heating up the sample leading to fractionation (Wiltsche & Günther, 2011). The high cost of femtosecond laser systems makes it impractical for general use. Femtosecond lasers, however, give better precision for quantitative analysis using matrix-matched standards than nanosecond lasers, although the accuracy is similar (Koch & Günther, 2011).

Ablating with laser pulses that last several nanoseconds causes heating in the target material. Due to its speed, a femtosecond laser pulse can ablate with almost no heating. By eliminating the thermal reaction, vaporisation of elements at different rates, or elemental fractionation, is avoided. A typical example of this is when brass is ablated with a nanosecond laser – heating occurs which vapourises zinc preferentially while the less volatile copper remains in the sample. For quantitative analysis this can result in misleading analytical results. The femtosecond ablation of gold, however, does not avoid the problems of heating. It has been shown that after only three successive pulses from a femtosecond laser, the gold is absorbing up to 100% of the delivered energy, causing heating and then melting, due to laser-induced nanostructures, and redeposition of ablated gold on the surface, reducing the amount of material in the ablated aerosol (Vorobyev & Guo, 2005).

An attempt was made to use Rand Refinery gold reference materials (the Au-DP series) for calibration, but quantitative analysis was not successful, as consistent calibration curves could not be obtained due to ablation rates (the amount of material ablated) varying with composition, and also sub-micron and micron-sized exsolution of some elements. For natural gold compositions, the effects of heterogeneity, often dependent on the alloy proportions, is even more pronounced. This is because as the amounts of silver vary there can be exsolution of silver to produce more than one phase (Samusikov, 2002).

4.3 Methodology used for gold profiling

The methodology employed for the gold profiling in this study includes a combination of techniques, in order to extract the maximum information for a sample of gold, which might be a very small sample. Due to the combination of speed, the small amount of sample consumed and the number of elements able to be detected, LA-ICP-MS was selected as the primary tool, used qualitatively to determine the relative abundances of all detectable elements, especially those which are present in amounts which are not detectable by the quantitative analytical technique using ICP-OES. These elements greatly expand the ability to discriminate between samples. The use of LA-ICP-MS at the FSL for profiling purposes enables the identification of elements which are indicative of the geological, beneficiation and adulteration processes encountered.

4.3.1 Application of LA-ICP-MS

Over the past decade, the LA-ICP-MS setup used at the FSL has changed as improvements in technology have decreased spot size and increased sensitivity and range of elements measured.

A quadrupole instrument, a SpectroMass ICP-MS (SPECTRO, Germany) was the first instrument used. It had low detection limits (low ppb) but due to the measurement rate a long ablation time was necessary, which reduced either the number of masses that could be measured, or necessitated a longer ablation, increasing the amount of sample ablated and thus smoothing out heterogeneity and the ability to identify all inclusions. This instrument had a large dynamic range of ~ 8 orders (ppt to %). This was used in combination with an LSX-200 laser ablation unit (CETAC, Omaha, NE, USA) as the sample introduction method.

In order to reduce the amount of ablated material for a single analysis, and thus improving the ability to record inhomogeneity in the sample, a Renaissance TOF-ICP-MS (LECO, St. Joseph, MI, USA) was acquired. This instrument, due to its time-of-flight detector, was able to analyse a wide mass range (up to ~50) 30000 times per second. Unfortunately, the instrument was not capable of analysing a wide concentration range and was only suitable for masses at low concentrations – ppm and below. However, due to its very fast acquisition rate, heterogeneity was accounted for and sub-micron inclusions were easily identified and analysed. The use of this instrumental setup has been described by Leach & Hieftje (2001; 2002) for the analysis and discrimination of metal alloys. One major problem with the TOF-ICP-MS is that the matrix of the material in gold profiling is gold. Due to the significant ion flux in this region, it is very difficult to resolve ^{194}Pt , ^{195}Pt , ^{196}Pt and ^{198}Pt in the presence of ^{197}Au , as the mass resolution is greater than 1 amu, and platinum is one of the elements of interest.

The 266 nm Cetac LSX200 laser was then replaced by a New Wave 213 nm laser, the next generation of laser ablation technology. This enabled greater control of the ablation energy, smaller effective spot size and a more stable signal.

With the advances in the rate of acquisition, and the need for a wide range in the measurement of analyte concentration, an Agilent 7500cx quadrupole ICP-MS was then acquired which has a reaction cell to reduce interferences. Although the instrument only has an acquisition rate of 10 Hz, it is able to measure 9 orders of magnitude concentration range,

as well as a wide range of analytes, which is selected to optimise the count rate, usually ~50 isotopes. The analysis of the samples takes approximately 1 minute per sample, and the total time for preparation and analysis of a single sample is roughly 3 minutes.

4.3.2 Standards

National Institute of Standards and Technology (NIST) standard glasses, NIST 610 and NIST 612, are used to optimise the instrument operating parameters (Gao *et al.*, 2002). After optimising the instrument set-up for maximum count rate, these standards were used at the beginning and end of each analytical run and after every ten samples analysed, allowing quantification of changes in mass response with time to be made. This procedure also enables inter-comparison and normalisation of data on a day to day basis, ensuring consistency of data over time.

The LA-ICP-MS was optimised for maximum counts daily using the NIST610 standard, and sample blanks and two standards (NIST610 and 612) were analysed frequently during the day. Samples were selected using the onboard NuWave software, and gold samples were ablated at a frequency of 15 Hz for 10 seconds. Two procedures were used to process raw data. In cases where the matrix was variable, the raw counts were normalised to the total number of counts recorded, allowing the relative contribution of different analytes to be evaluated. On samples with a more consistent matrix, a calibration curve was constructed using the sample blank, NIST610 and NIST612, and a qualitative estimate of the analyte concentration calculated from the calibration curves. Neither method produces quantitative data, but the results are internally consistent.

The choice of glass standards and not gold, in the gold profiling methodology, is predicated by the fact that optimisation requires a steady state signal. The fact that glass standards and gold samples are very different matrices, with concomitant differences in plasma loading, was not considered relevant as the protocol for the profiling interpretation is based on inter-element associations and patterns and not on absolute quantification.

4.3.3 Sample preparation

The use of LA-ICP-MS means that sample preparation is reduced to a minimum. Samples need to be small enough to fit inside the sample chamber, and the sample or sample mount should be relatively flat (~1 mm variation) so as not to obstruct gas flow. Normally, drillings taken from d'ore bars and pieces of gold seized during police operations, prills resulting from

fire assay and grains of alluvial or liberated gold are mounted on a Perspex holder using cyanoacrylate glue (Fig. 4.1).

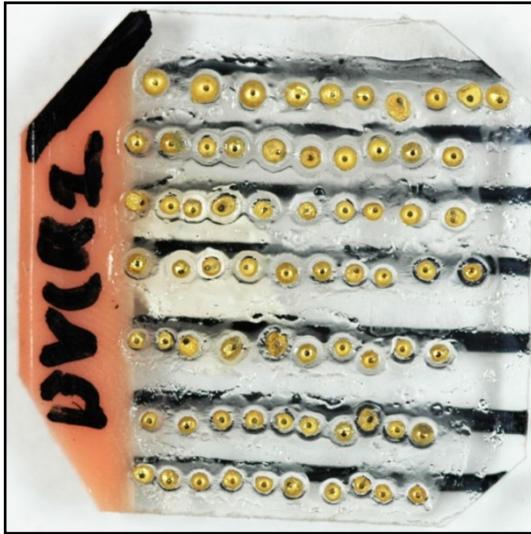


Figure 4.1. Small gold prills mounted in rows of 10 on a perspex mount with cyanoacrylate glue. The small black spots on the prills are due to ablated material from the ablation crater falling back to the surface. The whole mount is approximately 25 mm square.

4.3.4 Data analysis

The comparison of the gold samples is performed by considering the analytical data in conjunction with the geological and beneficiation information.

This process is not always amenable to straightforward statistical analysis, as representative databases of all the different sample types are usually not available, nor would it be practicable to create such databases to address short term needs. Not all deposits are represented in the South African gold database as only those which are actively mined are included.

Published information relating to gold compositions from different deposits, as well as gold produced by mines in different areas, is not commonly available, if at all, as it is usually proprietary information. It is therefore necessary to use information common to different gold ore deposit types and beneficiation processes to deduce the specific sequence of events which gave rise to the trace element characteristics of a gold sample.

The gold database maintained by the FSL contains gold samples from both legal and illegal sources, obtained from producing mining companies and recovered during police action; from South African and a number of other African countries. The database covers a variety of deposit types, other than the Witwatersrand Basin. Samples in the database, in addition to d'ore gold, include ore and concentrate samples as gold theft from the Witwatersrand gold mines is usually of gold-bearing material which is then subsequently processed to recover the

gold in metal form.

The association of elements, rather than elemental concentrations, forms the basis of the approach for most of the origin determination for gold. Variations in analyte signal between different ablation events, due to variations in coupling and transport efficiency, number of shots and morphology and colour of the substrate, are obviated by the use of inter-elemental ratios, and normalisation against the NIST 610 glass standard.

Once the sample has been analysed, the analytical data is examined to see if it is homogeneous or not, and then compared to the database samples. This comparison can be done using statistical analysis (Watling *et al.*, 2010). However, because the database consists of d'ore gold samples in the majority of cases, the comparison of a suspect sample which could have been produced in a different manner or be derived from material other than that used by the mining companies, or diluted with other material, such straight statistical comparisons are not usually helpful.

In the course of a criminal investigation, there is often a clue to the source of the suspect gold from the location of seizure, the mine at which the suspect works, information received, etc. Due to the nature of the process whereby the illicit gold was recovered, the illicit gold may have a different overall composition to that of the database samples supplied by the legally operating mines. It is then necessary to use only those elements which are common to both legal (floatation followed by cyanide leach followed by CIP) and illegal (mercury amalgamation) beneficiation processes for comparison.

5 Discrimination between illegally mined gold from two different ore deposits

5.1 Illicit mining in South America

The case study used here is from South America, where seized gold was analysed to determine whether it came from one of two putative origins. Extensive gold mining takes place across the northern part of South America, much of it by artisanal miners, who may or may not be legal, depending on the laws of the particular country (Veiga, 1997). The gold deposits range in age from Archaean to recent, and are mainly hosted in greenstone or ultramafic rocks on the Guyana Shield. Most of the northern part of South America is covered with laterite soils and these are often mineralised where they occur above primary gold mineralisation (Gibbs *et al.*, 1993). The majority of the artisanal mining utilises mercury amalgamation to recover the gold (García-Sánchez *et al.*, 2006), as opposed to the commercial CIP methods by most legal producers.



Figure 5.1. An artisanal miner panning for gold in the Condoto area, Colombia. (Negron, 2010)

A number of gold bars were seized at a few locations in the Caribbean and Europe, under suspicion of having been illegally exported from a South American country. The origin of this gold had to be determined, and a request was made to the Forensic Science Laboratory of

the South African Police Service to assist in this, due to their expertise in this field. The gold bars were sampled by drilling, and the aim was to determine which was the more likely origin for the gold - from the Chocó region in Colombia or from Bolivar State in Venezuela.

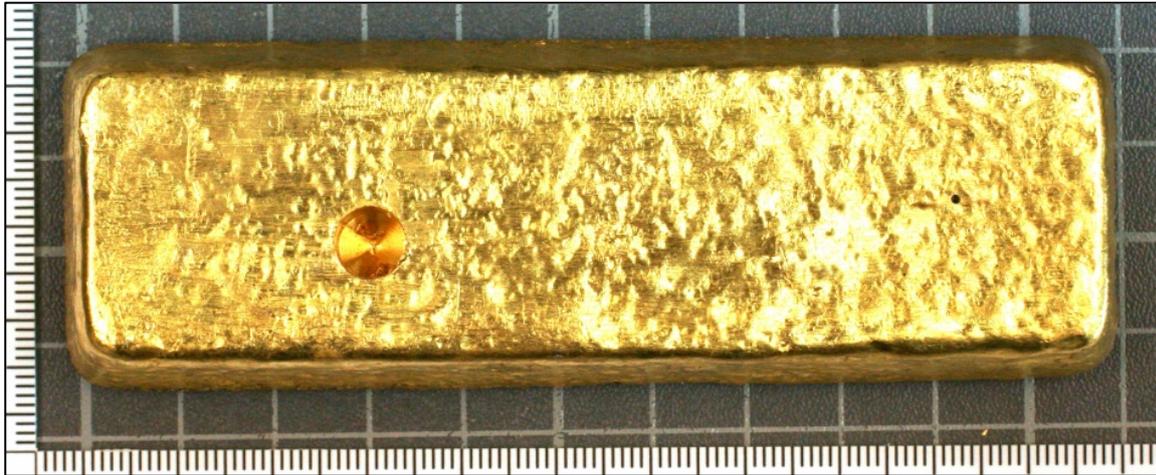


Figure 5.2. An artisanally produced gold bar showing the site from where a drill sample was taken for analysis.

Due to the fact that the Gold Database had no samples from this part of the world, samples had to be collected from the different areas that the gold in the bars may have come from. In order to be able to determine the origin, it was necessary to obtain gold samples representative of the manner in which they occurred, and in the manner how they were beneficiated. Owing to problems of legality, politics and potential danger to the collectors of the representative samples, it was only possible to collect gold samples for comparison from artisanal miners in the Chocó area of Colombia and the gold mines of Bolivar State, Venezuela. The control samples which were finally obtained from Colombia came from artisanal alluvial workings and had been recovered using mercury amalgamation. It was not possible to obtain similar artisanally produced gold from Venezuela, and the only samples obtained were from legal mines utilising the CIP process.

The use of this case in this thesis is to illustrate the complexity of comparing gold from different origins and processed using different methods. It also illustrates the need for an understanding of the geological background to the gold deposit.

5.2 Gold composition

In order to determine whether the illicit gold bars originated from the Chocó area in Colombia or Bolivar State in Venezuela, it is necessary to extract, from the analytical data, the elemental signatures which can indicate which origin is more likely. This has been done

for the simple alluvial case (*e.g.* McInnes *et al.*, 2008 and others) where the gold has not been processed after recovery, but the effects of processing, and by different means, also has to be taken into consideration as the processing method may add or remove elements to varying degrees.

The soils in Colombia and Venezuela, in the areas where gold is mined, are laterites which are depleted in silica via leaching, and enriched in aluminum and iron oxides. At the other extreme are bauxites, which are depleted in iron and enriched in aluminum oxides (see Jackson & Bates, 1997, for definitions). The initial kaolinised products of weathering are saprolites, which form in high rainfall regions. The deposits are different, however, in that in the Choco area the deposits are saprolites which formed from an alluvial deposit after weathering of the primary ore deposit, while the Venezuelan deposits from which the controls come are laterites formed mainly *in situ* above the ore deposits.

All the samples consisted of drillings from the suspect bars and the Venezuelan reference samples, and spongy gold produced after Hg has been removed from amalgam from Colombia. The samples were analysed using on an Agilent 7500cx ICP-MS with a NewWave 293 nm LAS for sample introduction. After blank correction, the raw counts were corrected using a drift curve obtained by ablating the NIST 610 glass standard on regular intervals between samples, in one run. The analyses of the suspect gold bars and the reference samples obtained from Colombia and Venezuela show distinct differences in their elemental composition. These differences have to be accounted for by looking at the source, beneficiation method and the nature of the processing.



Figure 5.3. Mining of gold from a saprolite deposit in the Choco area, Colombia. Note the grey colour, a result of leaching by aqueous flow. The degree of leaching can be seen to decrease with depth, as the soil darkens. (Negron, 2010).

The reference samples from Venezuela are enriched in Cu, Pb, Co, Ni and Zn, compared to the reference samples from Colombia, which show a distinct Ce enrichment and a relative depletion in Cu, Pb, Co, Ni and Zn. The suspect gold bars have a different composition to both of the reference samples, and these differences need to be identified and attributed to a specific cause, in order to determine from which source they derive.

5.2.1 Distinguishing between beneficiation methods

The two sets of reference samples were produced by different methods, Hg-amalgamation and the CIP process. The artisanal miners recover gold in South America by amalgamation (Veiga, 1997), which adds Hg to the gold metal composition, the amount depending on the smelting temperature used to drive off the Hg when recovering the gold, and the temperature and length of time the gold is molten if it is then cast into bars. Any metals present which have clean surfaces can also be amalgamated with the Hg, such as PGE alloys, scrap iron, etc.

The reference gold samples from the Chocó area in Colombia were obtained from artisanal miners utilising mercury to recover the gold. These samples consisted of the sponge gold left after the Au-amalgam was heated to drive off the Hg. The reference samples from Venezuela were obtained from the company Promotora Minería de Guayana (PMG), which recovers its gold via the carbon-in-pulp method from mines in Bolívar State. An effect of CIP is the enrichment in Ni if present in the ore material, as well as some other base metals. Generally, Au is adsorbed onto carbon the strongest, then silver followed by nickel and then copper (Laxen *et al.*, 1979). The degree to which the ions are absorbed can vary with changes in pH and ionic strength.

In Figure 5.4 three elements are plotted relative to each other – Hg and Ni, as discriminators of the extraction process used, and Al. Al was identified as a major discriminant in the natural process resulting in the formation of the Al-rich saprolites in Colombia, which can be considered to be correlateable with the flotation process used to produce the gold in the CIP process. The flotation of the in-situ sulphide-bearing ores from Venezuela, however, would be base-metal rich and Al poor, and the CIP process would further exaggerate the enrichment in Ni. The Hg content of the Colombian gold and the suspect gold bars is variable, which reflects the method by which it was recovered, namely mercury amalgamation.

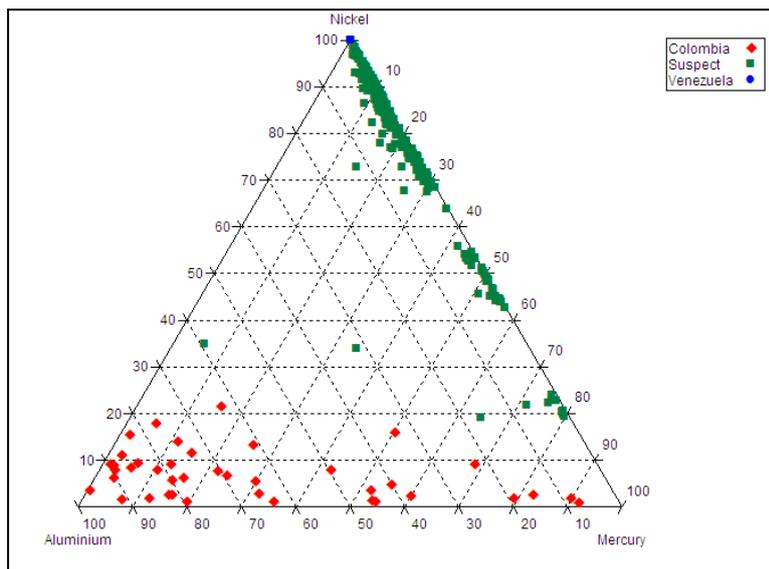


Figure 5.4. A plot of the aluminium (Al), nickel (Ni x100) and mercury (Hg) intensities from LA-ICP-MS analysis. The gold produced by the CIP process from Venezuela sits at the Ni apex. The gold bars and the gold from Colombia show a spread of values due to the relatively inconsistent artisanal process, as well as differences in material processed.

The gold samples of Colombian origin have a high Al content relative to the Venezuelan and suspect gold samples, which have a high Ni content compared to the Colombian gold samples. This discrimination is related to the geological settings of the gold deposits in Colombia and Venezuela. The higher Al contents in some of the suspect samples does not imply that they come from Colombia but rather that they happen to come from a laterite with higher Al (laterite has a continuous range of Fe to Al ratios). Consequently, Fig. 5.4 indicates a more bauxitic source for some suspect samples and the majority of the Colombian reference samples. The high Ni is attributed to a source area with a more typical laterite which is developed in-situ, and consequently some of the gold grains contained included and/or attached sulphide grains which were then smelted into the resulting gold. These differences reflect the source geology of the two different types of gold deposit.

5.3 Ce and V enrichment in gold from the Chocó area, Colombia

The gold and PGE deposits of the Chocó area, Colombia, are derived from recent ultramafic and basalt complexes, such as the Alaskan-type Alto Condoto ultramafic intrusion which has significantly high Au concentrations in zones with wehrlite mineralogy (Tistl, 1994; Tistl *et al.*, 1994). Due to the highly dissected topography, large alluvial deposits have formed under a thick blanket of tropical forest. These alluvial deposits are graded and sorted due to fluvial action, resulting in concentration of heavy minerals in specific areas. The coarser grained proximal deposits contain more PGE, while the distal deposits tend to be enriched in gold

compared to PGE. This is due to the malleable nature of gold grains which become flattened and broken up during transport. These small gold grains end up in the finer-grained deposits, which are often enriched in lighter, aluminium-bearing minerals such as clays. The clays result from the breakdown of the original feldspar as the alluvial deposit, which during prolonged chemical weathering under tropical conditions, is turned into a saprolite.



Fig. 5.5 This photograph illustrates the tropical conditions in the Choco area, with the Condoto ultramafic complex in the background. (Negron, 2010)

In environments such as that of the alluvial deposits at Choco, the high topographic relief combined high rainfall results in a strong flow of oxygenated water washing through these alluvial deposits. This highly oxidising environment produces a strong positive cerium (Ce) anomaly at the top of the soil profile (Boulangé *et al.*, 1990; Braun *et al.*, 1990; Braun *et al.*, 1998) where cerium is adsorbed and other REE remain in solution and are leached out by water flow. The cerium is deposited onto other minerals as the mineral cerianite and, together with gold (Greffié *et al.*, 1996), can be adsorbed onto clays and Fe oxyhydroxides such as goethite (Ohta & Kawabe, 2001; Valetton *et al.*, 1997). Further down the weathering profile (see Fig. 5.3), where the conditions are more reducing, the Ce anomaly is less pronounced or non-existent and its behaviour would be more in line with the other REE.

Artisanal mining of these sedimentary deposits results in a concentrate which is enriched in the fine gold grains which, during transport, have been flattened and deformed and contain trapped and included minerals such as clays and feldspars. The resultant gold, extracted by the amalgamation process and smelted to drive off the Hg, can therefore display variable

degrees of Ce enrichment relative to the other REE (see Figure 5.6). The gold samples from Colombia, which consisted of gold sponge resulting from the heating of amalgam, is derived from a number of locations and thus can have a highly variable composition, often due to included minerals, and the degree of leaching to which the various deposits have been subjected. This variation is clearly seen in Fig 5.6, with a trend towards Ce enrichment.

There is some overlap with the Colombian samples and the suspect gold bars. The suspect gold bars also derive from a number of sources, and thus would be expected to display a degree of leaching effects as well. However, many of the deposits in Venezuela are laterites which are developed *in situ* above the ore bodies, and have not been subjected to the extensive leaching experienced by the Colombian gold deposits. The majority of the suspect gold samples show some leaching compared to the control samples from the Venezuelan gold mine, which are not leached, and do not show the degree of Ce enrichment displayed by the Colombian gold samples.

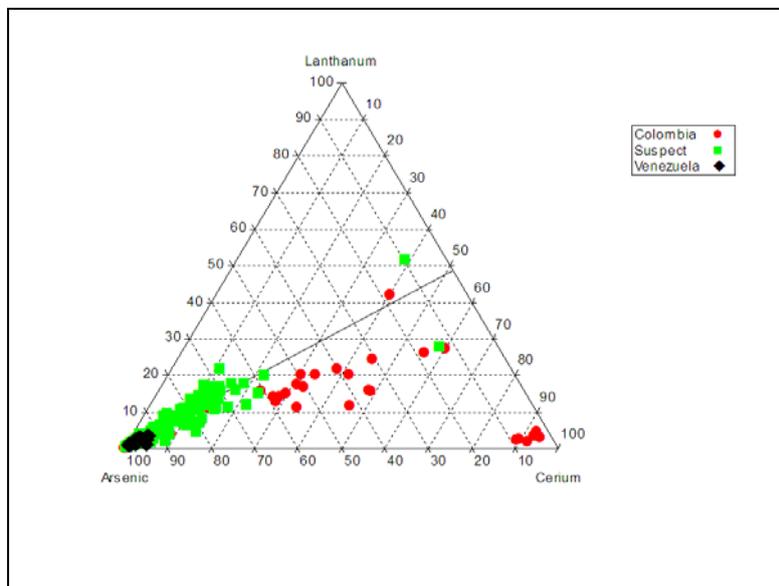


Figure 5.6. A plot of the arsenic, lanthanum and cerium intensities from LA-ICP-MS analysis, highlighting the difference between an oxidising environment, typical of the alluvial saprolites from the Chocó, Colombia area, and a more reducing laterite environment in Venezuela. Cerium in the more oxidising portions of the saprolite will be deposited from solution, whereas most other elements will remain in solution and be leached out. The As depletion shown for the Colombian gold also reflects the difference in degree of leaching affecting the deposits, and what is clear is that the suspect gold bars have a similar source to the Venezuelan gold.

A similar behaviour exists for vanadium (Van der Weijden & van der Weijden, 1995) (Figure 5.7). Many elements, however, which would be enriched in a typical laterite (Thornber & Wildman, 1979) are leached out in the conditions which produce these saprolites. In the typical Fe-rich laterites which are developed *in situ*, elements will be redeposited in the soil

and not leached away – arsenic is very mobile, so the relatively high proportion of As from Venezuela and the suspect samples shows that the degree of leaching experienced in their source areas was minor, compared to the reference samples from Colombia.

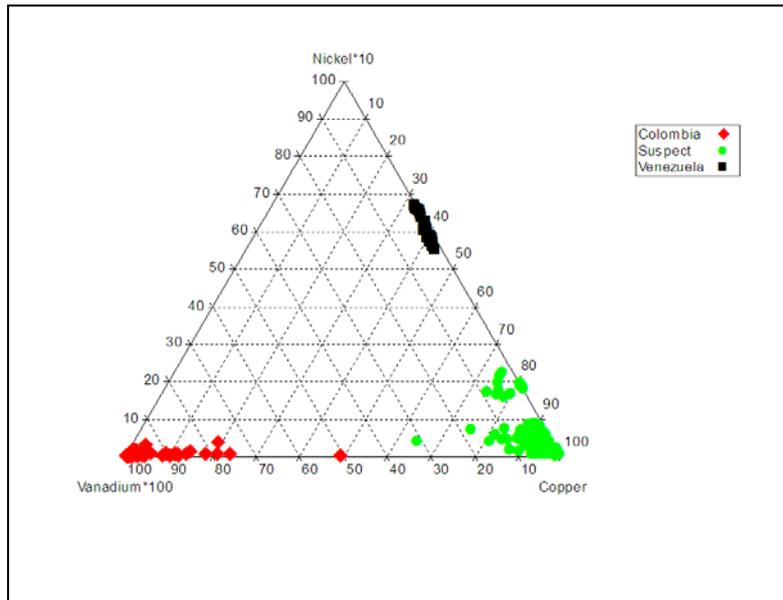


Figure 5.7. A plot of the vanadium (x100), nickel (x10) and copper intensities from LA-ICP-MS analysis. The Colombian gold shows a distinct enrichment in vanadium compared to the suspect and Venezuelan gold. The nickel enrichment in the Venezuelan gold is due to the commercial carbon-in-pulp extraction, which recovers nickel as well as gold from the leach solution, and distinguishes it from the artisanal gold recovery by amalgamation.

5.4 Ni and As enrichment in gold from Venezuela

The gold and PGE deposits in Venezuela occur in Archaean greenstone belts on the Guyana Shield, which occupy the northern part of the Amazon Craton between the Amazon and Orinoco river basins. The Guyana Shield consists of the Archaean rocks of the Imataca Complex, the Palaeoproterozoic Trans-Amazonian granite-greenstone belts and the Palaeoproterozoic sedimentary and igneous rocks of the Roraima Group, Uatumã Group and the Avanavero Suite (Gibbs *et al.*, 1993). The majority of gold mineralisation is hosted by the greenstone belts. In general, the craton has a flatter topography than that in Colombia.

Most of the gold and PGE recovered are mined in situ from soil derived from weathered bedrock, and underground from mineralised veins. The gold and PGE extracted here are recovered together with other associated minerals and elements distinctive of this type of deposit, such as pyrite with attendant nickel and cobalt (Menéndez, 1997).

Approximately 40,000 people are involved in gold mining in the Guayana region of Venezuela. Most of them are artisanal, small-scale miners, many of them illegal migrants from neighbouring countries (Logan, 2004). The mining of gold from an alluvial stream placer or from a quartz vein both depend on Hg for the amalgamation and recovery of Au.

In a laterite which has formed in a landscape of topographically moderate relief, the soils become metal enriched via co-precipitation with Fe and As in goethite. The degree of relative enrichment, as found experimentally, is $Cu > Pb > Co \gg Ni > Zn$ (Thorner & Wildman, 1979), in addition to Au (Greffié *et al.*, 1996).

Gold produced by either the CIP process or the amalgamation process, and originating in such an environment, would therefore be expected to have significant levels of base metals, including Ni and Cu, as well as elements such as As, which are all associated with base-metal sulphides. In Fig. 5.7 this difference is clearly shown, and the two different extraction processes, CIP and amalgamation, are clearly separated.

5.5 The source of the suspect gold bars

The discrimination between the gold originating from Colombia and that originating from Venezuela is clearly shown in Figures 5.4 by the nickel and aluminium distribution, which is a function of the types of ore deposits. It also shows that the suspect bars were a product of artisanal mining using Hg-amalgamation. In Figure 5.6 the Ce shows the degree of weathering to which the deposit has been subjected. The suspect gold bars clearly show that they do not have the same trace element composition as the artisanally mined gold from Colombia. Their trace element composition rather shows them having a geological origin similar to that of the gold samples from Venezuela.

The gold deposits on the Guyana Shield occur over a wide area in eastern Venezuela, Guyana, Suriname, French Guiana and north-eastern Brazil. Due to the lack of representative samples, it is not possible to identify the origin of the suspect gold bars, except to say that their trace element composition falls within the range that would be expected from gold produced in this area. The composition of the gold bars shows that they do not have the same origin as the gold reference samples from the Chocó area in Colombia, and could have the same or a similar origin as the reference gold samples from Bolivar State, Venezuela, with differences being explained by the differences in legal and illegal processing.

What can be clearly seen from the above results is that gold from different deposits can be distinguished on the basis of its trace element distribution, even if it has been processed and so is not in its original form when analysed. This discrimination, however, is very dependant on a good knowledge and understanding of the various genetic processes which resulted in the ore deposit, as well as the processes employed to extract the gold into its first transportable and tradeable form, d'ore bars.

6 Distinguishing between legally and illegally produced gold in South Africa

6.1 Introduction

Identifying the original source of gold recovered during police operations is of huge financial interest. Anything from the ore to the final metal product is stolen and the challenge is to develop techniques like elemental profiling to identify the original source of the gold, despite different beneficiation procedures applied by companies and criminal syndicates. The mineralogy of gold ores from the Witwatersrand mines is relatively consistent and the recovery of the gold is easily achieved with unsophisticated methods, such as panning, amalgamation, and cyanidation (Feather & Koen, 1975; Lloyd, 1978).

Elemental profiling has been used in forensic science for a variety of purposes. The trace element profiles of substances such as paint (Hobbs & Almirall, 2003), glass (Monteiro *et al.*, 2003) and precious metals (Watling *et al.*, 1994) have been used to prove a link between a sample of the material in question and samples from known provenance. There have been problems with the interpretation of the results of such profiling (National Research Council, 2004), and this has been extensively discussed and reviewed in the literature (Barton & Miskelly, 2006). Using such a database, which is representative of the population(s), should enable the attribution of the type and source of such material on a scientific basis, without having to worry about the terms “unique” or “identification” (Cole, 2009), and should produce results which have more weight when presented in court (Kaasa *et al.*, 2007; Saks & Koehler, 2005).

In the case of geological materials and the products processed therefrom, it has been shown that samples from the same source show significant uniformity in trace element distribution, and significant variation between different sources, leading to good discrimination between sources (Sie *et al.*, 1996; Keegan *et al.*, 2008). This discrimination is also successfully used to distinguish archaeological artefacts, such as coins, with different origins (Bugoi *et al.*, 1999).

There are, however, problems with the application of this type of forensic profiling. Most importantly, a sample of known provenance is needed for comparison. Without such a

sample, no meaningful comparisons can be made. For example, if there is no match between an unknown sample and the samples in the database, then one can only conclude that there is no match currently possible. This has been used in the field of gold exploration, where gold nuggets in placer deposits are matched to known deposits, and the non-matching gold samples can indicate further exploration targets (Leake *et al.*, 1997; Outridge *et al.*, 1998; Mortensen *et al.*, 2004).

This issue is extremely important in the field of gold profiling. The term “gold” describes a group of varied products containing some proportion of Au. These products range from native Au and Au-alloys, to Au produced by mines for further refining, to pure refined Au and Au-alloys incorporating refined Au and other metals for use in jewellery and other applications. These Au-bearing products represent small volume, high value products, with little or no obvious indication of provenance, and are thus obvious targets for theft.

In South Africa it has been challenging to successfully implement gold profiling. South Africa has a large number of gold mines, a wide range of genetically distinct gold deposits in discrete geological environments (Department of Minerals and Energy, 2006; Robb & Robb, 1998; Ward & Wilson, 1998), and is also the final refining destination for quantities of gold from all over Africa and South America. Furthermore, most of the South African gold mines exploit gold hosted in Archaean alluvial fans of the Witwatersrand Basin (Goldfarb *et al.*, 2001; Hallbauer & Barton, 1987; Frimmel, 1997). Detrital gold in different fans reflects the whole hinterland with different geological characteristics in the source areas. Although gold in each fan is a mixture of original deposits in the source areas, differences can still be expected.

Thus most mines in South Africa are situated on geologically similar deposits, and there is often more than one mine on a particular deposit. Furthermore, a large amount of gold theft in South Africa does not occur from the processing plants, but actually from the ore face itself. Raw ore is processed by primitive means such as amalgamation, and then sold on to large organised syndicates, who customarily mix gold from several localities and types together. This means that a wider range of gold products and compositions are commonly seized by the police in South Africa, necessitating a more complex approach to the forensic identification of the source of such gold.

Under South African law, it is not legal to process gold or possess gold, which has not been refined to over 99.9% purity and has not undergone any manufacturing process, without a permit (Precious Metals Act, 2005). The use of elemental profiling to distinguish between legal gold alloys and illegally processed gold, which represents gold stolen from mining operations, provides a legal mechanism for the seizure of such material.

6.2 The effects of processing on gold composition

In the CIP process, the raw ore is crushed and milled, run through a flotation circuit to concentrate heavier minerals, and then leached with a cyanide solution. The dissolved gold in the cyanide solution is then adsorbed onto activated carbon particles, and then either smelted or processed by an electrowinning circuit to produce the final gold bullion. This processing upgrades the concentration of gold from less than 10 g/t in the ore to close to 100 wt % Au in the bullion. The individual processing steps remove some elements and add other elements to the gold, but only the final electrolytic processing done at the refinery can produce pure 99.999 wt % Au. The final electrowinning stage is usually done at a refinery, to which the gold mines have sent their run-of-mine gold bullion, known as doré. Doré is produced after smelting the final concentrate, and can vary in composition depending on the type of ore processed, usually containing 80 – 90 wt. % Au. Where the word “bullion” is used in this work in the figures, it refers specifically to doré.

When it comes to theft of gold, the main source is from the ore, by illegal mining, and also theft of concentrates before smelting. In illegal processing, these materials are often amalgamated with mercury, which in addition to extracting all the native gold particles, also amalgamates with other metals present, such as copper from blasting caps. In addition, other incompatible elements, like iron derived from tools, can be incorporated into the amalgam as inclusions adhering to other metals. The resulting amalgam is then heated and the mercury is driven off to a level that the metal becomes a golden colour. The resulting gold-rich metal is rich in impurities, especially in mercury.

Sophisticated criminals might try the addition of other elements, either as other metal alloys or as chemical mixtures, to mask the “fingerprint” of the gold source. Typically, an attempt is made to present the illegally processed gold as having a legal origin, being derived from melted scrap gold, of an industrial or jewellery origin. Fortunately for the forensic analyst, the large range of elements present in gold and the various isotope ratios of minor and trace

elements present a formidable challenge to any such attempt. In addition, the material added will also have its own characteristic signature, so the identification of this signature will allow the additive to be subtracted from the bulk and the original profile of the gold identified.

6.3 Methodology and materials

In order to investigate the compositional variation of gold that has been processed or refined to different degrees, a large number of samples were collected, consisting of:

- Alloy - 61 commercially available jewellery and other Au-alloys;
- Jewellery - 71 pieces of jewellery, typical of jewellery recovered by pawn shops which would be the type of gold jewellery sold to the refineries as jewellery scrap. This group contains gold-plated or coated brass, which has a very low effective Au content;
- Bullion - 477 bars of doré from 23 different African gold mines, all produced via the CIP method; and
- Suspect - 249 samples of gold-containing material seized during police action, considered to be of “suspect” or illegal origin, including material recovered from slag in crucibles where pieces of copper and brazing rods were being melted together with gold-bearing material.

6.3.1 Analytical procedure

The samples were prepared using *aqua regia* dissolution, and then analysed utilising a Spectro Vision ICP-OES. The following analytical lines were used: As 189.042; Au 242.795, 267.595, 274.825, 201.200, 174.050; Be 313.042; Bi 190.241; Ca 396.847; Cd 226.502, 228.802; Co 228.616; Cr 205.552, 283.563; Cu 324.754, 219.958, 224.700; Fe 259.941; Ir 263.971; Li 670.780; Mg 279.553; Mn 257.611; Mo 202.030; Ni 231.604, 341.476; Pb 220.353; Pd 340.458, 360.955; Pt 265.945; Rh 343.489; Ru 240.272; Sb 206.833; Se 196.090; Sn 189.991, 147.516; Sr 407.771; Te 214.281, 238.578; Ti 334.941; Tl 190.864; V 292.464, 292.402; Zn 206.191.

Standards were prepared from multi-element and single element liquid SRM's, with concentrations of 0.5ppm, 1ppm and 10ppm. These were prepared in 100 ml volumetric flasks with 10 ml ultra-pure *aqua regia*, and made up with milli-Q water to the 100 ml mark. During calibration the instrument was rinsed with 10% *aqua regia* in between samples. The

aqua regia was prepared by distilling hydrochloric and nitric acid with a Milestone DuoPUR sub-boiling distillation system.

Samples were prepared in duplicate by drilling, using a new drill bit for each sample. 0.1 gram of sample was placed in an acid-cleaned 50 ml glass beaker, 10 ml concentrated ultra-pure aqua regia added and then heated on a hot plate under reflux until the sample was dissolved. The solution was then transferred quantitatively to an acid-cleaned 100 ml volumetric flask, using milli-Q water (conductivity of 18 million ohm.cm⁻¹), and made up to 100 ml.

The following analytes were detected and quantified: As, Au, Bi, Ca, Cd, Co, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Pd, Pt, Rh, Sb, Se, Sn, Te, Ti, Zn. Ag and Hg were not analysed, as due to the method used, these elements either precipitate out of the acid solution prior to analysis, or (partially) volatilise during the heating process.

6.4 Results and discussion

6.4.1 Variation in manufactured (legal) gold alloys

Manufacturing jewellers buy certified gold alloys from a refinery, but are then free to mix different alloys in different proportions in the finished product. The refineries themselves sell a variety of different alloys, containing different elements not only to dilute the gold, but also to alter the colour and hardness of the gold, as well as casting or metallurgical properties (Ott, 2002; Rapson, 1990; Raub & Ott, 1986). (See Appendix A for some typical alloy compositions).

For instance, Cu-rich gold is redder than Ag-rich gold, even if both contain the same amount of gold. Therefore it is important to check the consistency of the elemental profile for legal gold alloys before considering illegal gold alloys.

Analysis of commercially available gold alloys and of manufactured jewellery items show that many elements are present in quantities close to, or below, the ICP-OES detection limit in these matrices under the analytical conditions chosen. Elements such as As, Ca, Fe, Mg, Sb, Sn, Se, Te, Ti, Pb, and Bi are present either in extremely low quantities or in quantities below the detection limit of the instrumentation used. Sufficient analytes are present in measurable quantities to allow discrimination between gold samples of different provenance.

An obvious starting point for an investigation of the composition of gold alloys is to assess the Au content directly. For most uses of gold, the pure metal is too soft on its own and is therefore hardened by the addition of alloying elements such as copper, silver, nickel, palladium and zinc. This is an area of much research, with novel alloys and manufacturing methods having been developed for specific uses (Levey *et al.*, 2002; Gusmano *et al.*, 2001; Bernardin, 2000; Cretu *et al.*, 2000; Corti, 1999).

Pure gold is yellow and other common colours of gold alloys such as red, white and green are due to the ratios and type of elements added. In the South African context, stolen mine gold when seized is normally yellow in colour, and therefore gold jewellery and alloys which are not of this hue are unlikely to be used in activities where the stolen gold is stated to be of jewellery origin.

Commercial gold alloys are available in set gold concentrations, which can clearly be seen in Figure 1, where the Au and Cu contents of the jewellery samples, the alloys and the doré are compared. Clusters of jewellery samples and alloy samples occur at 9 carat (37.5 wt %), 14 carat (58.33 wt %), 18 carat (75 wt %) and 22 carat (92.5 wt %) Au. The alloys are considerably less variable than the jewellery, which often has a lower gold content than the alloys from which it is supposedly made, or consists of base metal which is plated or coated. This may also be the result of dilution during the melting of the alloys prior to the casting of the manufactured article, and the recycling of scrap jewellery, which would include solder and other diluents. Cu is the most commonly used diluent in commercial alloys, as Cu is present in high quantities (35-50 wt %) in most 9 carat gold, and 5-20 wt % in 18 carat gold.

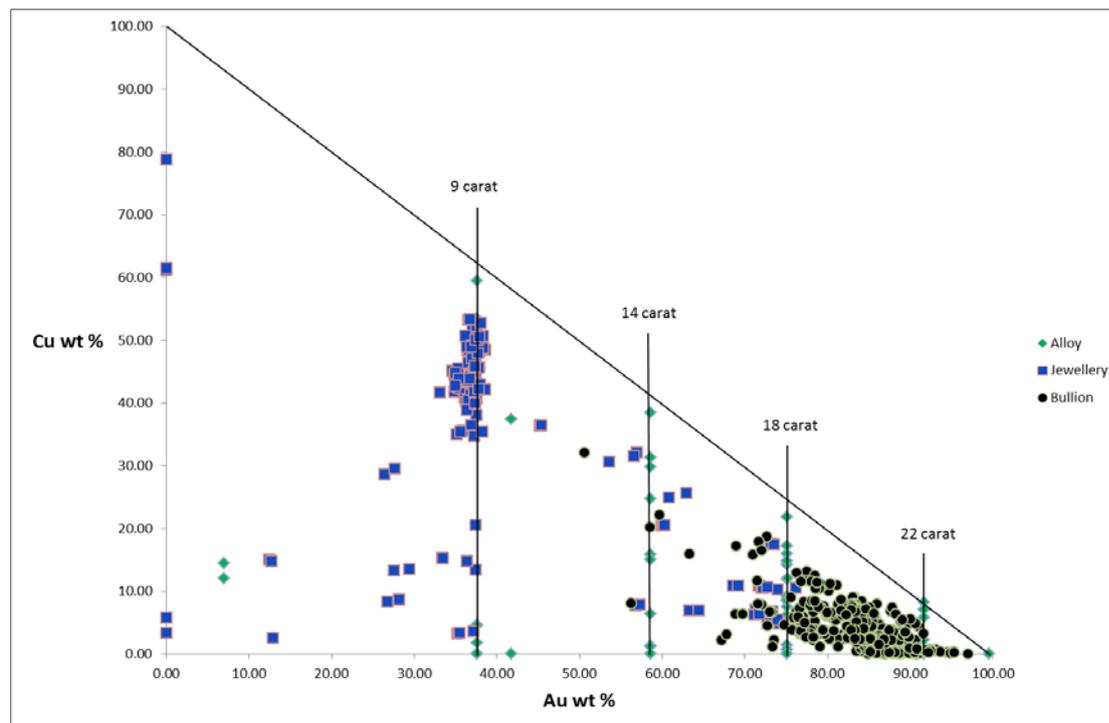


Figure 6.1. Comparison between the Au and Cu contents of commercial jewellery alloys, manufactured jewellery and doré (bullion in the key). The majority of the Au alloys are 9 ct and 18 ct.

Another element common to all jewellery alloys and manufactured jewellery is Zn, which is present in concentrations of up to 20 wt %. Zn is added to gold alloys to improve hardness, to aid in casting and as a diluent (Raub & Ott, 1983). The concentration of Zn in the gold alloys and in the manufactured jewellery is similar. Ni, Co and Pd are present in some commercial alloys, but not in all. The manufactured jewellery can contain not only these three elements, but also As, Cd, Pt and Rh. As and Cd are mainly from solders used in older jewellery, while Pt and Rh were used in older jewellery when they were relatively inexpensive. When detected, these elements can be present in relatively high concentrations, up to 20 wt % of the total abundance.

Comparing the manufactured jewellery to the commercial jewellery alloys, several comments can be made. Firstly, the commercial alloys are much more consistent in their composition than the manufactured items. Secondly, the older manufactured jewellery contains elements that are no longer commonly used as alloying elements or in solders. Thus, the collected data set can be considered to contain historical samples as well as contemporary samples, and so is not biased towards modern compositions.

6.4.2 Comparison between mine doré and gold jewellery alloys

D'oré, as supplied by mining companies to the refinery, has undergone significant processing using the Carbon-in-Pulp (CIP) extraction method (Fleming, 1992; Laxen *et al.*, 1994). Comparing the commercial gold alloys and manufactured jewellery data to the mine doré data in Figure 6.1, it is immediately apparent that the d'oré reaches generally 70 wt % or more Au. At the same time, the Cu content is generally lower than that of the refined alloys. Extending the comparison to include Zn, the other element found in almost all jewellery, the Zn and Cu content is generally higher than d'oré, with only a few jewellery alloys close in composition to some doré.

It is possible to consider the relative abundance of other elements sometimes present in jewellery, namely Cd, Pd, Pt, Ni, and Co, in terms of the ratios between these minor constituents. Jewellery and doré have comparable Pd/Cd ratios, but doré has very different Pd/Pt and Pd/Co ratios, owing to the low concentrations of Pt and Co in this type of gold. High Cd/Pd ratios are indicative of jewellery, as is the presence of Co. It is thus possible to use these elements to distinguish between manufactured jewellery and doré. These elements are not consistently present, however, and cannot be relied upon for a clear and easy method.

For forensic purposes, a simpler discrimination scheme is preferred, and rather than use elements present in both jewellery and d'oré, it is possible to characterise the source of gold solely on elements that are present in d'oré, but not in refined gold. The element of interest is thus Pb, which is present in all natural gold deposits. Other discriminating elements are As, Sb, Sn, Se and Te, which are undesirable in refined gold, and are removed during the final refining process.

Pb was not detected in any of the jewellery items, but is present in the doré in concentrations mostly in the range of 300 to 5000 ppm. Lead is usually found in gold ores, and due to the beneficiation process will become alloyed with the gold in the doré. The presence of Pb in high concentrations in most bullion samples means that analytical methods of lower sensitivity, such as handheld XRF spectrometers, can be used to easily identify suspect gold-bearing material. For the analytical procedure used in this study, with a detection limit of 1 ppm for Pb, the use of the Pb content of the analysed samples was 100% successful in discriminating between jewellery alloys and d'oré.

The other elements of interest are present in only some of the gold deposits. Tin is present in some bullion. Antimony is present in two samples of d'oré from greenstone gold deposits in Murchison and Barberton (Ward & Wilson, 1998), and As, Se and Te are present in occasional samples. The dataset of d'oré used in this study is heavily slanted towards gold hosted in sedimentary deposits of the Witwatersrand, so it is likely that these elements will be present in higher concentrations in deposits from other parts of the world. The presence of any of these elements is sufficient to classify the gold-bearing material as semi-processed and not refined.

During this study, it was noted that many of the elements of interest are likely to be present at levels below the detection limit of the ICP-OES. Though the use of Pb, As, Te, Se, Sn, and Sb is sufficient for the purposes of differentiating jewellery from bullion, some d'oré samples of high gold purity do not have levels of these elements measurable by ICP-OES. A more sensitive method of analysis such as ICP-MS should be considered in order to improve the discrimination achieved from trace element profiling of gold.

6.4.3 The origin of suspect samples of gold

During the course of operations directed at combatting the illegal gold trade, numerous suspect samples of gold have been seized by the SAPS and given to the FSL for analysis and evaluation. 249 such suspect samples have been analysed for this study, and can be used to test the ability to empirically determine the source of the gold-bearing material and its legality according to South African law.

In Figure 6.2, a PCA analysis shows the results of a comparison between the various samples, with the majority of jewellery and the d'oré quite distinctly separated by their Au and Cu contents, with the suspect gold samples from criminal investigations mainly in-between these two extremes. Au and Cu comprise the majority of the discrimination, and a much clearer picture is given in Figure 6.3 where they are plotted against each other. The suspect material covers a much broader range of Au values than either the d'oré or the jewellery, and has Au contents ranging between 40 and 95 wt %.

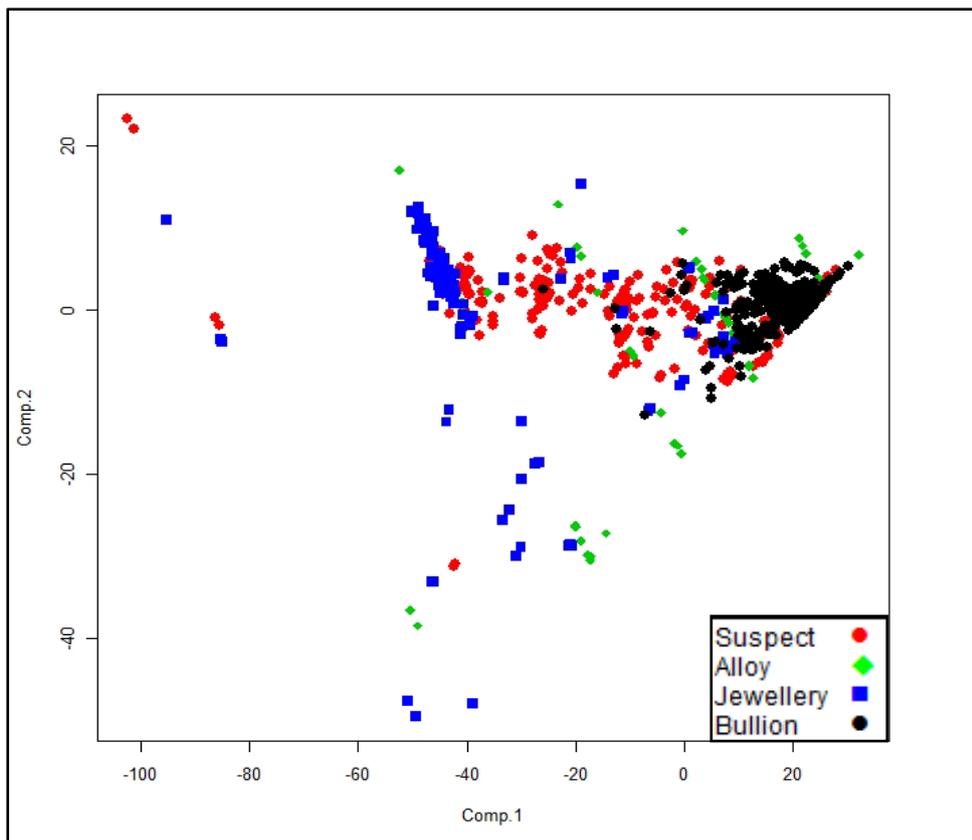


Figure 6.2. PCA analysis of the samples used in this case. The elements which contribute the majority of the discrimination are Au and Cu, and this is shown for the two principal components. Overall, the rest of the analysed elements have only a small overall contribution. The main feature is that the suspect samples plot in the space between the bullion and the 9 ct gold jewellery (which makes up the majority of the jewellery samples).

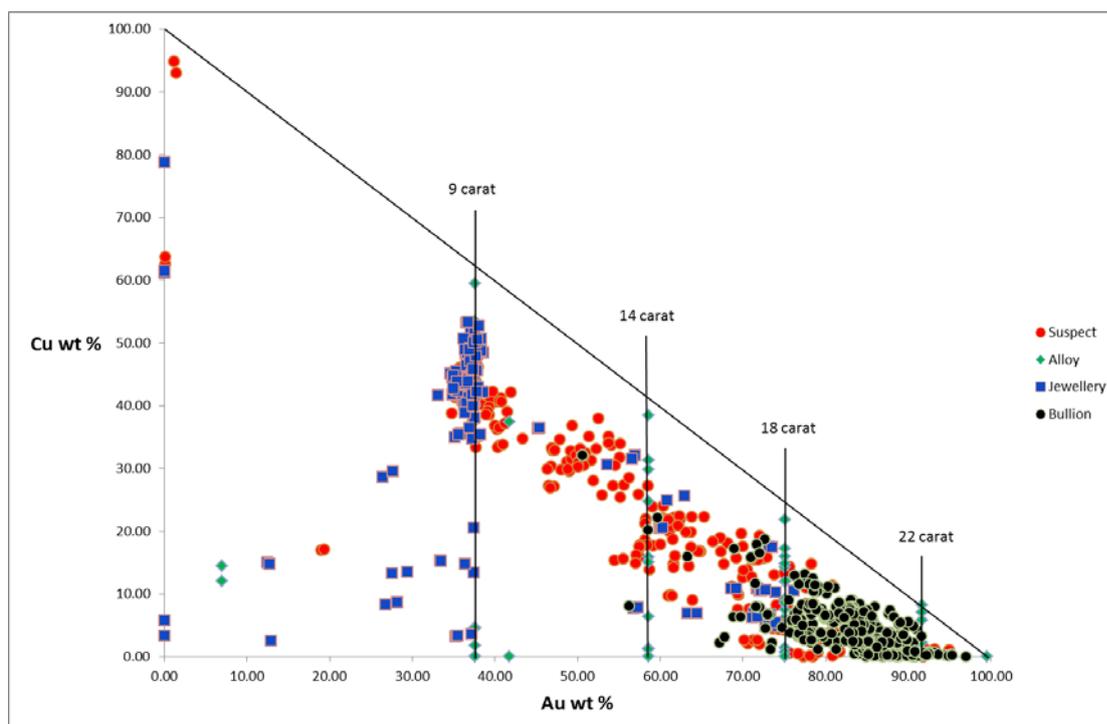


Figure 6.3. Comparison between seized gold (suspect; in red) and gold from known sources (alloys, jewellery and bullion), based on Au and Cu content. The commercially produced alloys (in green) show the groupings according to carat value. Pieces of brass and copper, and Au-free jewellery (possibly Au-coated jewellery with a negligible Au content), are shown against the y axis.

The suspect Au values are not clustered together like the jewellery values, and extend to lower Au values than the bullion. This spread, together with observations made at the crime scene where pieces of copper and brazing rods were being melted together with scrap jewellery and doré, leads to the conclusion that the suspect samples include material that is not jewellery in origin. This conclusion cannot be considered definitive solely on the basis of the Au/Cu ratio in the samples. However, if the suspect samples are in fact illegally processed gold, then it is apparent that the original high gold content of the stolen mine gold, as represented by the bullion, has been diluted by adding copper-bearing material, as well as scrap jewellery. This is very evident as most of the suspect samples plot between 80 and 40 wt %, in an attempt to simulate the range expected for jewellery scrap.

Attempts to utilise PCA to clearly identify the different groups produced no distinct discrimination apart from the first two components, Au and Cu (Fig. 6.2). This can be attributed to the fact that there are a number of different materials, at different stages of the gold beneficiation and production process, and these different materials also have a wide range in composition. Ternary plots were able to produce a clearer discrimination.

In Figure 6.4, the relative proportions of Au, Cu and Zn are shown for the complete dataset. The doré contains little Cu and even less Zn, and is clustered around the Au apex. The commercial alloys, made for a variety of uses, show a large variation in all three elements. The jewellery clearly shows the carat alloys, with or without zinc, with variation due to dilution by other alloying elements, predominantly in the 9 carat range. The suspect material follows the brass dilution trend for the majority of samples, with the remainder showing a Cu dilution trend and a few in-between. The only conclusion to be drawn from the combination of the observations made at the crime scene when the suspect material was collected, and the distribution of the suspect samples as shown in Figure 6.4, is that the suspect material is consistent with doré which has been diluted to varying degrees with copper or brass to produce a gold alloy between 9 carat and 18 carat which could be passed off as jewellery scrap.

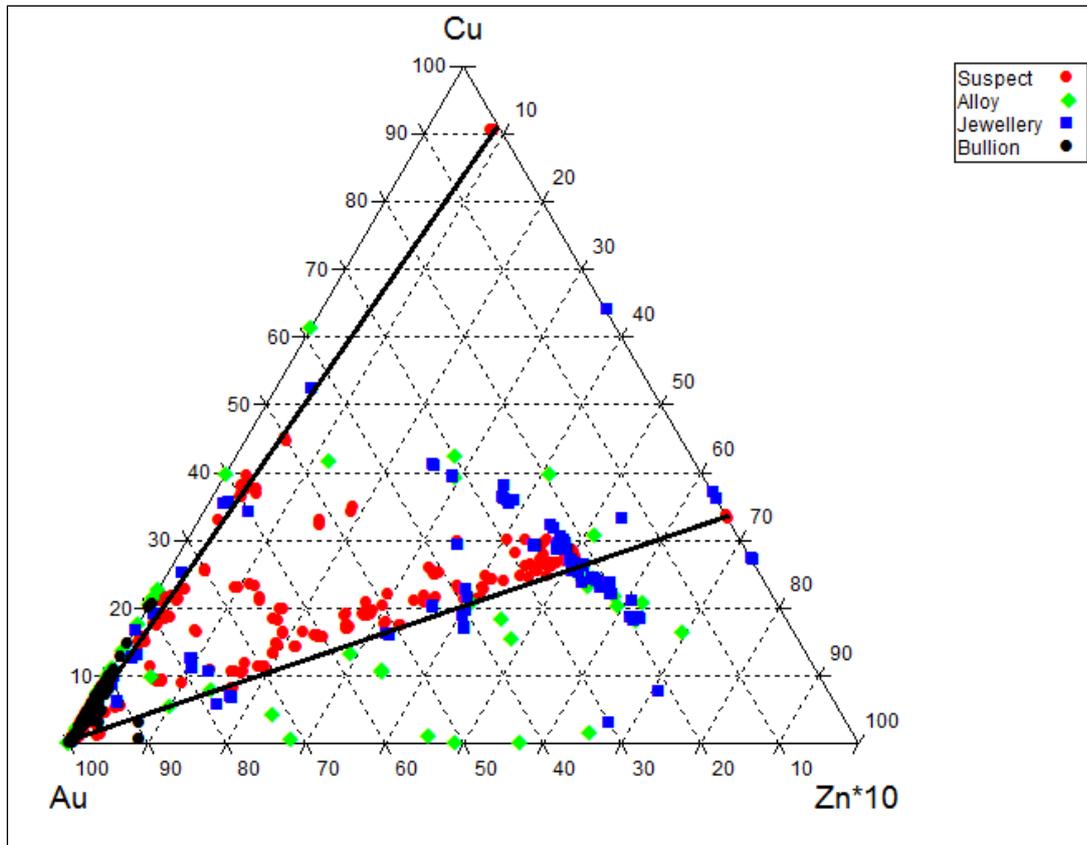


Figure 6.4. Relative proportions of Au, Cu and Zn (x10) (wt %) plotted for the complete dataset. The two lines show a dilution trend for brass (lower line) and a Cu dilution trend (upper line).

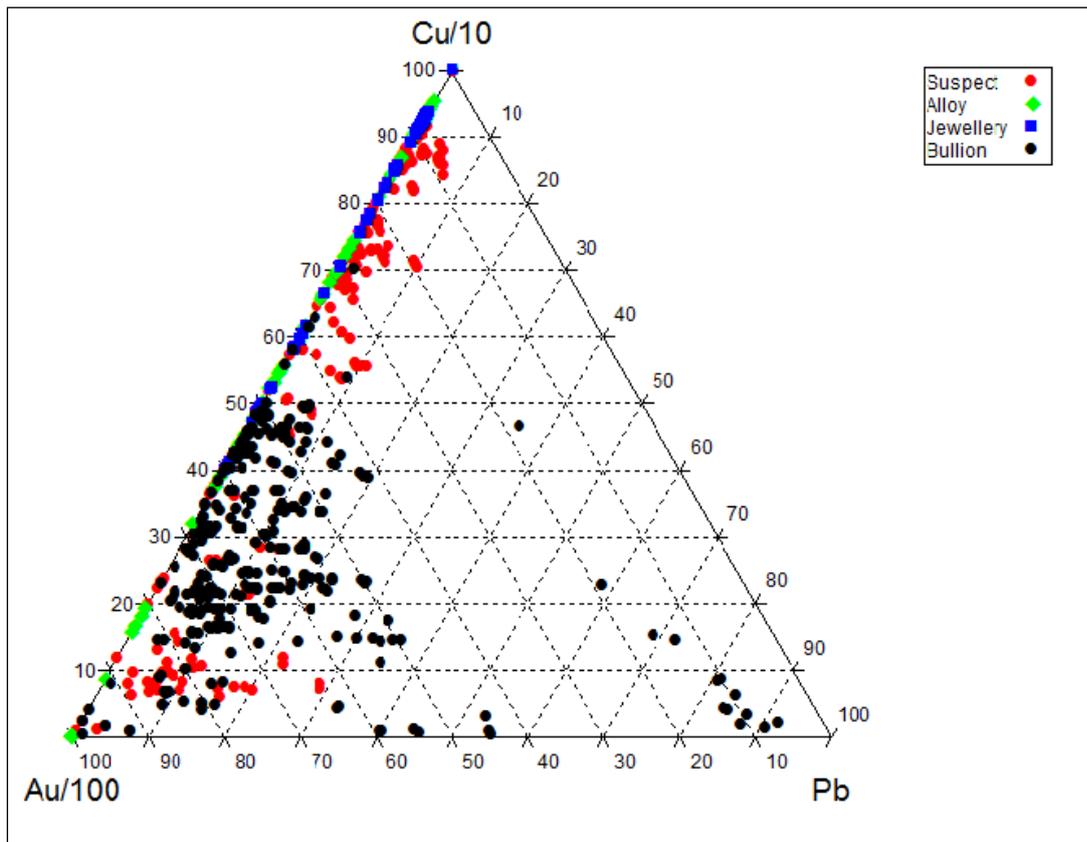


Figure 6.5. Relative proportions of Au, Cu and Pb (wt %) plotted for the complete dataset. The alloys and jewellery contain no Pb.

Looking at the trace elements, lead and tin show the best utility for discriminating between stolen mine gold, jewellery and alloys. Pb is distinctive of unrefined gold, which does not contain significant quantities of Sn, and jewellery does not contain Pb or Sn (with the exception of a few very specialist alloys used in electronic components which would not normally be found as scrap). The presence of Sn can be attributed to the use of brazing rods (commonly used brazing rods are Cu:Zn alloy with Sn added) for diluting the stolen doré. This is confirmed by the presence of some of the suspect material of this composition. Other samples consisted of brass or pure copper.

In Figure 6.5 there is a clear distinction made between alloys and jewellery, and the majority of the d'oré, with the d'oré being restricted in its Cu content. The suspect samples show a range of Cu content from d'oré to Cu metal, but the majority show the presence of Pb, showing that there is a component present in these samples which corresponds to gold with an unrefined origin, similar to the bullion which is the unrefined gold extracted by the mines.

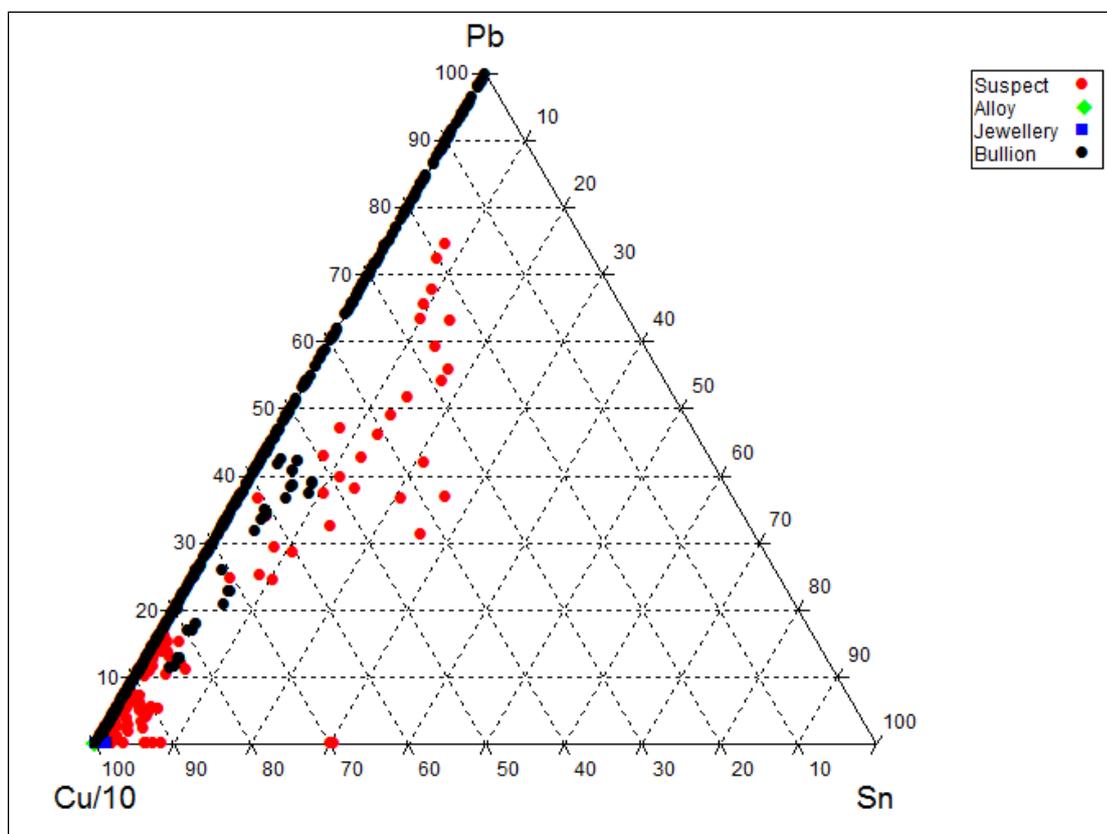


Figure 6.6. Relative proportions of Cu, Pb and Sn (wt %) plotted for the complete dataset. The alloys and jewellery contain no Pb and plot at the Cu apex.

Figure 6.6 shows a plot of Cu, Pb and Sn which clearly shows that the majority of the suspect material plots near the Cu apex and shows the presence of Sn in significant amounts. This corresponds to dilution of unrefined gold with either copper or brass, and Sn-bearing brazing rods. At low concentrations of Cu, the relative proportions of Sn in doré increases, where detected, and this accounts for the tail of d'oré (bullion in legend) and suspect material towards the Pb apex. The suspect material corresponds to diluted d'oré.

6.4.4 Diluents used in the illegal gold trade

The analysis of the gold-bearing material seized during police actions clearly shows that the gold in these samples has been diluted with other material in order to achieve gold concentrations similar to those in legal jewellery alloys. It is obviously of interest to the forensic analyst to identify the material(s) used as the diluent, as these may be responsible for the unique geochemical characteristics of the illegal gold products. Amongst the material commonly confiscated during police action against suspected gold thieves are pieces of copper wire, as well as brazing rods. Both copper wire and brazing rods are stolen from mines, and are obvious choices for diluents in the illegal processing of gold.

6.5 Conclusions

It is possible to distinguish between legal alloys derived from refined metals, such as jewellery and unrefined, semi-processed gold in the form of doré, based on the presence of major and trace elements in the gold.

Other elements commonly associated with native gold, such as As, Se, Sb, Sn and Te, can be used to identify gold bullion, if these elements are present at levels high enough for detection. None of these elements normally occurs in jewellery.

Elements present in relatively large amounts in gold, such as Cu, Zn, Pb and Sn, can be used to distinguish between jewellery and unrefined gold (d'oré and gold recovered illegally by artisanal means). The compositions of jewellery and unrefined gold are sufficiently different to allow easy discrimination between the two forms of gold on the basis of their Pb content. Jewellery alloys are made from refined metals, and contain no Pb, whereas d'oré as produced by the Carbon-in-Pulp (CIP) method of cyanide leaching still contains significant Pb.

Normal statistical methods such as PCA do not result in sufficient discrimination between the different Au-bearing materials, as they are not representative of a single variable population. Instead, expert knowledge of the elemental composition of different materials and the beneficiation and processing methods is required to identify the nature and origin of the suspect Au-bearing material.

Samples of gold seized during police operations include some samples that are most likely stolen mine gold, but generally show a unique geochemical signature. High levels of Sn, the presence of Hg, along with low but measurable levels of Pb, are likely to indicate crude processing and beneficiation through mercury amalgamation and low-temperature smelting. These elements are sufficient to identify the seized material as illegal according to South African law.

7 Variation in d'oré gold composition from different mines within the Witwatersrand Basin

The gold extracted from the Witwatersrand Basin has been mined historically from a number of goldfields situated around the outer margin of the basin, as well as a single goldfield on the inner margin on the rim of the Vredefort meteorite impact (Fig. 7.1). A comprehensive overview of the goldfields is given in Robb & Robb (1998). The majority of the gold mined from the Witwatersrand Basin is found in the Central Rand Group, with some in the Ventersdorp Contact Reef lying unconformably on top, as shown in Fig. 7.2. The legal requirement to supply samples for the precious metal database (Precious Metals Act, 2005) only affects producing mines. This has had the result that the Free State (Welkom), Klerksdorp and West Wits (Carletonville) goldfields are represented with numerous samples, as they have been producing over a long period. Prior to the legislation taking effect, the major goldmining companies (AngloGold Ashanti, Gold Fields and Harmony) were all contributing regularly as part of the development of the database.

The d'ore gold samples were collected and identified as being from a specific shaft or mine, and were not defined on the basis of geological criteria. For this reason, some producers could have submitted samples with distinct differences between samples, as a result of the geological variation within the boundaries of the mine property from which it is stated to have originated. The d'ore samples were all collected as drillings from cast d'ore bars from the smelthouses of the specific mines, and a more precise identification of geographic and geological origin is not possible. This, however, means that the beneficiation process used at a particular mine/smelter is consistent for all the samples originating from that source, and differences between samples are a reflection of the ore composition and not changes in process.

Before the LA-ICP-MS methodology was well-developed, all samples submitted to the database were initially analysed quantitatively by ICP-OES, this being the routine method for analysis of precious metals at the FSL at the time. In this manner, 124 d'ore gold samples from the West Wits, 155 from the Klerksdorp, and 158 from the Free State goldfields were analysed. The only elements which were consistently present were Au, Ag, Cu, Ni, with lower amounts of Pb, Zn, and Fe. All other elements were either at, or below, detection limits, or not consistently present. (See Appendix B for d'ore compositions)

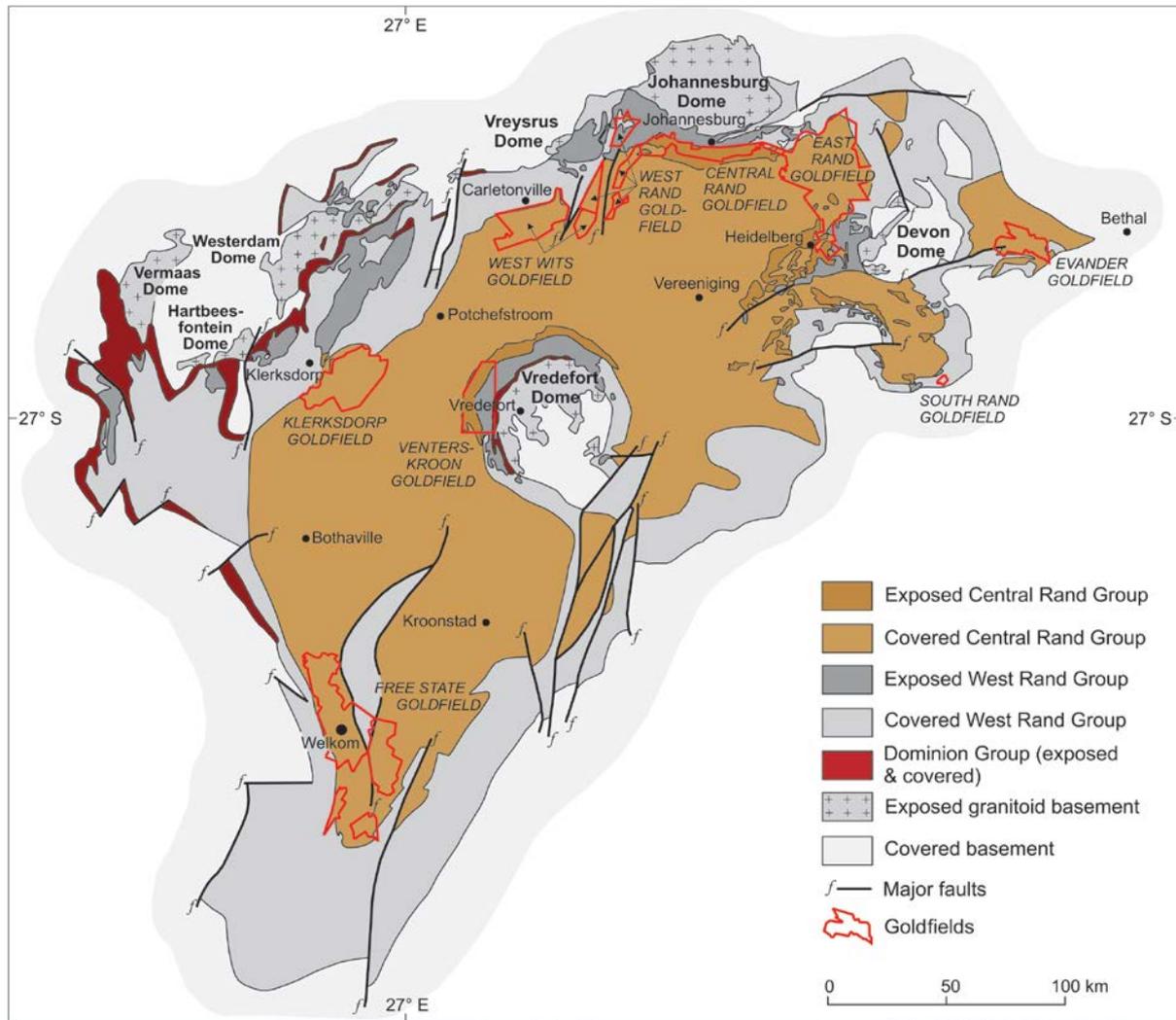


Figure 7.1. The Witwatersrand Basin, showing the location of the goldfields (after Robb & Robb, 1998).

The d'ore samples were then analysed using laser ablation and the LECO Renaissance ICP-TOF-MS. This instrument has a limited concentration range (high ppm to ppb), so it was used to analyse for the trace elements for which the ICP-OES method was not sensitive enough. The d'ore gold, which is unrefined and contains a variety of elements other than Au, was found to be inhomogeneous. This inhomogeneity was found to consist of relict refractory phases, exsolution, nucleation along grain boundaries, and domains of different composition. For this reason only Pb, due to its solubility in gold, was selected for examination of its isotope distribution.

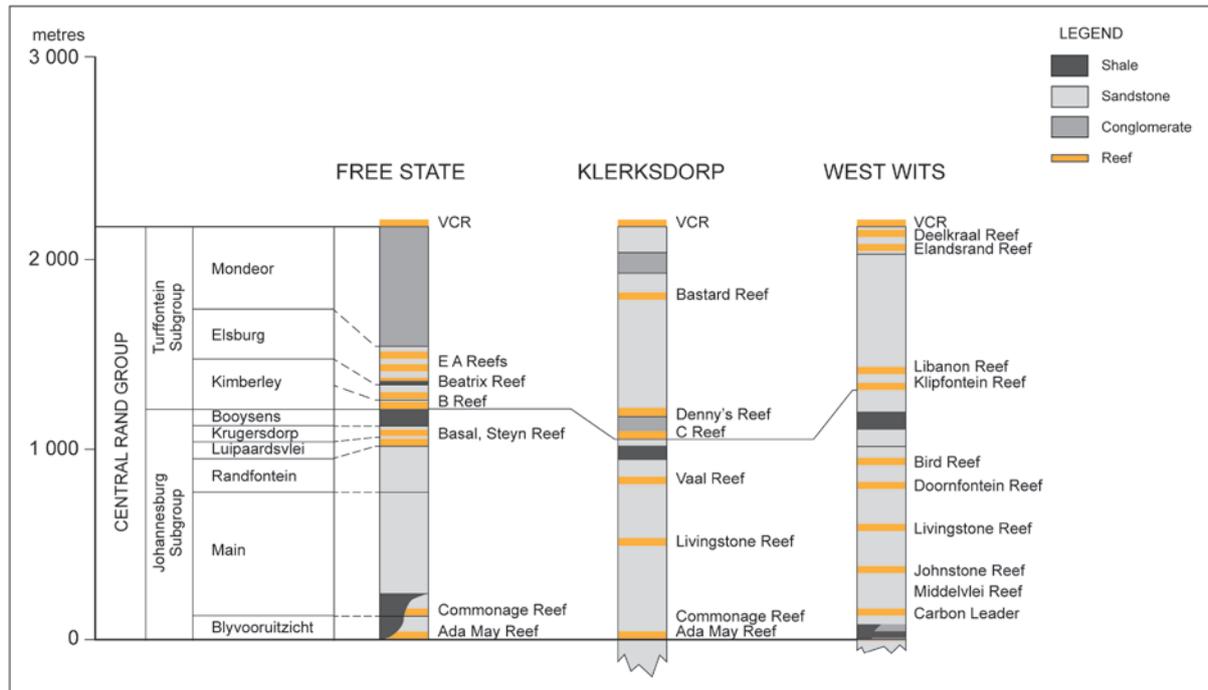


Figure 7.2. Comparison between the stratigraphy of the Central Rand Group in the three goldfields (after Robb & Robb, 1998).

7.1 Discrimination between goldfields

The gold mines of the Witwatersrand Basin recover not only gold, but also uranium and sulphur. In the majority of cases this is accomplished by a combination of gravity concentration (Penman, 1987) and flotation (Broekman *et al.*, 1987), followed by the cyanide leach process (Young, 1987) after which the gold is recovered by means of adsorption onto activated carbon (Bailey, 1987). However, for gold to be efficiently extracted from solution, it is inevitable that other base metals with similar behaviour would be extracted at the same time, which means that Cu, Zn, Ni and Pb, amongst others, are also preferentially removed from the leach liquor (McDougall *et al.*, 1980; Fleming & Cromberge, 1984). The abundance of these elements in the d'ore gold can therefore be indicative of the geological and geochemical variations in the ores themselves. Zn is used as a precipitant in the gold recovery process at some mine plants (Adamson, 1972), so Zn abundance could have an additional source of variation and should not be used without more information about the process used for each sample.

7.1.1 Discrimination using elemental abundances

When comparing the compositions (ICP-OES, wt%) of the d'ore gold produced in the three goldfields, the Klerksdorp goldfield shows a distinct enrichment in Ni compared to the other

two goldfields (see Fig. 7.3). This is also reflected in the scatter between Cu and Au in Fig. 7.4. The implication is that the reefs being mined which show high Ni in the extracted d'ore gold, have an additional Ni-bearing phase. This implies that the gold-bearing reefs in these areas are different to those which have low Ni in the d'ore gold. There is also a distinct difference in the behaviour of Ni relative to Pb, as shown in Fig. 7.5.

These differences in behaviour between the three goldfields are indicators of a difference in overall content in the reefs of the Central Rand Group, which reflect either differences in source rocks or post-deposition processes (*e.g.* Robb & Meyer, 1995; Frimmel & Minter, 2002). Hayward *et al.* (2005) noted that there was also an apparent geographic variation in the chemistry of gold grains, which showed a strong geographical variation with respect to Ag and Hg, and that some West Wits gold had similar signatures to some Free State gold.

If the source of the gold was by alluvial deposition from a now-eroded hinterland, one would expect to see distinct differences in the composition of the gold produced in the three different goldfields. Hydrothermally deposited gold would be more homogeneous in composition, as precipitation out of solution is a chemical process and would tend to result in a more even regional composition for the gold.

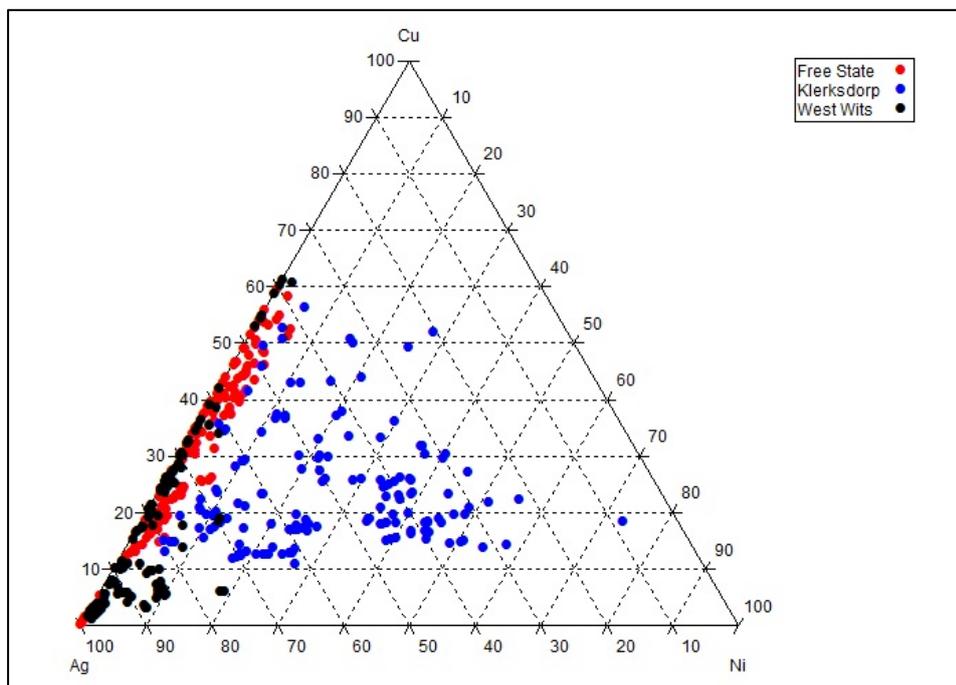


Figure 7.3. The variation in element proportions between d'ore gold from mines in the Klerksdorp (blue), Free State (red) and West Wits (black) goldfields. The Klerksdorp goldfield shows a high proportion of Ni relative to Ag and Cu, with some samples containing up to 15 wt % Ni (ICP-OES). The Free State appears to have a higher Cu to Ag ratio than the West wits, although there is much overlap.

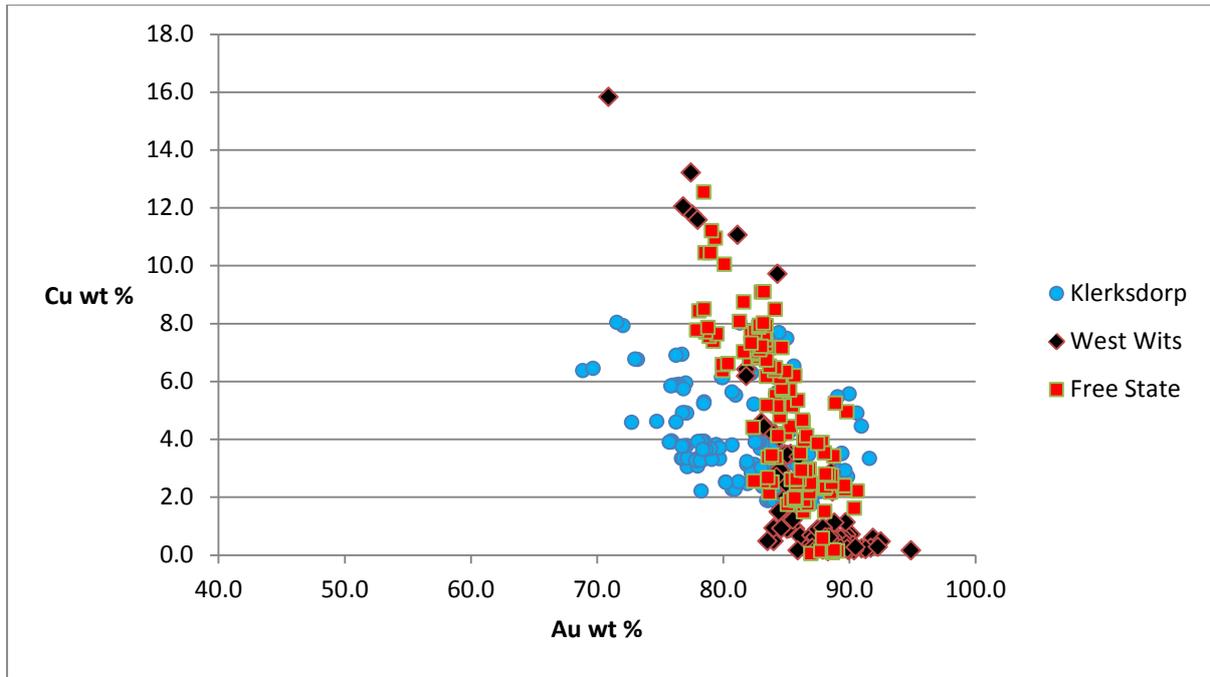


Figure 7.4. A plot of Au vs Cu for d'ore gold from the Free State, Klerksdorp and West Wits goldfields. The variation in Au for the Klerksdorp goldfield is due to the higher Ni content.

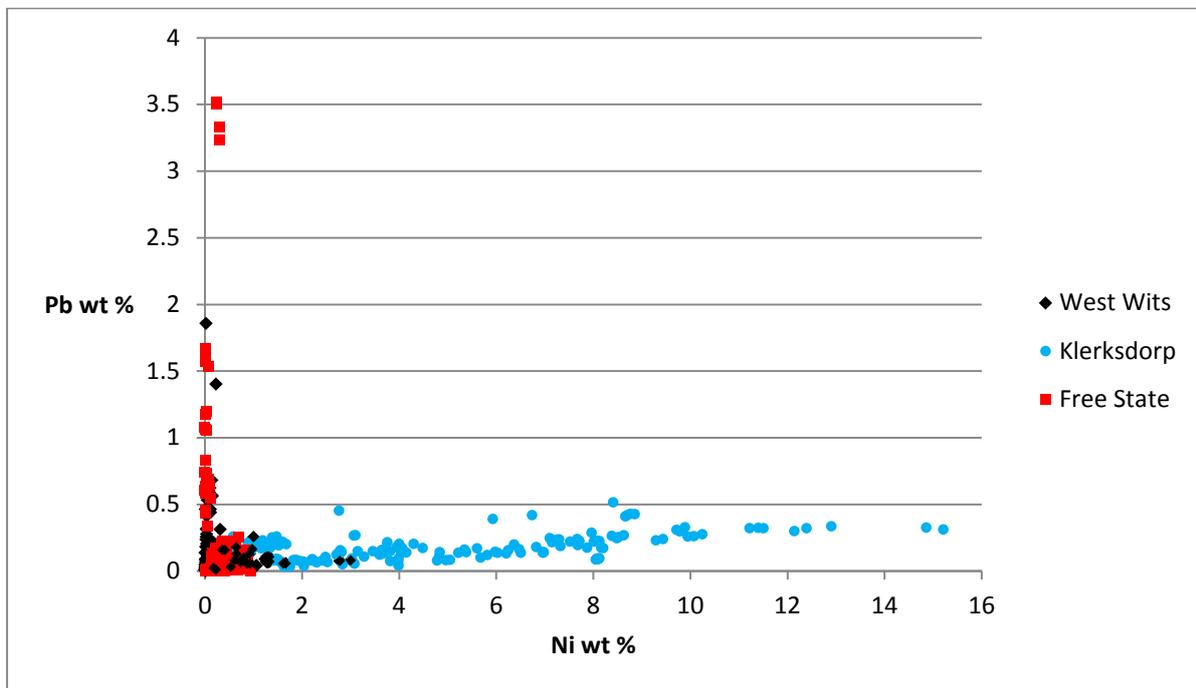


Figure 7.5. A plot of Ni vs Pb (ICP-OES, wt%) for d'ore gold from the Free State, Klerksdorp and West Wits goldfields. The Klerksdorp goldfield shows how the high Ni content discriminates it from the other two goldfields. The Free State and West Wits goldfields show similar behavior for both elements, with the exception of St Helena in the Free State with the enrichment in Pb, and Driefontein in the West Wits which shows an enrichment in Ni.

7.1.2 Pb isotope variation

A pronounced enrichment in radiogenic Pb in the gold-bearing reefs in the Witwatersrand Basin has been reported (Burger *et al.*, 1962; Nicolaysen *et al.*, 1962; Rundle & Snelling, 1977; Zartman & Frimmel, 1999). This was shown to be more pronounced in the Klerksdorp and West Wits goldfields than the Free State goldfield, and to be more pronounced towards the base of the Central Rand Group in the reefs which have substantial carbon content, such as the Carbon Leader Reef (Rundle & Snelling, 1977; using a small sample set (16) of whole rock reef samples).

The source of the Pb has been attributed to post-depositional hydrothermal mobilisation of Pb from uraninite, which shows strong and heterogeneous enrichment in ^{206}Pb and ^{207}Pb and is found throughout the basin (Zartman & Frimmel, 1999). The relatively low ^{208}Pb proportion is due to the source of the radiogenic Pb coming mainly from uraninite in the sediments, with $\text{Th}/\text{U} = 0.06$, much lower than would be expected from most sedimentary and igneous rocks (Zartman & Frimmel, 1999). Varying amounts of Th would therefore affect the amount of ^{208}Pb present.

Both the ICP-MS and LA-ICP-MS analyses performed on the d'ore samples showed anomalous behaviour for all the radiogenic isotopes. However, the results for the different techniques show differences which could be due to instrumental artefacts. When analysing the NIST 610 and NIST 612 glasses by LA-ICP-MS, the amount of ^{208}Pb varied, while the $^{207}\text{Pb}/^{206}\text{Pb}$ remained constant. For NIST 610 the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio was ~ 0.96 . This is an uncorrected value derived from raw data, but it compares well with the value of ~ 0.91 reported by Baker *et al.* (2004). In d'ore samples from St Helena mine, which contain up to 3% Pb, there was a significant difference in the Pb isotope ratios compared to samples containing low Pb levels, which showed anomalously high proportions of ^{208}Pb .

As the Pb isotope analyses were not the direct aim of the project, no standardised analyses were performed, other than using the two NIST glasses for comparison. Notwithstanding this, little or no ^{204}Pb was detected in most of the samples analysed, whereas substantial amounts of the radiogenic isotopes were detected, in agreement with previous findings. The ratio of $^{207}\text{Pb}/^{206}\text{Pb}$, however, was not constant for all the samples, and in some the variation was considerable and distinct, indicating that a real variation exists in the relative proportions of these isotopes in some parts of the Witwatersrand Basin, especially in the Klerksdorp goldfield and the Driefontein and Oryx mines, which also show the Ni enrichment.

Baker *et al.* (2006), in a study of Pb isotopes in archaeological copper and silver artefacts, showed that the analysis of high (> 500 ppm) and low (< 100 ppm) Pb artefacts by LA-ICP-MS results in an offset in the data for samples with a low Pb content when compared to TIMS and bulk dissolution analyses. They concluded that this was “probably an effect of relatively high matrix to lead ratios varying space-charge effects in the plasma”, and that while laser ablation was suitable for metals containing high concentrations of Pb, it was not suitable for metal containing low Pb contents.

Due to the analytical uncertainties in the Pb isotope results in this study, further analysis using bulk dissolution needs to be done to be certain of the behaviour of the Pb isotopes before any conclusions can be drawn.

7.2 Discrimination within goldfields

7.2.1 Klerksdorp goldfield

In the Klerksdorp goldfield, the reefs mined are the Vaal Reef, Ventersdorp Contact Reef ("VCR") and the Crystalkop ("C") Reef, of which the Vaal Reef has the majority of the reserves and produces most of the gold. High gold values in the Vaal Reef often occur at the base of the reef, associated with high uranium values and carbon. The lower gold grade VCR, about one kilometer above the Vaal Reef, has approximately 15 percent of the estimated reserves concentrated mainly in the western part of the goldfield. The thin Crystalkop Reef, which also has a carbon-rich basal contact, comprises less than one percent of the reserves. Most of the mines in the Klerksdorp goldfield mine the Vaal Reef as their principal gold ore, with the exception of Tau Lekoa mine to the west, which mines the VCR.

Within the d'ore gold samples from the Klerksdorp goldfield some systematic variation is observed between Cu and Ni (Fig. 7.7). This is interpreted as a direct reflection of the reef mineralogy and composition, with the VCR having a greater Cu content than the Vaal Reef. All the mines, with the exception of Tau Lekoa, mine mainly the Vaal Reef, and show an increase in Cu content in some samples which is interpreted as being due to the addition of VCR to the ore.

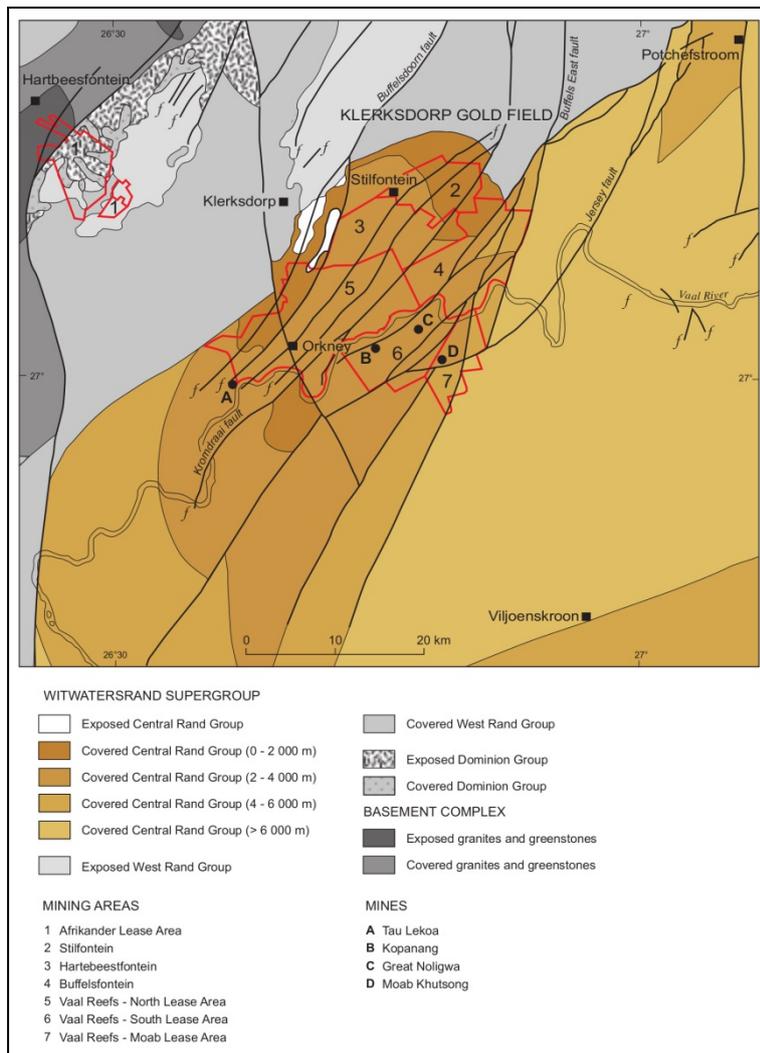


Figure 7.6. The Klerksdorp goldfield (modified after Robb & Robb, 1998), showing the locations of the Tau Lekoa, Kopanang and Great Noligwa mines in the former Vaal Reefs areas.

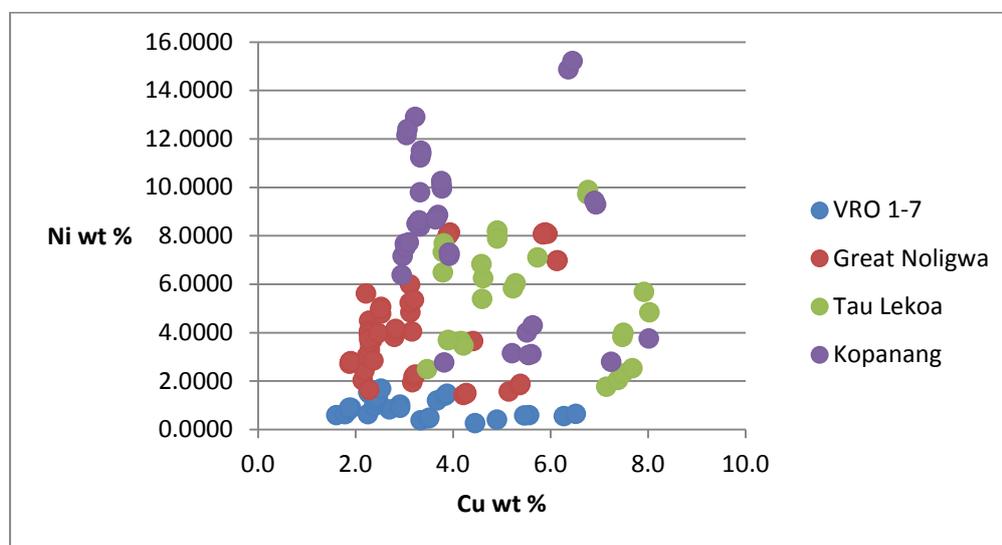


Figure 7.7. A plot of Cu vs Ni (ICP-OES, wt%) for d'ore gold from the Klerksdorp goldfields. The gold produced from the VRO 1-7 shafts, which are situated in the north of the Vaal Reefs area, are much lower in Ni than the other mines. Tau Lekoa, situated in the west and which mines the VCR, appears to have a greater amount of Cu than Great Noligwa and Kopanang in the east, which mine mainly the Vaal Reef.

7.2.2 Free State goldfield

The most important reef in the Free State goldfield is the Basal Reef, at a similar stratigraphic position to the Vaal Reef in the Klerksdorp goldfield. This is the main source of gold at St Helena Mine. Beatrix Mine, approximately 50 km south of Welkom, on the eastern side of the Ararat fault, mines the Beatrix Reef and the Beatrix-VS5 Composite Reef. The Oryx Mine, to the west of Beatrix, was originally started as a uranium mine, due to the very high uranium content of the Beisa Reef, but was later converted to a gold mine.

In the Free State goldfield (Fig. 7.9), discrimination between between St Helena mine and the Beatrix and Oryx mines can be made on the basis of the distribution of Ni and Cu between the three mines, with a clear distinction can be made between Oryx and St Helena (Fig. 7.8). Beatrix and Oryx show a distinct enrichment in Ni compared to St Helena, even though the levels are much lower than those found in the Klerksdorp goldfield. The process which caused the Ni enrichment does not appear to have affected the Cu content, as it behaves differently. It is possible that this reflects differences in the Cu content within the ores themselves, and that there is a geological or mineralogical control.

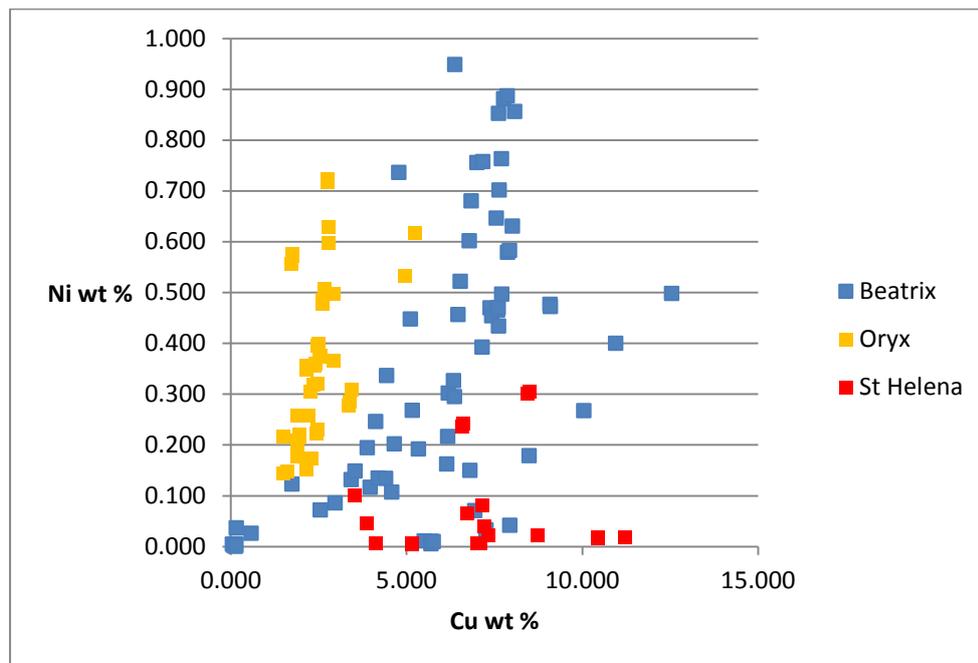


Figure 7.8. A plot Cu and Ni for the Beatrix, Oryx and St Helena mines in the Free State goldfields. The three mines extract their gold mainly from three distinctly different reefs, the most probable reason for the differences in the relative amounts of the two elements.

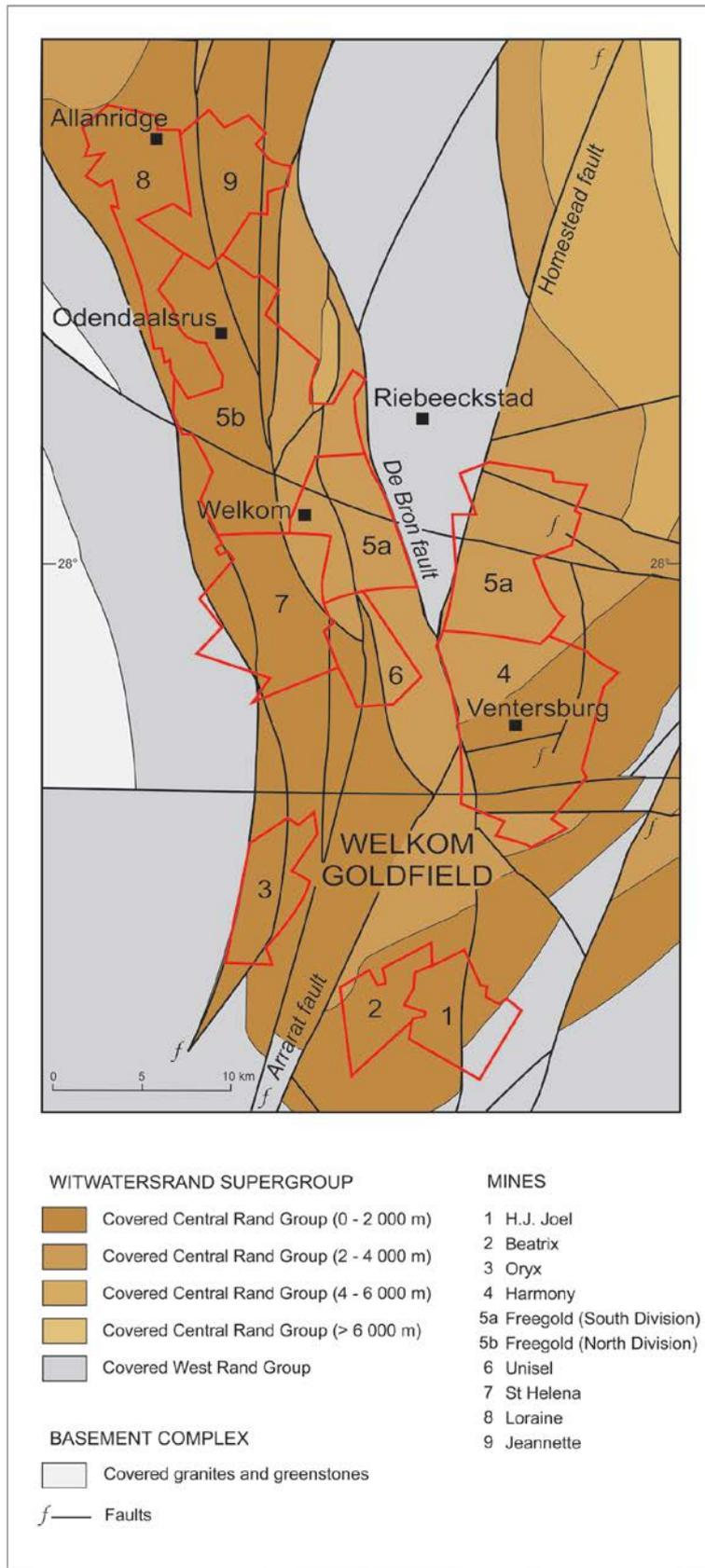


Figure 7.9. The mines in the Free State goldfield (modified after Robb & Robb, 1998).

Saager (1969a) showed that within the Free State goldfield there is a variation in the bulk ore Ag/Au ratio, which is highest in the northwest, correlating with the direction of transport of the sediments towards deeper water, away from the southeast. This increasing ratio is not seen in the composition of the individual gold grains, and indicates that Ag is mineralized separately, and not only in gold (von Rahden, 1965). Ag is widely disseminated within the ores of the goldfield, and several Ag minerals have been identified, including silver (Ag), proustite (Ag_3AsS_3) stromeyerite (AgCuS) and dyscrasite (Ag_3Sb) (von Rahden, 1963, 1965; Saager, 1968).

7.2.3 West Wits goldfield

The West Wits goldfield is cut in two by the Bank fault (Fig. 7.10), with Kloof, Libanon and Leeudoorn situated to the east of the fault. Kloof and Leeudoorn mined the VCR and the Kloof Reef, while Libanon mined the Main Reef. Driefontein, at the time when the d'ore samples were produced, was the only mine recovering most of its gold from the Carbon Leader Reef. The rest of the mines to the east of the Bank Fault produced most of their gold from the VCR.

The difference in the source of the gold ore is clearly seen in the distribution of Cu and Ni, where Driefontein is distinguished from the rest by its higher Ni content. In Fig. 7.11 it is possible that there is a slight geographical trend with increasing Cu content from east to west within the VCR, which is similar to the increase in the ratio of U to Au within the Carbon Leader westward across goldfield (Buck & Minter, 1985). As there is no geographic control on the samples, other than from which mine they came from, a correlation with distance from each other and distribution within the goldfield cannot be made. The variation in the Cu content must be related to a variation in the ore composition, which is either due to primary mineralization or secondary processes thereafter.

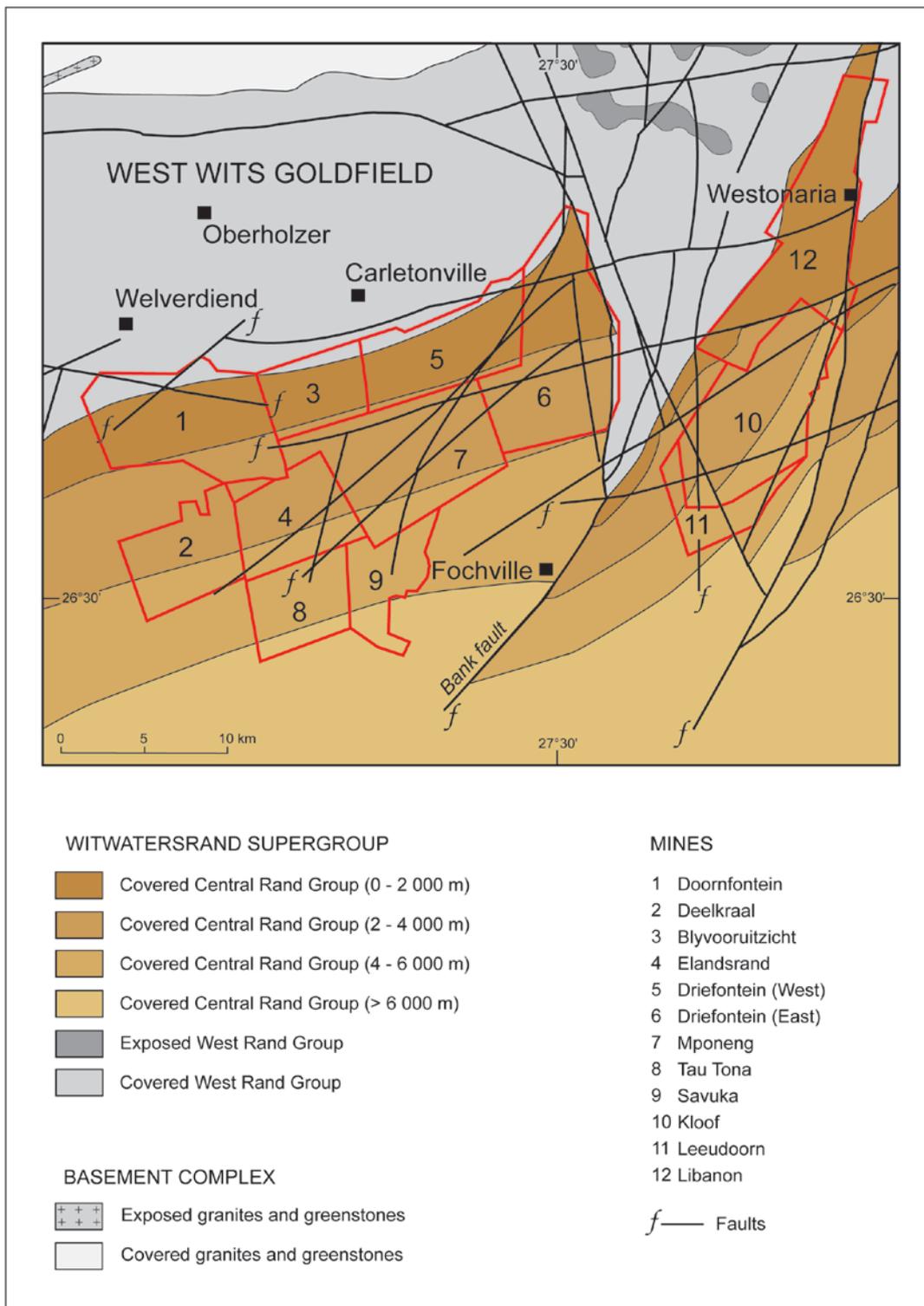


Figure 7.10. The mines in the West Wits goldfield. Driefontein was created in 1981 with the merger of West Driefontein and East Driefontein mines. Tau Tona (to the west) and Savuka (to the east) were named after the split up of Western Ultra Deep Levels (modified after Robb & Robb, 1998).

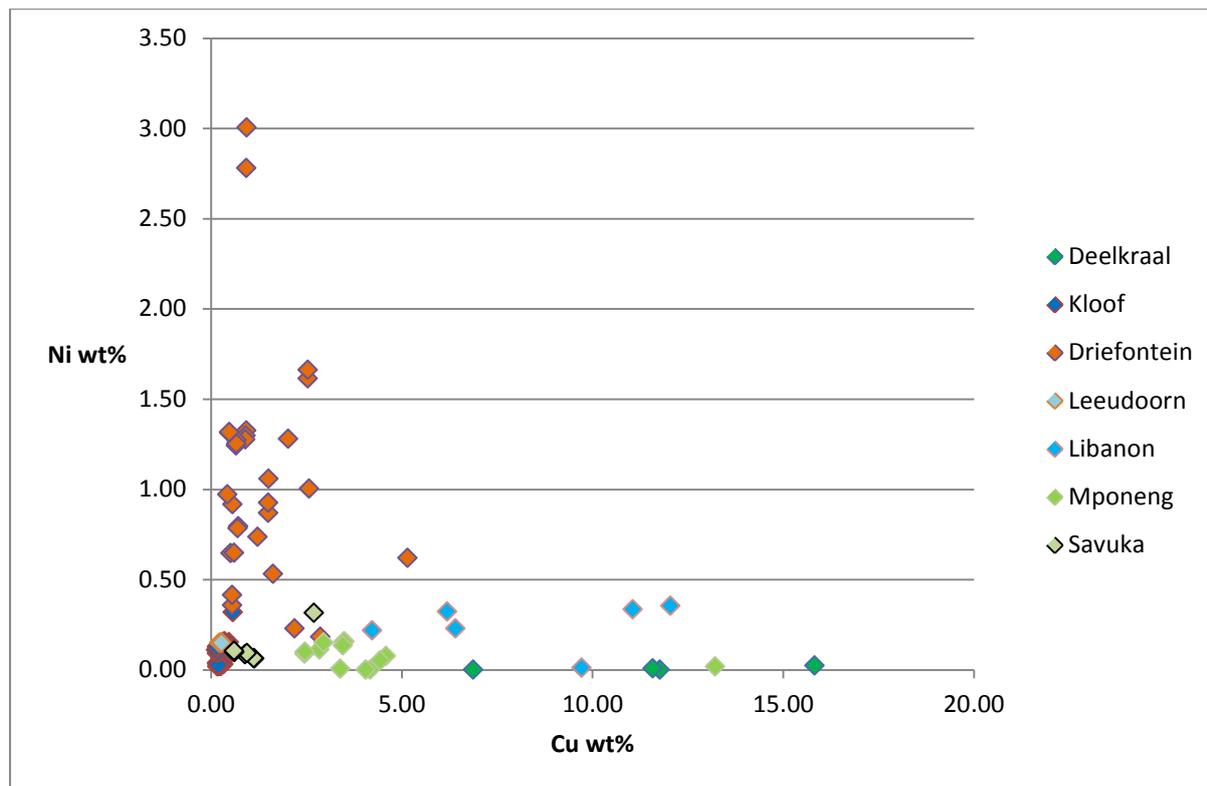


Figure 7.11. A plot of Cu vs Ni for the mines of the West Wits goldfield. Driefontein d’ore is highly enriched in Ni and low in Cu, and produced mainly from the CLR. Mponeng and Deelkraal, which mined the VCR, show an apparent increase in Cu from east to west. Savuka, which mines VCR with some CLR, shows similar behavior to Driefontein, but to a lesser degree. Libanon, which mined the Main Reef, shows similar behavior to Kloof and Leeudoorn, which mined VCR and some Kloof Reef.

7.3 Discrimination between mines

Using the various characteristics identified above, a d’ore gold sample from any of the mines on the database may allow identification of the goldfield it originates from, and a variable degree of probability exists of identifying the mine which produced it. Using a single characteristic, however, will not be sufficient to ensure discrimination.

The analyses of the d’ore gold from the three goldfields have shown that, overall, a few elements can be used consistently for a varying degree of comparison and discrimination between various sources. The elements are those which are consistently present in the ICP-OES results and not below detection limits.

Within the southern African context, discrimination can also be made between gold coming from the Witwatersrand Basin which has an anomalous Pb isotope distribution, due to the high U associated with the gold mineralization, especially in reefs which contain carbon such as the Vaal Reef (Klerksdorp goldfield), the Carbon Leader Reef (West Wits goldfield) and the Basal Reef (Free State goldfield) (Horscroft *et al.*, 2011), and gold from other types of

deposits or as manufactured alloys, which show a more typical relationship between the isotopes. The presence of anomalous radiogenic Pb isotopes is distinctive of gold recovered from the Witwatersrand Basin.

Once the recovered suspect gold has been analysed and has been identified as having originated from the Witwatersrand Basin, and possibly the goldfield or mine, the issue of legal ownership is then addressed. In some goldfields ownership of all or a large proportion of the mine shafts and mines vest in a single owner. Here, identification to the goldfield would be sufficient grounds for returning the gold to its rightful owner.

One of the problems which is encountered in the database is the distribution of samples from the different producers, and the fact that only producing mines submit d'ore gold samples. Furthermore, the only producers who regularly submit samples as required by law are the larger, more established mining companies. The wide variation seen in the composition of the extracted gold from a single producer, due mainly to variations in the composition and type of reefs mined, makes it difficult to discriminate between shafts in close proximity, unless the geological variation is marked, such as mining areas separated by a large fault.

In situations where the discrimination is not unequivocal, additional information is required, such as information received during a criminal investigation (*i.e.* where the material was seized, was the suspect a worker at a particular mine, etc.). This information, although not chemical or geological in nature, is part of the information which can be used to identify provenance to an as closely circumscribed geographic origin as possible.

8 Variation of composition of gold prills between reefs at the Driefontein mine

The majority of samples in the gold database consist of drillings from d'ore gold bars, which are usually the product of the mining activities at a single shaft, or a few close shafts mining the same reefs and supplying a single mine smelter. This mixture is dependant on a number of factors, such as gold grade, ease of extraction and processing economics, and is not constant over time. This gold is unrefined and represents the product of mineralisation and extraction, and compositional variation between them should represent differences in mineralisation.

In order to determine whether a sample of d'oré gold is representative of the gold mined at a particular shaft, it is necessary to determine whether the composition of the gold extracted from a single reef is sufficiently distinct from the other reefs in a single shaft so as to affect the overall profile obtained for the doré. As has been shown in Chapter 6 there is a distinct variation between the d'ore gold produced in the Witwatersrand Basin both within goldfields and between goldfields, and also that there appears to be a correlation between the composition of the gold produced and the specific reef from which it is extracted. In Chapter 5 it has been shown that post-depositional processes due to weathering, transportation and chemical activity can produce a distinct trace element fingerprint, or profile, which is clearly detected in the resulting d'ore gold.

The composition of the gold that the mines produce will vary from each smelt according to the proportions of different reefs mined and the relative proportions of different reefs combined in the metallurgical processing plant. It is necessary to determine whether the trace element content of the d'ore gold is representative of the trace element content of the in-situ gold that undergoes metallurgical processing and changes as it is converted into d'ore gold at the mine smelthouse.

8.1 Use of prills as indicators of reef gold composition

In order to sample the gold in the reefs in a consistent manner, it was decided to look at the composition of the gold prills which were produced as part of the routine grade determination during routine mining. Fire assay of gold-bearing ore is a standard method for determining

gold grade during mining (Haffty *et al.*, 1977), and each stope is routinely sampled in order to determine the optimum feed to the processing plant. Due to the large tonnages mined in the gold mines of the Witwatersrand Basin, fire assay is the method of choice for grade determination, as it is quick, cheap, consistent and reliable.

The prills are formed during fire assay of reef samples, and they provide the best available record of the in-situ gold composition at the sampling point. If the prill compositions can be correlated with the bullion composition from the same mine, then it would be sufficient merely to sample the doré for gold profiling purposes. It should be remembered, however, that the flotation process to concentrate the gold, and the gravity and magnetic separation processes during which PGE are removed from the ore, will have an effect on the d'ore composition which will not necessarily be reflected in the gold prill produced by fire assay, as some PGE, like Pd, are also collected during the fire assay process.

The variation in prill composition would allow the determination of the distribution of gold-associated elements within a reef, which is a direct reflection of the mineralogical associations with the gold, and could give some insight into the processes which led to the gold mineralisation.

8.2 Sampling and analysis

Due to the logistical problems associated with collecting samples underground during mining operations, and the subsequent fire assaying, it was decided to utilise the prill samples as produced by the mine during routine operation. Accordingly, duplicate prills for mining operations for approximately one month (December, 2005) at the Driefontein Mine near Carletonville were obtained. The sample mass and fire assay method was constant for all samples. The reefs being mined at the time were the Carbon Leader Reef (CLR), the Main Reef (MR) and the Ventersdorp Contact Reef (VCR). The majority of the ore processed, however, was supplied by the CLR and VCR, and as these two reefs are situated towards the bottom and on top of the Central Rand Group, they should show the greatest degree of variation in relation to each other. For this reason it was decided to concentrate on these prills first, to evaluate differences.

The prills were each individually weighed, mounted (see Fig. 4.1) and then analysed utilising an Agilent 7500 Cx ICP-MS connected to the New Wave 213 nm laser ablation system.

The gold content was determined by difference - it is assumed that the sample comprises only the analysed elements and gold: $\% \text{ Au} = 100\% - (\text{total } \% \text{ of other trace elements})$. The wt% of the other elements was obtained with a calibration using the NIST 610 and NIST 612 glasses and a gas blank. The amounts obtained by this process are semi-quantitative at best, and are used to identify relative differences. Ideally, the prills do not contain much Pb, Bi, Se, Tl or other volatile elements, as these are removed during cupellation, together with Pb (Haffty *et al.*, 1977). The values for some PGE (Ru, Os and Ir) are also under-reported for lead-collection fire assay (Diamantatos, 1977).

8.3 Prill composition in the Carbon Leader Reef

The 86 prills displayed an asymmetrical mass distribution, with proportionately more low weight prills than high weight prills (Figure 8.1). The prills have a variable Au content (Figure 8.2) and contain large amounts of Ag, Pd and Pt (Figures 8.3 to 8.5).

8.4 Prill composition in the Ventersdorp Contact Reef

The 140 prills showed two populations by mass. The first population has a narrow mass range. The second population of larger prills has a strong tail of larger prills (Fig. 8.6).

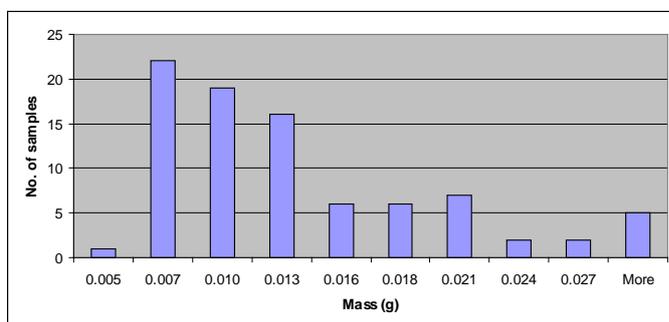


Figure 8.1. Mass distribution of Carbon Leader prills from Driefontein Mine

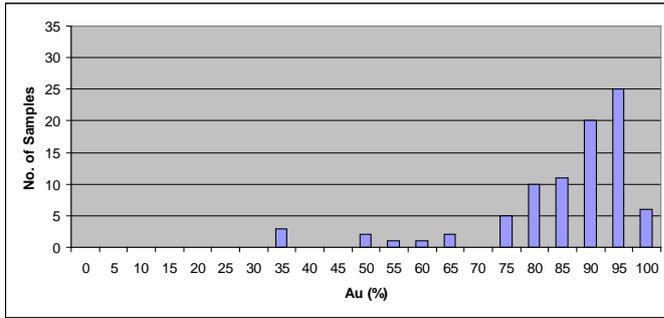


Figure 8.2. Distribution of Au (wt%) in Carbon Leader prills from Driefontein Mine

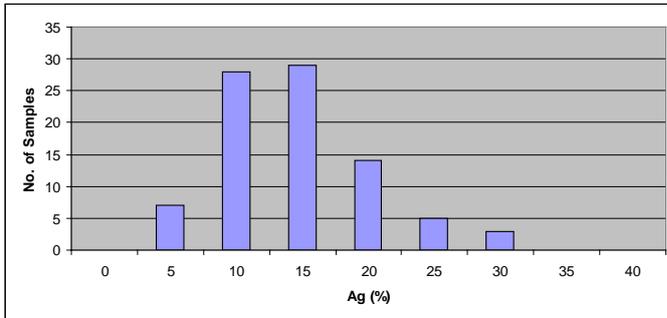


Figure 8.3. Distribution of Ag (wt%) in Driefontein Carbon Leader prills

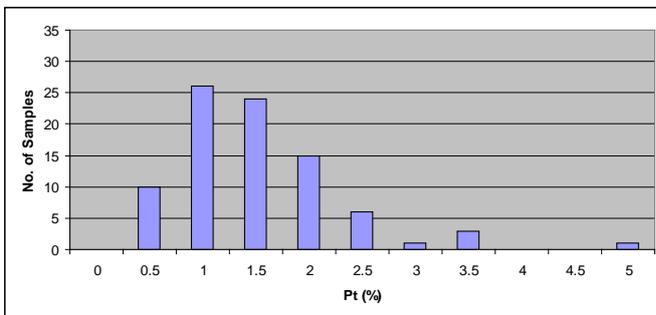


Figure 8.4. Distribution of Pt (wt%) in Driefontein Carbon Leader prills

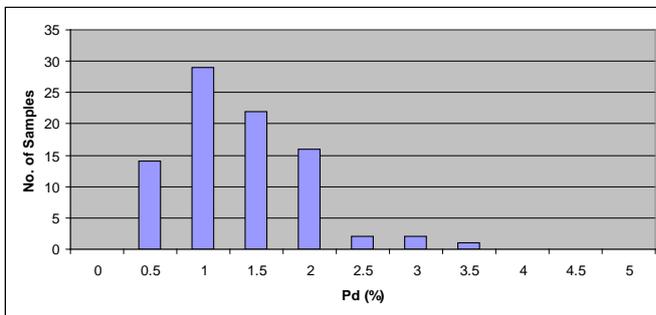


Figure 8.5 Distribution of Pd (wt%) in Driefontein Carbon Leader prills

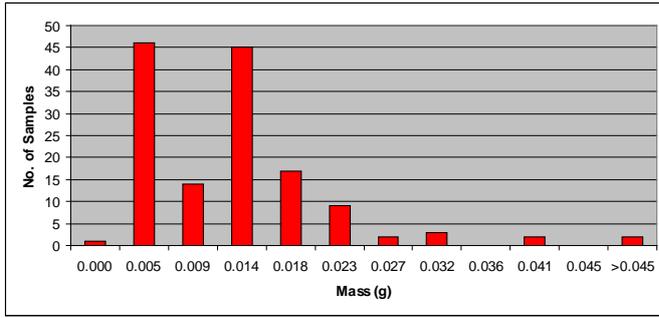


Figure 8.6. Mass distribution for Driefontein VCR prills

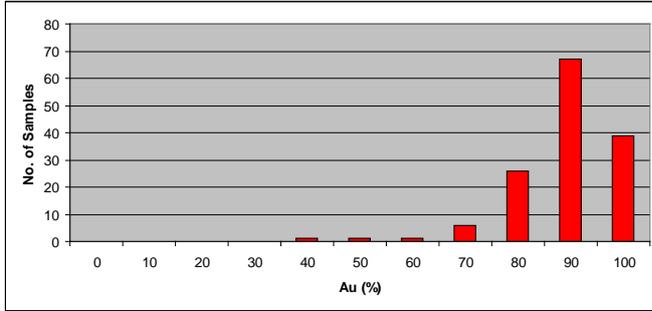


Figure 8.7. Distribution of Au (wt%) in Driefontein VCR prills

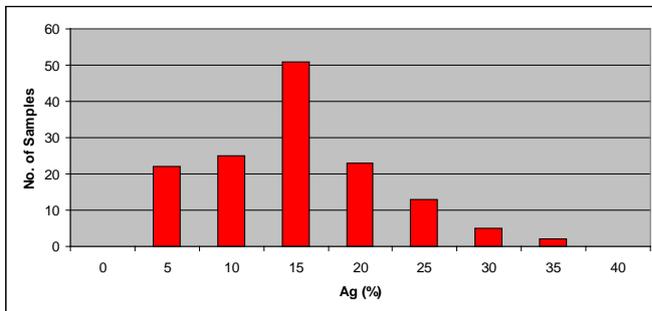


Figure 8.8. Distribution of Ag (wt%) in Driefontein VCR prills

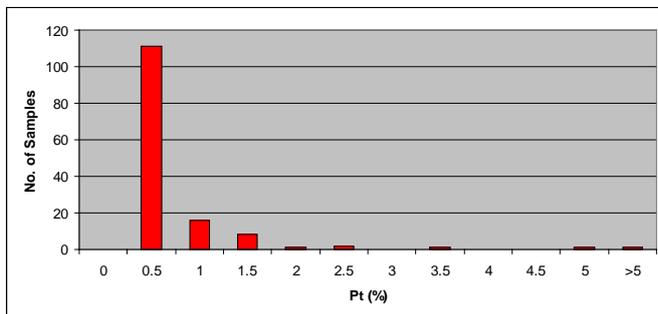


Figure 8.9. Distribution of Pt (wt%) in Driefontein VCR prills

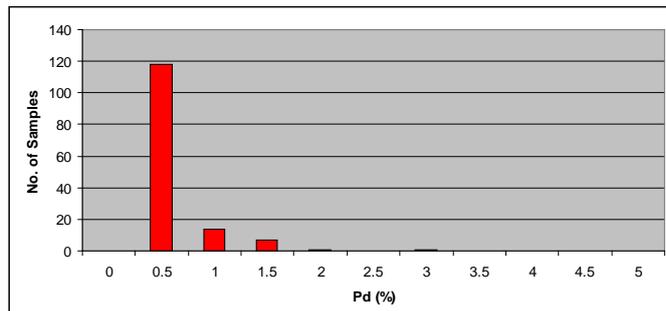


Figure 8.10. Distribution of Pd (wt%) in Driefontein VCR prills

8.5 Differences between the CLR and VCR

The mean gold content (by difference) of the VCR prills (85.05%) is higher than in the CLR (80.11%), and the mean Pt and Pd contents are quite different, with very large variability in the VCR compared to the CLR.

The Carbon Leader Reef at Driefontein shows median prill values of ~ 1.5% for both Pt and Pd (Figures 8.4 & 8.5). This contrasts with the VCR prills, which have occasional high PGE contents, but generally show low median distributions of ~ 0.5% for both Pt and Pd (Figures 8.9 & 8.10).

The use of gravity and magnetic concentration showed that there are higher levels of metallic PGE minerals in the VCR than in the CLR (Feather & Koen, 1975). The fire assay method used is optimised for the extraction of Au, and some PGE which occur as PGM might not be collected as efficiently as gold. The main difference observed in the PGE in the prills is the variation of Pt and Pd values in CLR vs the VCR (Fig. 8.11). The distribution of Pt and Pd in the CLR prills is similar (Figs 8.4 & 8.5). However, the distribution of the two elements in the VCR shows a different behaviour, with Pt having a number of prills showing much higher Pt values, in excess of 5% (Fig. 8.9). The lower Pt and Pd concentrations observed in the VCR, which has higher overall values than the CLR (Feather & Koen, 1975), shows that the Pb-collection fire assay technique is favouring PGE in some minerals over others, and therefore the PGE are distributed differently in the VCR compared to the CLR.

A plot of the relative proportions of Pt, Pd and Sn for the prills from the CLR and the VCR (Fig. 8.12) shows that the CLR has proportionally lower Sn than the VCR. The Sn distribution in the VCR, while overlapping with CLR, shows an area of high Sn. These high Sn prills appear to indicate a systematic relationship with Pt, while the low Sn prills, which overlap with the majority of the CLR prills, appears to indicate a systematic relationship between Pt and Pd.

The prill compositions show that there are some clear differences between the proportions of some elements in the CLR and the VCR at Driefontein mine, but that a clear distinction between the two based on a single sample, such as a seized piece of stolen gold, is not likely. The mode of recovery of the raw material which is processed to produce the illicit gold will also play a dominant role in the final composition, as shown in Chapter 6. What we see from

this is that illicit gold from either reef or a combination of the two will all have a very similar composition, and so the probability of identification as to a specific mine or area is strengthened.

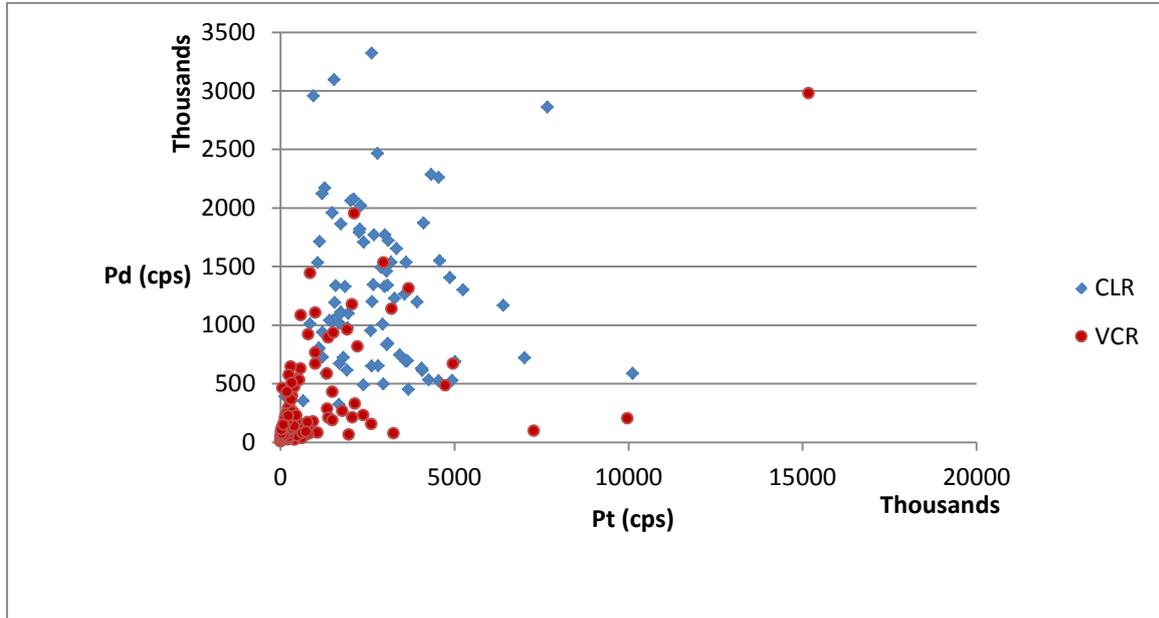


Figure 8.11. A plot of the Pt and Pd contents of the prills from the VCR (red dots) and the CLR (blue diamonds). There is a broad spread in the ratios between the two elements, with some overlap between the two populations which would be expected due to an alluvial component in both reefs. The difference in behavior of the two elements between the two reefs shows a difference between the CLR prills compared to the VCR prills, which could be attributable to another mineralizing component present in the CLR.

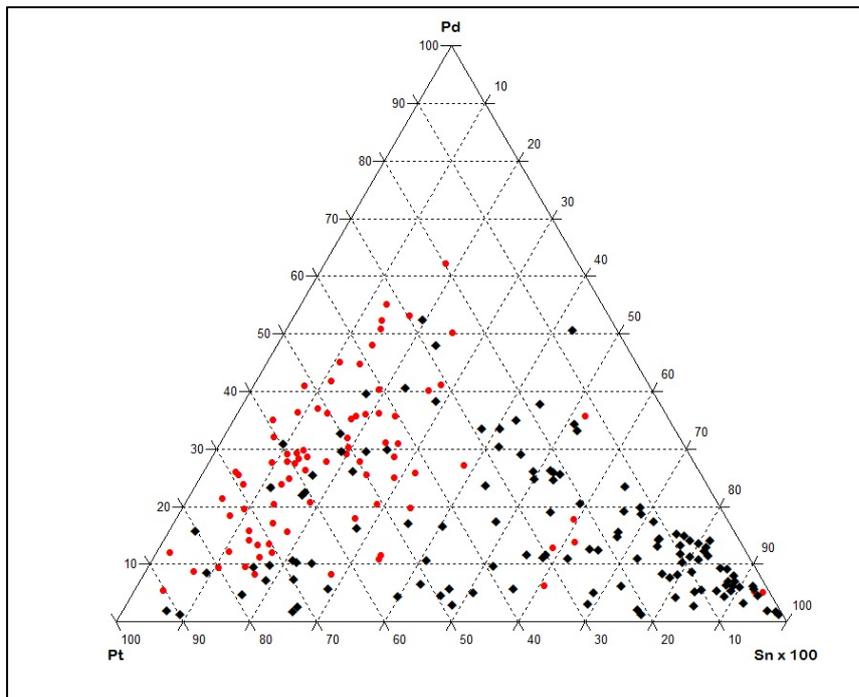


Figure 8.12. This plot of the relative proportions of Pt, Pd and Sn for the prills from the Carbon Leader Reef (circles) and the Ventersdorp Contact Reef (diamonds) shows that the CLR has proportionally lower Sn than the VCR. The Sn distribution in the VCR, while overlapping with CLR, shows an area of high Sn. The high Sn prills appear to indicate a systematic relationship with Pt, while the low Sn prills indicate a systematic relationship between Pt and Pd.

9 Identification of source of stolen gold against the database

A test case for determining whether the database is effective in determining origin arose when twelve pieces of illicit gold were seized during the course of a clandestine operation. The seizure was made in the vicinity of the Driefontein mine, and information received was that some of the gold had been stolen from the mine itself. It was necessary to determine whether the gold had in fact come from the mine, in order to return it to its rightful owners. Fig. 9.1 illustrates some typical pieces of seized illegal gold, called “buttons”, which were inside the shoes of the suspect when arrested. Eleven pieces of gold were seized in three separate batches during the same operation - a group of 6 items (Group A, items 11 to 16), a single item (Group B, item 100), and a group of 5 items (Group C, items 31 to 34, 37).



Figure 9.1. Gold “buttons” hidden in the shoe of a suspect. This is a typical size and shape of gold produced illegally from material stolen from mines in the Witwatersrand goldfields.

The samples were drilled and analysed quantitatively by ICP-OES and then a number of drillings from each sample were analysed by LA-ICP-MS. The analyses showed that the suspect samples contained elevated levels of certain elements, such as As, Sn and PGE, which were not typical of the d’ore gold in the database (see Fig. 9.3 for a few comparisons). There is a substantial amount of platinum-group element minerals associated with the gold-mineralised reefs within the Witwatersrand Basin, of which alloys of Ir, Os and Ru constitute approximately 80%, with sperrylite (PtAs_2) and other arsenides also common (Feather, 1976; Malitch & Merkle, 2004). In addition, other heavy minerals such as cassiterite (SnO_2) are

found with the PGE minerals in heavy mineral separates and gravity concentrates in mine plants (Feather & Koen, 1975). The gravity separation process therefore reduces the amount of these elements which might be liberated during the floatation, CIP processing and the smelting process.

The adsorption of Au onto activated carbon in the CIP process is most effective within a specific pH range, and this affects which elements are recovered efficiently (Stange, 1999). The high pH at which Au is best recovered is also the range at which the best recovery of Ag, Co, Mn, Cd, Cu, Ni, Pb and Zn is effective (Laxen *et al.*, 1979; Koshima & Onishi, 1986). The gold extraction process used at the mine processing plants also removes elements such as Hg, As and Sn, so the presence of high levels of these shows that the processing method to produce the d'ore gold at legal processing plants has not been used. High amounts of these elements is indicative of a manual concentration process, such as panning or amalgamation (alloys), and therefore these samples are considered to have been illegally processed by other methods.

In order to identify the type of material processed to produce the buttons, the differences seen in the compositions of the suspect samples had to be identified, and the reason for these differences identified. Groupings which are identified will therefore represent gold extracted from different materials which were stolen at different stages of the beneficiation process utilized at the mines. If the source material for all the suspect was the Driefontein mine, then what factors and conditions would give rise to the different groups? A good indication of the different sources can be gained by examination of the elements of difference, as well as the homogeneity of the material.

Principal component analysis of the suspect samples together with Driefontein samples from the database resulted in the suspect samples showing three different behaviours, differentiated mainly by Cu, Ag and Pt. The Driefontein samples group with suspect samples items 11 to 16 and item 34.

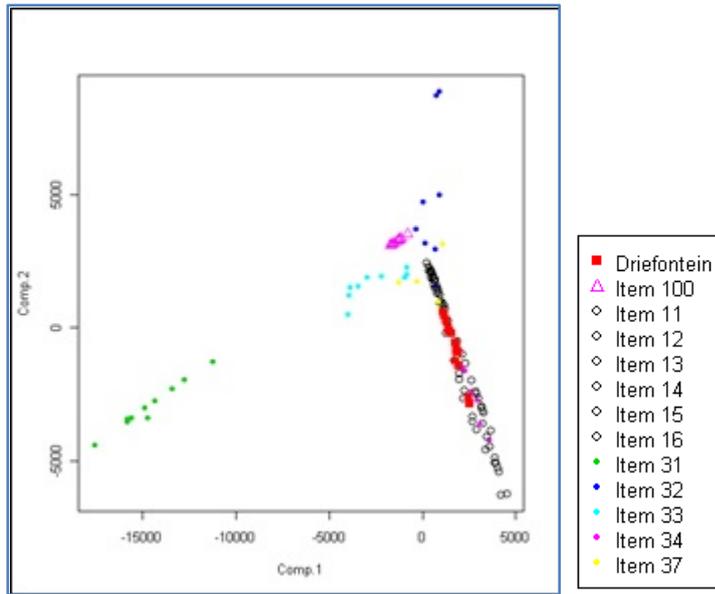


Figure 9.2. Principal component analysis of the suspect samples and Driefontein samples from the database. The main components that separate out are Cu, Ag and Pt, with the suspect samples appearing to fall into three separate groups. The Driefontein bullion samples are distinct from items 31, 32, 33 and 37 and item 100. Items 11 to 16 and item 34 group with the Driefontein bullion d'ore samples.

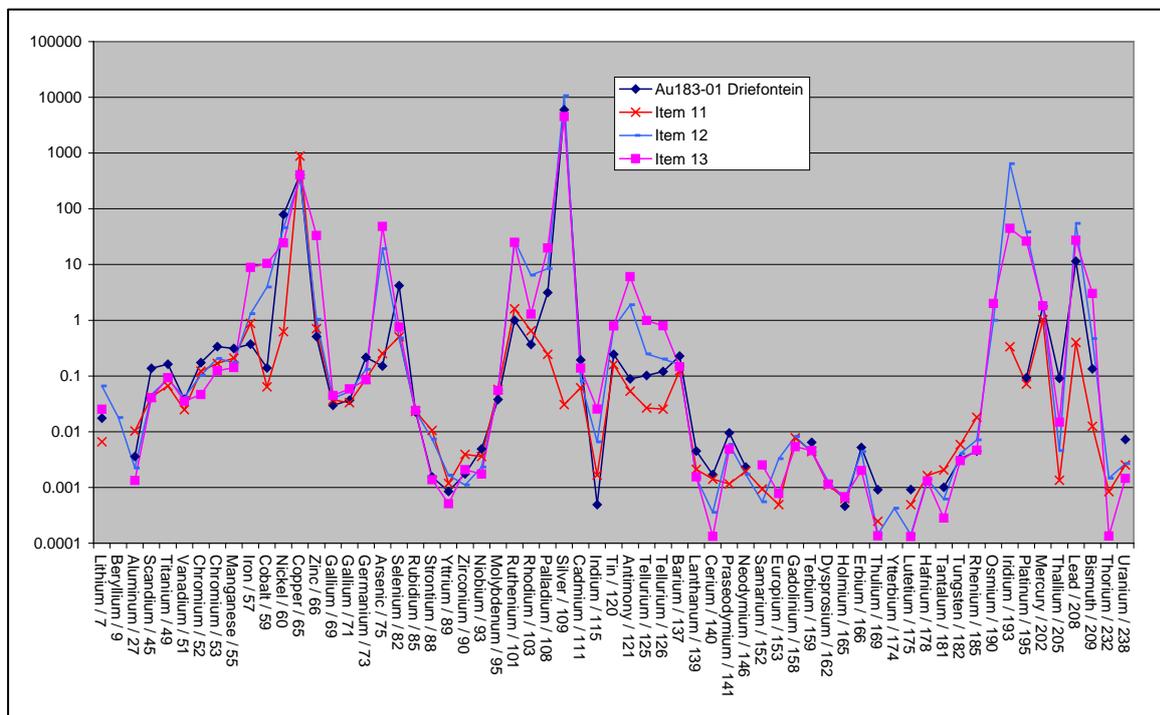


Figure 9.3. Three of the suspect gold samples plotted against a representative sample from the Driefontein mine from the database showing the similarity in elemental abundances (counts per second obtained by LA-ICP-MS).

A plot of two of the elements which show differences between the groups, Pt and Sn, is shown in Fig. 9.4. This plot shows that the samples from Group A form two tight clusters close to each other, with little variation within each sample. These samples appear to be relatively “clean” (fewer elements present) and consistent, as though the source material they

had been produced from had already been through a beneficiation process prior to being processed to extract the gold. Group A falls within the field for the samples from Group C, which have a very contrasting behaviour, with a wide spread between and within samples.

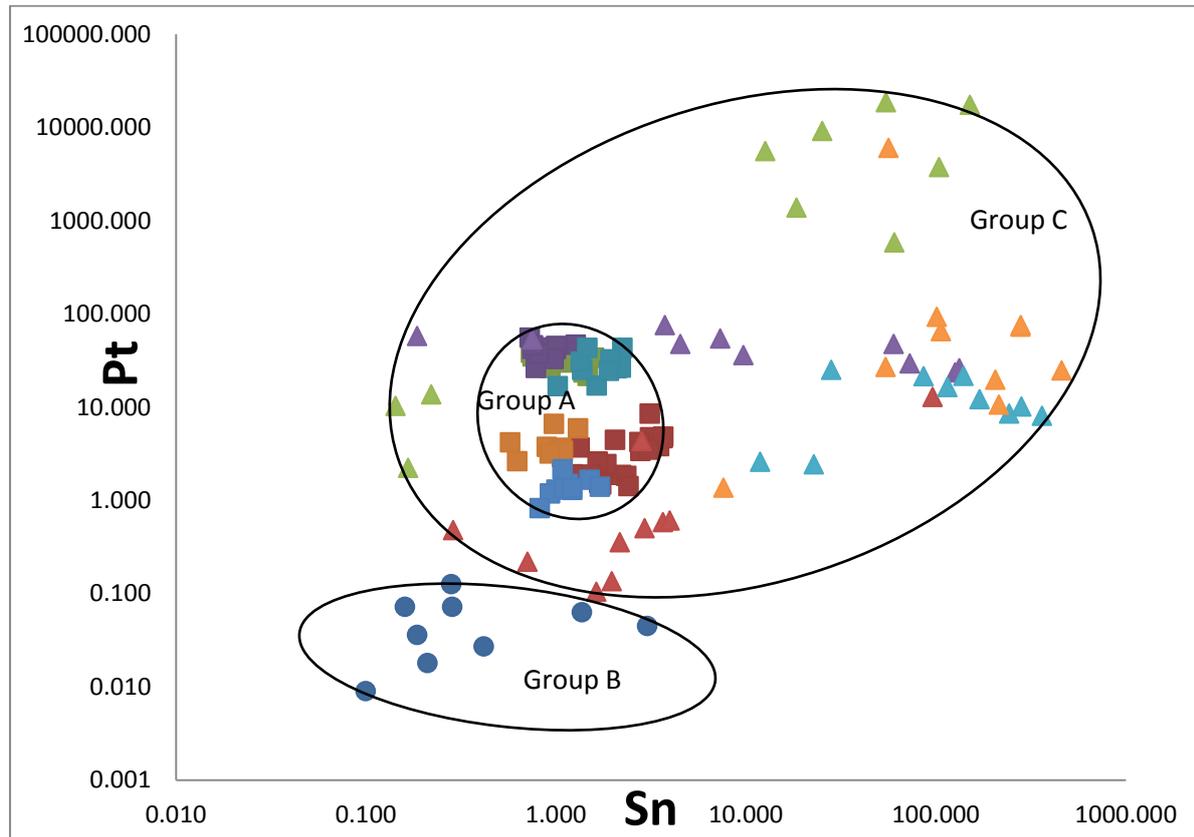


Figure 9.4. Plot of Sn and Pt for the suspect gold samples. Group A (squares) and Group C (triangles) are distinctly enriched in Pt and Sn compared to Group B (circles), showing that the raw materials processed to extract the gold were different. The large variability in Group C is indicative of various batches being processed, while the tight clustering of Group A shows that possibly two batches of the same material were processed to produce that gold. The data points which have the same shape and colour are all from the same sample, and it can be seen that Group C shows a large variability, possibly due to poorer extraction as well as the inhomogeneous melting together of smaller pieces of gold.

In Fig. 9.4 Group B shows low Pt and Sn levels and Group A has similar Sn and higher Pt levels. Both groups form relatively tight clusters and could represent material which has been processed to some degree before production of the gold buttons, leading to a more homogeneous composition, while Group C is highly variable, with some samples highly enriched in Pt and Sn. A plot of these three groups using Pt, Pd and Sn (Fig. 9.5) shows a systematic relationship between Pt and Pd in Group A, a systematic relationship between Sn and Pd in Group B and a relative depletion in Pd and enrichment in Sn in the quite variable Group C.

In Group A two distinct subgroups are identified. These two subgroups are clearly separated by their to Co, Ni, As, Sn and Sb and the PGE abundances (see Fig. 9.3) and this is clearly

shown for As in Fig. 9.6. The variation between and within the various gold buttons in the three groups (A, B and C) is attributed to an interplay of different factors. Material being stolen at different parts of the beneficiation process will give different elemental distributions, while the tightness of the distribution of the analyses of a single sample shows how homogeneous the source material was.

The relative homogeneity of the gold in Group A could possibly be attributed to a derivation from flotation concentrates, which would give rise to a homogeneous fine-grained milled material. The two different subgroups could be due to the material coming from different parts of the process after flotation, which could account for their clear discrimination based on relative As abundance (Fig. 9.6), or possibly to a different source of ore being milled at the time of theft.

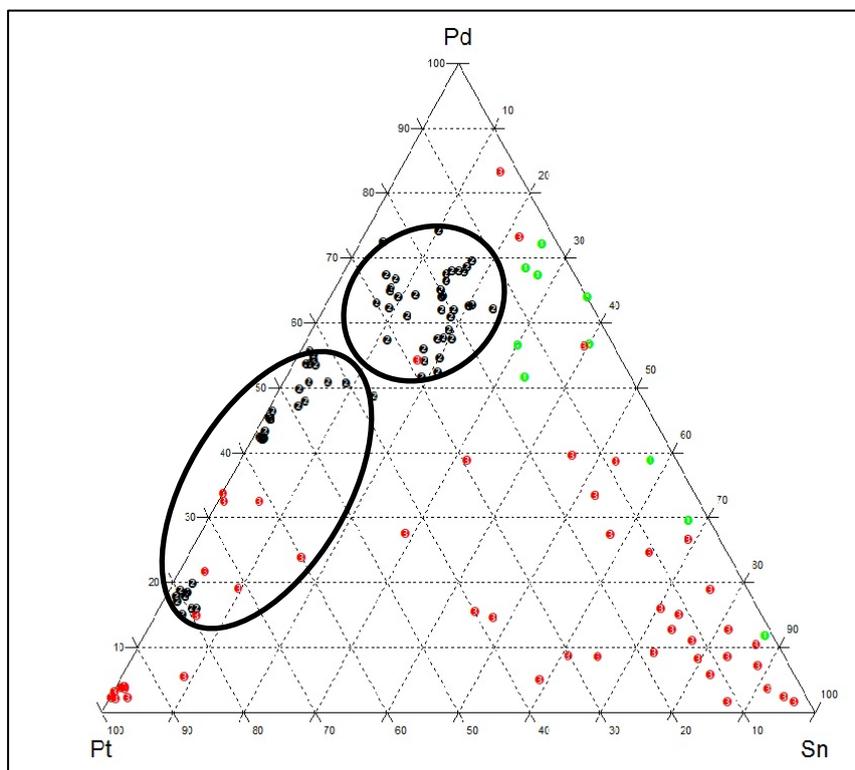


Figure 9.5. The suspect samples showing relative abundances of Pt, Pd and Sn. Group A (black circles) shows a systematic relationship between Pt and Pd. The ringed clusters show the two subgroups of Group A. Group B (green circles) show a systematic relationship between Sn and Pd. Group C (red circles) is quite variable, but does show a relative depletion in Pd and enrichment in Sn.

At Driefontein mine the Ventersdorp Contact Reef and Carbon Leader Reef are the main sources of gold and have different mineralogies (Feather & Koen, 1975), so variation in d’ore gold and stolen gold from the mine could reflect these differences. However, the many differences between the different groups, which are not consistent between all three groups,

indicate that the final gold product is also very dependent on the material from which the gold is extracted, and the manner in which it is extracted. This is clearly shown in Fig. 9.7 where Groups B and C show a systematic relationship between Pb and Sn, whereas Group A shows a relative enrichment in Pb while displaying the same systematic relationship. This could be a reflection of the mineralogy of the material processed, possibly modified after flotation, with the extraction process contributing to these differences. For elements such as Pb which are volatile, the temperature at which the gold is smelted will affect the content of such elements, so this cannot be used as a diagnostic tool for origin. However, it can show similarities between different batches of samples which were smelted from the same type of material under the same conditions, and thus link samples to a single origin.

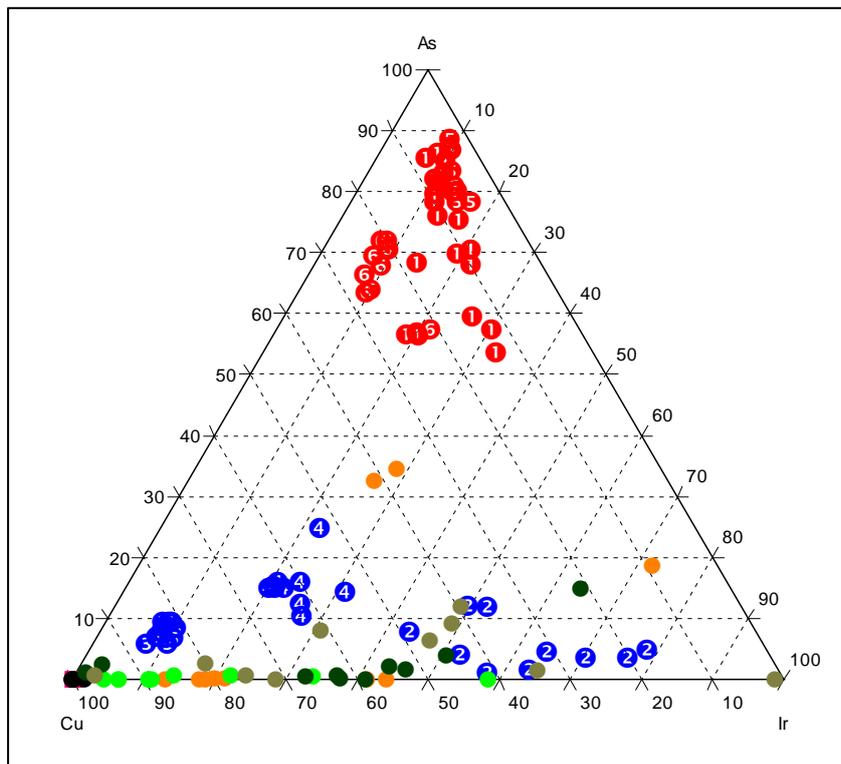


Figure 9.6. Plot of the suspect samples. Data points with the same colour or number are repeat analyses of the same sample. Group A is subdivided into a relatively As-rich subgroup (red numbered filled circles) and an As-poor subgroup (blue numbered filled circles). Group B sits at the Cu apex, and Group C (filled circles) show a large variation in relative Ir abundance. Group A shows tighter clusters of its repeat analyses, compared to a much wider spread for Group C.

Identifying these differences without the original material is dependent on knowledge of the original mineralogy and the effects of all the processes, and the answer obtained cannot be proven beyond doubt without experiment. This limits the applicability of a comparison against a database where the samples in the databases are the products of a different process to those of the illegally obtained and processed gold.

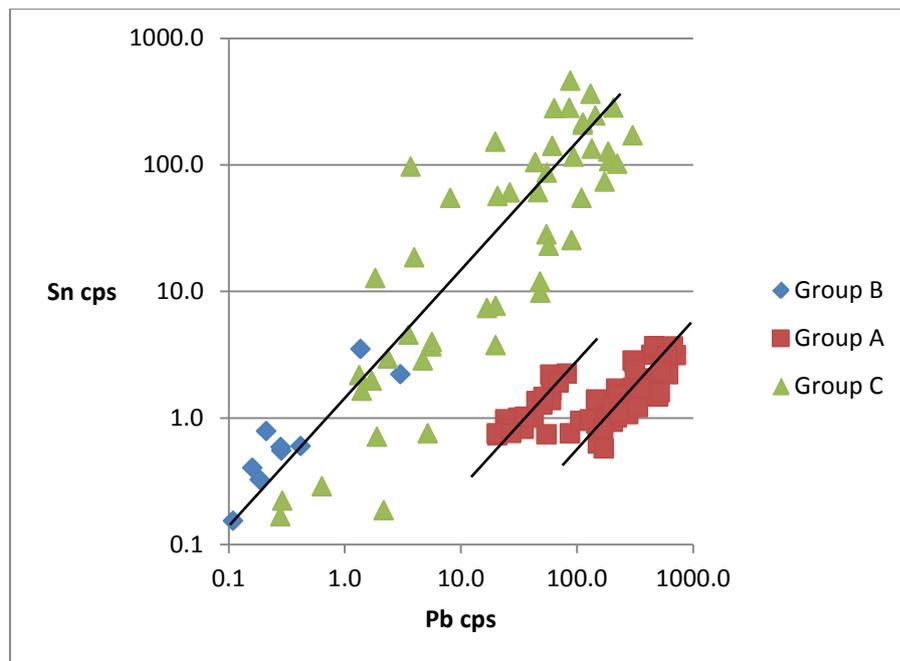


Figure 9.7. A plot of Pb vs Sn (LA-ICP-MS, cps) showing the tight clustering of the two subgroups of Group A (squares) and the broad range occupied by Groups B (diamonds) and C (triangles). The systematic trends in the different groups show the same slopes, and this is attributed to the loss of these two volatile elements during smelting, with a lower concentration attributed to a higher smelting temperature.

In naturally occurring gold in the Witwatersrand basin, the predominant elements associated with Au are Ag and Hg, with traces of Cu and a few other elements (von Gehlen, 1983; Oberthür & Saager, 1986; Erasmus *et al.*, 1987; Reid *et al.*, 1988; Frimmel *et al.*, 1993; Frimmel & Gartz, 1997; Hayward *et al.*, 2005; see Chapter 2.5). During the beneficiation of the gold ore to produce d'ore gold, only trace amounts of the Hg would be retained, while Cu is enriched, being recovered from other minerals which are concentrated during the flotation process (see Fig. 9.8). The amount of Cu seen in the suspect samples would thus potentially indicate at which stage of the beneficiation the source material was derived.

In Fig. 9.8 Group A is shown together with native gold and the d'ore gold in a plot of Cu vs Ag. The two subgroups previously identified in Group A are clearly distinguished, with the high As subgroup showing Cu at below the detection limit. As the information received was that the gold came from Driefontein, the starting material used by the illicit miners could have been ore, flotation concentrate, mill-liner concentrate or even gold amalgam, among others. A potential source of the suspect samples with no detectable Cu could thus be inferred to be from native gold. Within the gold mines, Hg is often placed in drainage channels where gold flakes, liberated during mining, are washed from the stopes and caught by the Hg. When the Hg has been amalgamated with the Au flakes it is recovered and smelted directly. This route therefore avoids the inclusion into the amalgam of Au enclosed in minerals which

would not be released during blasting, but only after milling, due to the physical properties of the associated minerals. The association of the As in this subgroup with the Au could be attributed to the inclusion of As-bearing pyrite attached to the gold into the amalgam. A typical mineralogical association within the Witwatersrand Reefs is that of Au with As-enriched pyrite, as described by Foya *et al.* (1999) for Type III As-enriched pyrite.

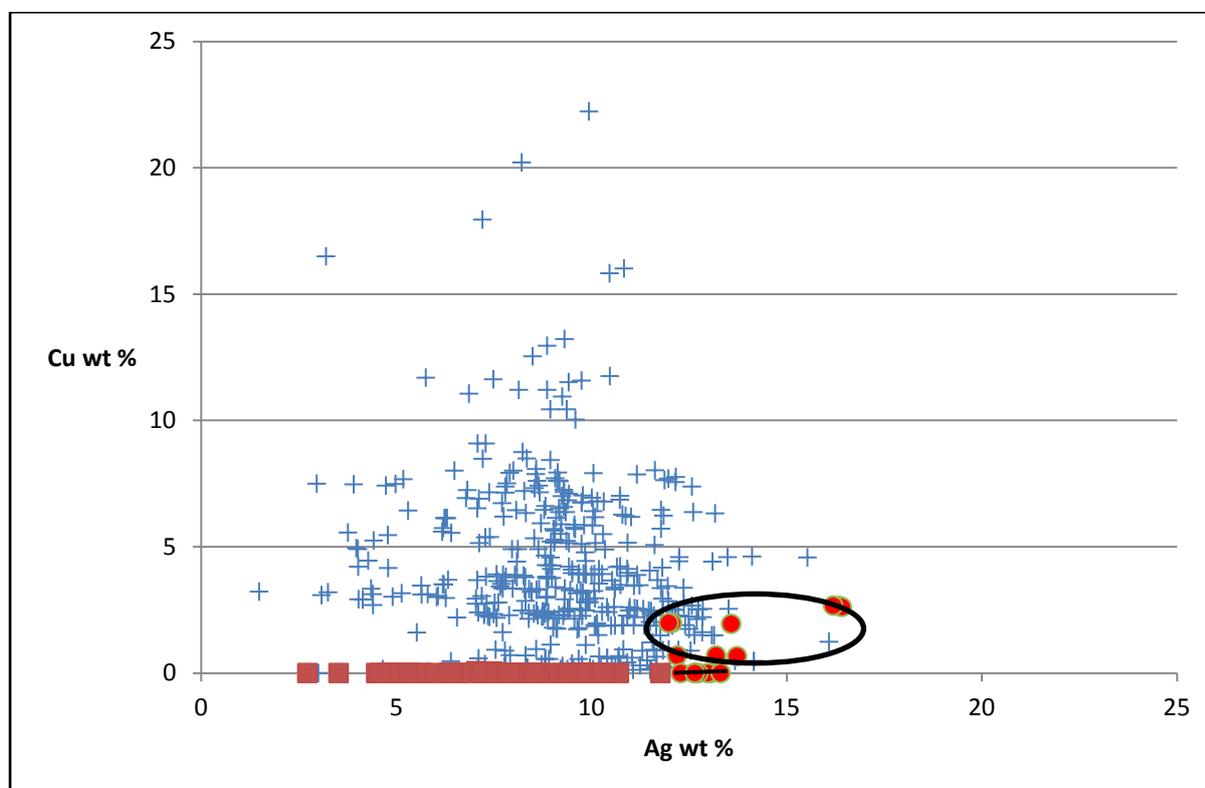


Figure 9.8. A plot of Cu vs Ag showing the distribution of the two elements in native Au from the Witwatersrand reefs (63 samples, Erasmus *et al.*, 1987) (squares), d'ore gold from the Witwatersrand (421 samples) (crosses), and the two subgroups from the suspect samples Group A (circles). The subgroup with no Cu consists of the same samples which show the relative enrichment in As in Fig. 9.6.

Amalgamation of gold is most effective when the Au particle size is in the range 10 – 1000 μm (Harris, 1990), so amalgamation of milled and floated ore, which is then heated in a furnace or by means of a blow-torch to drive off the Hg, would result in a fairly pure gold metal. Gravity separation methods prior to flotation would remove a number of the metallic phases, while ore which is milled and amalgamated directly will contain a wide range of metallic minerals, mainly PGE phases (Cousins, 1973; Feather & Koen, 1975; Feather, 1976; Malitch *et al.*, 2000; Malitch & Merkle, 2004), which would dramatically change the trace element composition of the gold produced after amalgamation. A wide range of metallic elements and alloys form amalgams, including Pt and Pd (Gumiński, 1989, 1990a, 1990b).

Factors affecting the recovery of gold include the mineralogy of the gold-containing minerals and the associated sulphide minerals, their grain size, the nature of the gangue minerals, the coatings on the gold grains and the extent of chemically bound, or "invisible" gold (Cabri, 1988; Harris, 1990). Milling will homogenise the ore, as well as breaking down the mineralogical boundaries (inclusion in other minerals, coatings, etc.) to amalgamation by creating new metallic surfaces which can then react with the Hg. This is especially true with respect to Au, which is often coated with Fe-oxides and the PGE alloys which are often coated with minerals such as sperrylite (PtAs_2) (Feather, 1976; Malitch *et al.*, 2000) which would prevent amalgamation taking place.

The relative PGE abundances in the suspect gold samples are very variable. In the Cu-bearing subgroup of Group A the most abundant PGE is Ir, followed by Ru, Pd, Pt and then Rh. Os is not considered as it is very volatile during the smelting process, and variable temperatures could affect its abundance considerably. This abundance trend mirrors that described by Cousins (1973) for abundances of PGE in platinoid minerals from the Witwatersrand Basin, with the exception of Pd, which he stated was absent or only present in trace amounts. The As-bearing subgroup of Group A shows higher levels of Pd (see Fig. 9.5) which is consistent with the amalgamation of transported gold grains. Pd is highly soluble in Au, so the relative enrichment in Pd compared to Pt can be seen as another indicator of the type of material processed to produce the gold buttons.

Among the PGE in the Witwatersrand reefs, Os and Ir, which together account for approximately 70% of the PGE occurring in platinoid minerals, are strongly correlated. Pt, Rh and Ru are also strongly correlated by mineralogy, forming another suite of mineral species (Cousins, 1973; Feather, 1976). The distribution of PGE in Groups B and C is highly variable within and between samples, and appears to be a very strong indicator of differences in source material processed to produce this illicit gold. In Group B and one sample from Group C, Ru and Rh predominate, in another sample Pt is present almost exclusively, and in yet another Ir is present at more than 80% of the PGE. This highly variable behaviour points to material being processed which has not been floated, but has been mineralogically sorted by some mechanism, either prior to theft or during the illicit beneficiation process.

The presence of the PGE in the illicit gold, with the various proportions and relationships described above, shows that the gold is consistent with having been derived from the gold mines within the Witwatersrand Basin, and not from other deposit types which have distinctly

different associated mineralogies (which are typical of their genetic processes) such as epithermal vein deposits (Watling *et al.*, 1994).

From the examination of the suspect samples, those from the Cu-containing subgroup of Group A have the characteristics of having been produced from flotation concentrate, and are the most likely to correspond in composition to the d'ore gold produced at the mines of the Witwatersrand Basin. The Cu content of the majority of d'ore gold from the Klerksdorp and Free State goldfields is above 2 wt %, while the West Wits shows a cluster of samples at around 1% (Fig. 7.4). This, combined with information from mine security and police investigation that the suspect gold was stolen from Driefontein mine, shows that a comparison between the Cu-containing subgroup of Group A and the d'ore gold from the West Wits goldfield can be justified. The plot of Cu against Au in Fig. 9.9 shows that the suspect samples have the most overlap with the d'ore samples from Driefontein mine.

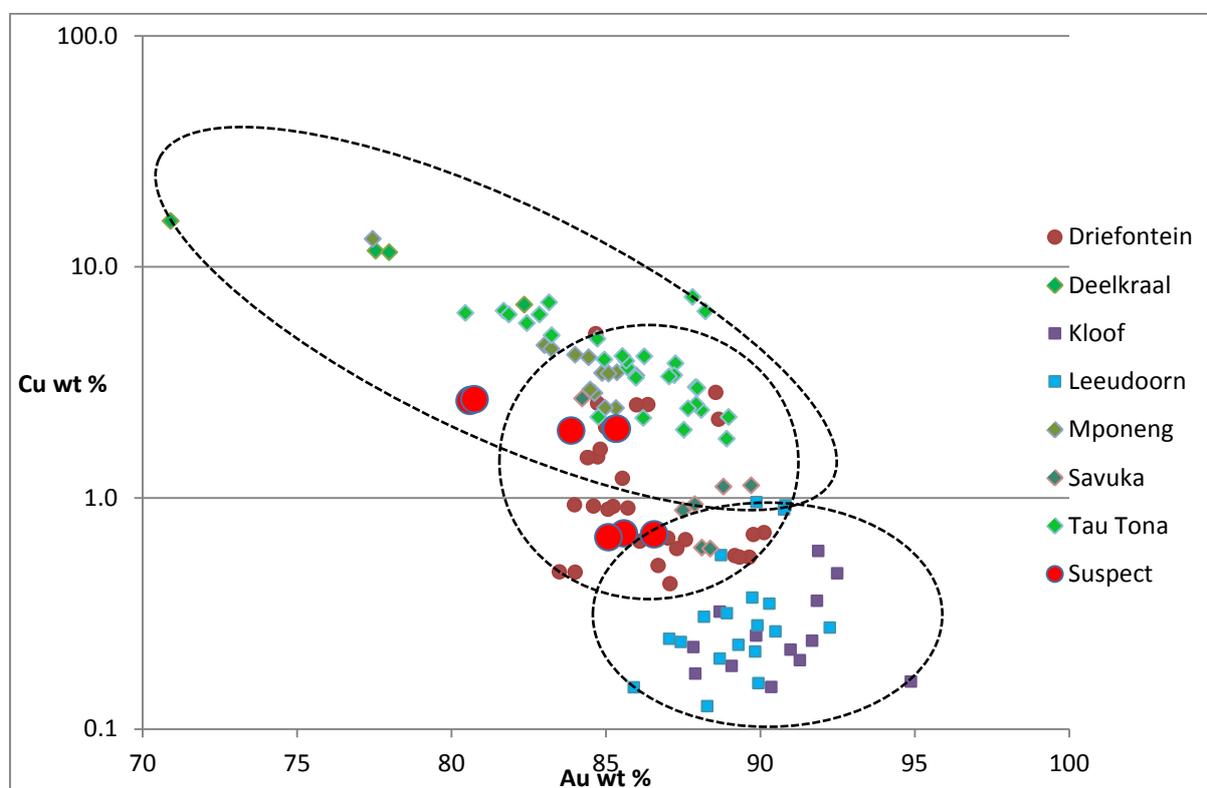


Figure 9.9. Suspect gold samples from Group A plotted against the mines in the West Wits goldfield. Based on their Au and Cu concentrations, they correspond to the d'ore gold produced from Driefontein mine.

The variation in composition between the the different suspect samples and the d'ore gold has been shown, in the discussion above, to be due to a number of different factors which are attributable to differences in ores both within and between goldfields, as well as the

beneficiation method used to extract the gold and the stage in the beneficiation process from which the illicit gold is extracted.

The elemental profiles of the suspect gold samples shown in Fig. 9.3 show both subgroups of Group A, reflecting the differences between the low and high As groups. The profile of Sample 11, belonging to the low As subgroup, shows a very similar profile to the Driefontein d'ore sample from the database which would have been produced from flotation concentrate.

The interpretation of the analytical results cannot be a simple comparison between suspect and database. The information revealed the analysis of a piece of illicit gold can assist in a criminal investigation, even though the exact origin of the gold cannot be precisely determined.

A good knowledge of the mineralogy of the deposit and the processes used to beneficiate it to produce the final gold product, legal or illegal, can thus assist in the following:

- Identification of the type of deposit from which the gold was recovered, based on trace element distributions – high PGE being distinctive of the Witwatersrand Basin.
- Identification of what type of material was stolen and processed to produce the gold – the suite of elements shows what has been removed or enriched, and can point to the step in the beneficiation process from which the material processed illegally was stolen.
- Identification of the process used to produce the gold metal – presence of high Ni content would show that the CIP process has been used.
- Identification of the geographical area from which the gold-bearing material was stolen, which could be a goldfield, mining area, or shaft – this can only be done if the material under investigation is similar to samples in the database, whether in its entirety or in areas which are distinctive of a particular source or process.

10 Composition of gold grains from the Witwatersrand Basin

There has been much debate on the source of the gold within the Witwatersrand Basin, in order to determine whether the gold has an alluvial or hydrothermal origin, or a combination of the two. The morphology of individual gold grains within the reefs of the Central Rand Group have been attributed to two clear groups – those of alluvial origin (e.g. Hallbauer & Utter, 1977; Minter *et al.*, 1993; Frimmel, 1997; Minter, 1999; Utter, 1980) and those having a hydrothermal crystallisation origin (e.g. Barnicoat *et al.*, 1997; Jolley *et al.*, 1999). Within the Carbon Leader Reef, however, what appears to be originally detrital gold grains have the appearance of hydrothermally crystallised gold, and grains that can be unequivocally attributed to an alluvial origin are rare (Oberthür & Saager, 1986; Hayward *et al.*, 2005).

The composition of the gold grains (as discussed in Chapter 2.5) has not resulted in a clear and unambiguous interpretation of formation of the Witwatersrand gold deposits. However, the study by Hayward *et al.* (2005) has shown that the degree of heterogeneity of gold grains within the CRG precludes chemical homogenisation from widespread hydrothermal events, (with the exception of gold in late-stage veins (Frimmel, 1997)), and that *in situ* recrystallisation of originally detrital gold grains, rather than remobilisation, took place in a number of areas. They conclude that fluids were of limited volume, locally variable and not capable of transporting gold very far.

The preceding chapters have shown that there is a difference in the overall composition of the d'ore gold recovered from the VCR and CLR, and that at Driefontein mine the gold in the VCR can be of two possible genetic origins, alluvial and another, possibly hydrothermal. The gold in the CLR, however, appears to have one main genetic origin. The distinct difference in the composition of the d'ore gold from the Klerksdorp goldfield and Driefontein mine in the West Wits goldfield compared to the rest of the West Wits goldfield also indicates that two different processes were at work. It was therefore decided to look at grains of native gold to see whether there was variation between individual grains, and specifically to evaluate the composition of gold grains towards the base of the Central Rand Group, where the greatest Pb isotope anomalies are observed.

10.1 Samples and analytical procedure

In Chapter 7 it was shown that the d'ore gold composition from the Klerksdorp goldfield was distinctly different to that of the West Wits goldfield, with the exception of the Driefontein mine which showed some similarities. The main source of gold in the Klerksdorp goldfield is the Vaal Reef, which is found in the lower half of the CRG (Fig. 7.2). A number of gold grains from the Vaal Reef, obtained from a gravity concentrate, were selected for analysis. Spot analyses were performed using the LA-ICP-MS method described in Chapter 4.

In addition to the grains from the Vaal Reef, gold grains from the Merensky Reef were analysed as outgroup, because according to Malitch & Merkle (2004) the majority of PGM found in the Witwatersrand Basin are detrital in origin, probably derived from Archaean ultramafic rocks, and so there is a possibility that the gold associated with these PGM might also be found. This gold is thought to be the result of hydrothermal remobilisation from magmatic sulphides (Merkle *et al.*, 2008). As one hypothesis for the origin of the gold mineralisation within the Witwatersrand Basin is as a hydrothermal process which has an extra-basinal component (*e.g.* Graton, 1930; Phillips & Law, 1994; Barnicoat *et al.*, 1997), it was thought that a comparison between this type of gold and that found in the Witwatersrand Basin would be logical. The majority of publications attribute the origin of the gold in the Witwatersrand to originally granite-greenstone sources (*e.g.* Robb & Robb, 1998; Frimmel & Gartz, 1997).

Samples of columnar carbon from the CLR from the Blyvooruitzicht mine, which is situated next to the Driefontein mine in the West Wits goldfield, and which consisted of solid carbon with gold mineralisation, were also analysed. This columnar carbon is well-described by Mossman *et al.* (2008), and represents the remnants of microbial mats. The gold is found as fine particles within the carbon, and was selected because of the possible relationship between the carbon and the Pb isotope anomaly, described in Chapter 7.1.2. The d'ore gold compositions from Blyvooruitzicht mine are similar to those of the rest of the West Wits goldfield, and different from Driefontein mine and the Klerksdorp goldfield.

The electron-microprobe work by Hayward *et al.* (2005) on Witwatersrand gold grains and Merkle *et al.* (2008) on gold grains from the Merensky Reef have shown that the gold grains are heterogeneous and contain inclusions, so bulk analyses have limited utility in working out genetic relationships based on elemental distributions. Accordingly, the gold grains were

analysed by LA-ICP-MS (Agilent 7500 CX with New Wave UP213) in order to determine elemental distribution within the grains. The resolution of the laser spot is not as small as that which is achievable by an electron microprobe, but elemental concentrations of a wide range of elements down to ppb levels is possible. Areas of sample were mapped on a grid pattern, with continuous ablation via successive line scans to determine elemental distributions (Fig. 10.1). A laser spot size of 10 μm was selected, with a scan speed of 10 μms^{-1} and a sampling rate of ~ 0.25 s. This translates to an effective sampling area of $2.5 \times 10 \mu\text{m}$. The average size of each scanned area was $\sim 500 \times 500 \mu\text{m}$, and this is large enough to allow analysis of most of the gold grains encountered, from a few μm to several hundred μm in size. The plotting of the maps was done using a Microsoft Excel add-in developed at the University of Graz, Austria. The utility of this methodology in increasing the resolution compared to spot analyses has been discussed by Sanborn & Telmer (2003), who showed that LA-ICP-MS line scans could produce similar or better information about elemental distribution in a heterogeneous solid than spot analysis, and do it quicker as well. Woodhead *et al.* (2007) discussed the benefits and disadvantages of LA-ICP-MS imaging, and identified that a major advantage of the technique was that elemental and isotopic maps could be produced over a wide dynamic range.

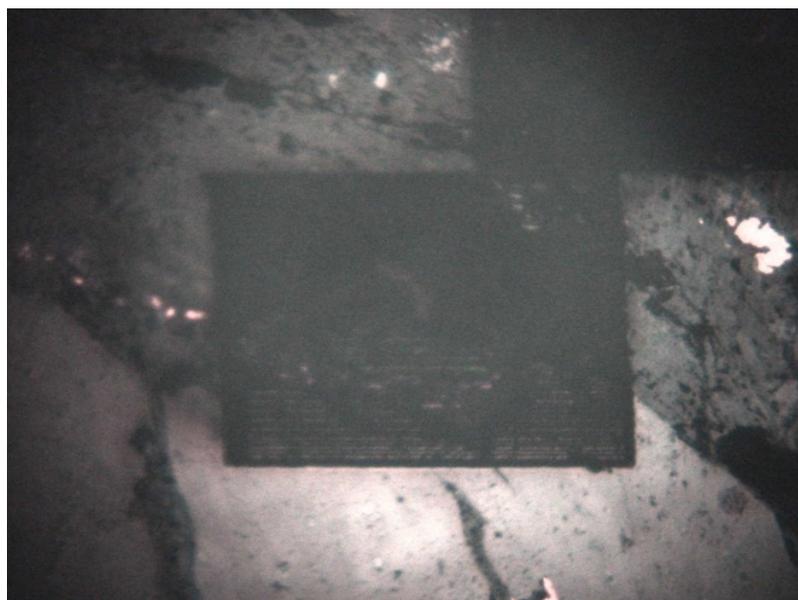


Figure 10.1. A $600 \times 400 \mu\text{m}$ area which has been sampled using a $10 \mu\text{m}$ spot size which is ablated continuously from left to right, with a sampling rate which equates to a $2.5 \mu\text{m}$ horizontal resolution.

Elements analysed for were represented by the following isotopes, which were selected in order to avoid interferences from other ions and isotopes, and which were expected to be encountered based on the work in the preceding chapters: ^{13}C , ^{27}Al , ^{29}Si , ^{33}S , ^{47}Ti , ^{51}V , ^{53}Cr ,

^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{82}Se , ^{101}Ru , ^{103}Rh , ^{105}Pd , ^{107}Ag , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{193}Ir , ^{195}Pt , ^{197}Au , ^{202}Hg , ^{208}Pb , ^{209}Bi , ^{232}Th and ^{238}U . These isotopes were selected by conducting a full mass scan of the samples (gold matrix) and identifying all peaks, and then determining whether the isotopic distribution for each element was consistent with the natural abundances and selecting the largest mass which was unaffected by significant interferences.

Table 10.1. LA-ICP-MS spot analyses for three types of gold grains from the Vaal Reef (VR) and gold grains from the Merensky Reef (MR). The abundances are shown as raw counts per second.

	^{35}Cl	^{52}Cr	^{56}Fe	^{60}Ni	^{63}Cu	^{75}As	^{105}Pd	^{107}Ag	^{118}Sn	^{195}Pt	^{197}Au	^{202}Hg	^{208}Pb	^{209}Bi	^{238}U
VR			127	57	9487			6156983	107	10	76307543	1147277	37		
VR		110		207	10	8202		5761648	133	17	60983123	1203458			
VR			107		14656			6276164	40		86887843	805262	17	23	
VR			107		4983	263	97	7636356	37	17	75740903	460929	10	20	
VR			773	50	12169	167		4185393	37		74008523	346516	253	203	7
VR		4092	74926	23	170	15299	320	5589501	83		76316683	662098	780	260	60
VR		35350	1468436	1374	900	8422		9121948	400		94286363	2231136	5029	4579	6374
VR		554	37571	253	47	21403	734	7933363	213	3	85656823	905882	3831	103	2188
VR		3162	125500	1114	470	44780	2054	8602748	530	3	93325843	1274331	25220	223	134294
VR		1905	665457	4608	620	58978	3229	9300661	483	43	80284903	923435	23691	170	55167
VR	49012	17		80	13	9663	597	6327793	47	7	84109483	713121	20	10	
VR	22674	113		20	17	16491	387	4295062	37	3	74946643	572784		17	
VR	35209	73				17598	503	4216918	50	13	74377643	583924		13	
VR	24169	37		40	3	10731	550	5456068		10	65829503	357938	7	23	
VR	79			107		10123	507	5464776	10	20	65309273	387672		40	
MR		177		137	17	4719	87	520831	16407810	147707	14968	43664823	155867	7	25267
MR		10176	497214	1190	2154	11995	50	517706	23887800	154705	2621	48076003	112494	113	8240
MR		173		177	40	10446	17	846311	15978720	9942	5296	48541043	278791	137	267015

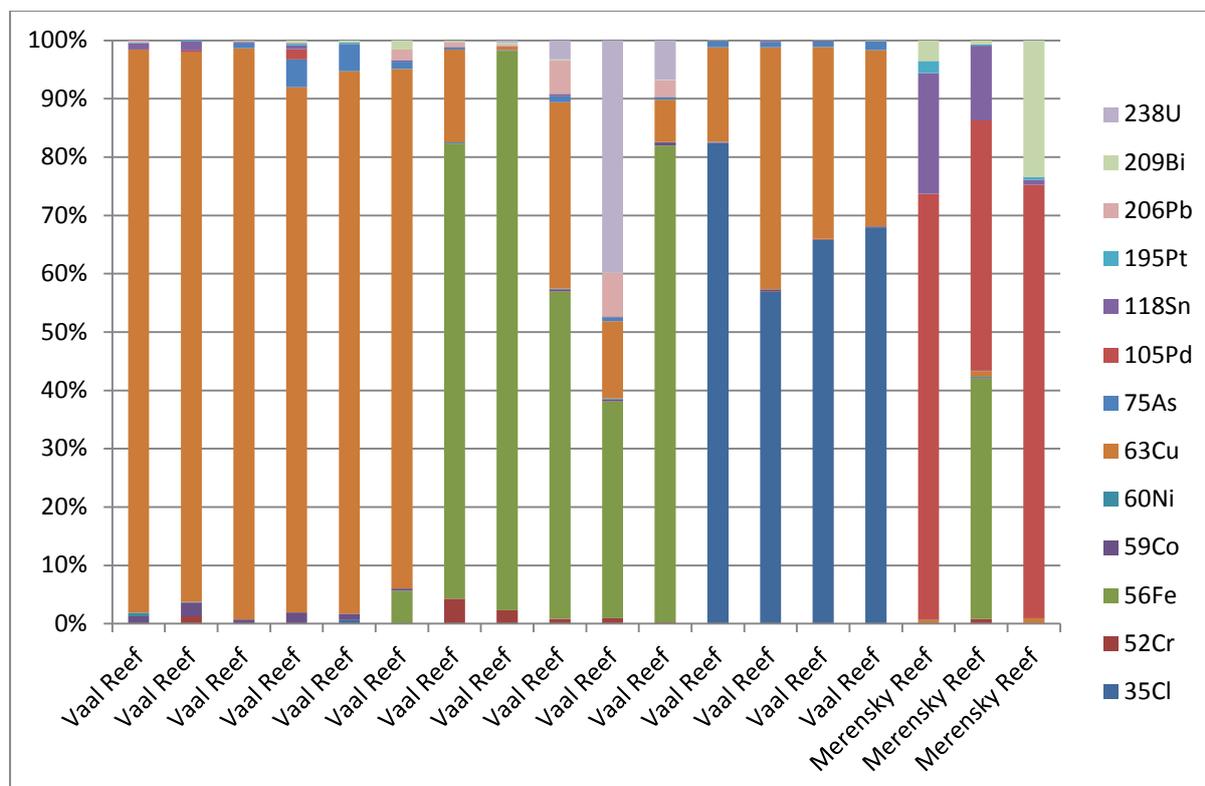


Figure 10.2. Bar graph showing the relative amounts of the elements present in the gold grains from the Vaal Reef and the Merensky Reef, after subtracting Au, Ag and Hg, and using the data shown in Table 10.1. Three groups of gold grain compositions are identified from the Vaal Reef, all three of which are quite distinct from those from the Merensky Reef.

10.2 Composition of gold from the Merensky Reef

The gold grains from the Merensky Reef, which are from a mafic layered complex, are very different from the gold grains found in the Vaal Reef. Considered to be of hydrothermal origin, Merkle *et al.* (2008) found that these gold grains contain a suite of inclusions with compositions which are typical of those found in PGM – Pt, Pd, Ru, Rh, Ag, Bi, Sn, Te and As. Analysed using EPMA with a spot size of $\sim 1 \mu\text{m}$, the majority of these elements were found to be present as micron to sub-micron sized inclusions of PGE minerals, and that the gold matrix contained Au (60-80%), Ag (15-35%), and up to 6% Pd. No other elements were detected by EPMA.

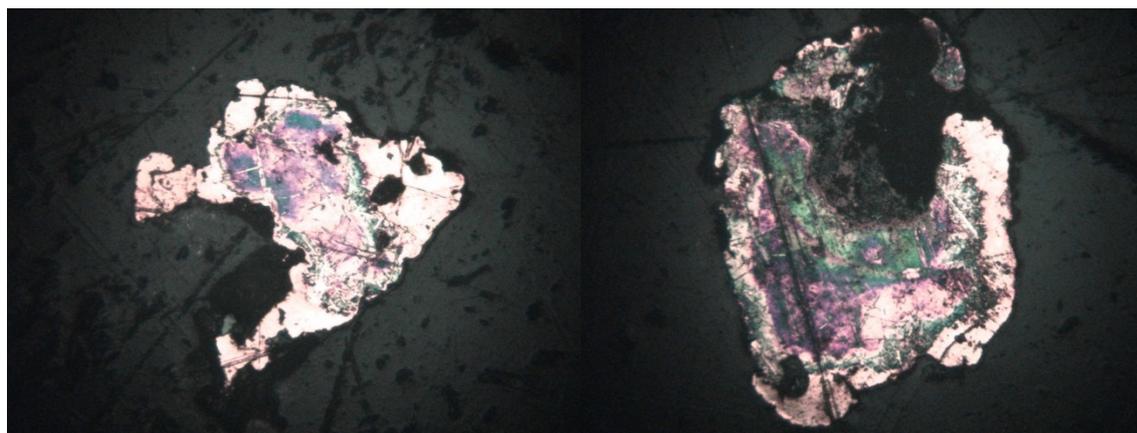


Figure 10.3. Gold grains from the Merensky Reef. The oxidation in the cores of the grains clearly shows crystallization and zonation. The grains are quite inhomogeneous and full of inclusions of other mineral phases. The oxidation is attributed to the high Ag content. The grains are approximately $300 \mu\text{m}$ in maximum dimension.

The grains analysed in this study were the same ones as those analysed by Merkle *et al.* (2008). A single $50 \mu\text{m}$ spot was ablated on each grain, to get an indication of the elements one would expect to see in gold from the Witwatersrand Basin, if the gold grains were alluvial and of an origin similar to the Bushveld Complex. The same elements detected by EPMA were also found using LA-ICP-MS. In addition, Hg and traces of Cu were detected. No other elements were detected in any significant amount, including U and Pb (Table 10.1).

10.3 Composition of gold from the Vaal Reef

The results of analyses of gold grains from the Vaal Reef, in the Klerksdorp goldfield, are presented in Table 10.1. A graphical representation of the relative abundances of the elements (after subtracting the contribution of Au, Ag and Hg) in Fig. 10.2 clearly shows three distinct populations within the gold grains. Notwithstanding the fact that there will be different responses under ablation and ionisation by the different elements, the presence and absence of elements such as Cu and Cl was used to identify the different groups.

The first population shows small amounts of Cu, but is otherwise relatively clean. The second population is distinguished by the presence of significant amounts of Fe, U and Pb, associated with Cu, Cr, As, Co, Bi, Ni and Sn. The third population shows the presence of significant amounts of Cl, but apart from traces of As it is very clean. What is very clear is that there are almost no PGE in the gold grains from the Vaal Reef, whereas the gold from the Merensky Reef has substantial amounts of PGE, especially Pd, as well as Sn and Bi.

10.4 Composition of gold from the Carbon Leader Reef

The columnar carbon from the CLR at Blyvooruitzicht mine showed areas of seemingly homogeneous solid carbon (the columns) and heterogeneous interstices containing a variety of material, including small gold grains. The results of the LA-ICP-MS mapping (as described in paragraph 10.1) show that the carbon columns (the grey areas in Fig. 10.4) consist mainly of carbon, with other elements at very low levels or not detected. All other elements which are present occur between the columns and in the interstices (as seen in Fig. 10.5). The distribution of the elements and their relationships, however, show domains which vary in size, down to the 2.5 μm resolution of the laser, and different elemental associations. The distribution of Al between the columnar carbon, as shown in Fig. 10.5, is compared with the distribution of Au, Ag, Pb and U in Figures 10.6 to 10.9. for the same area.

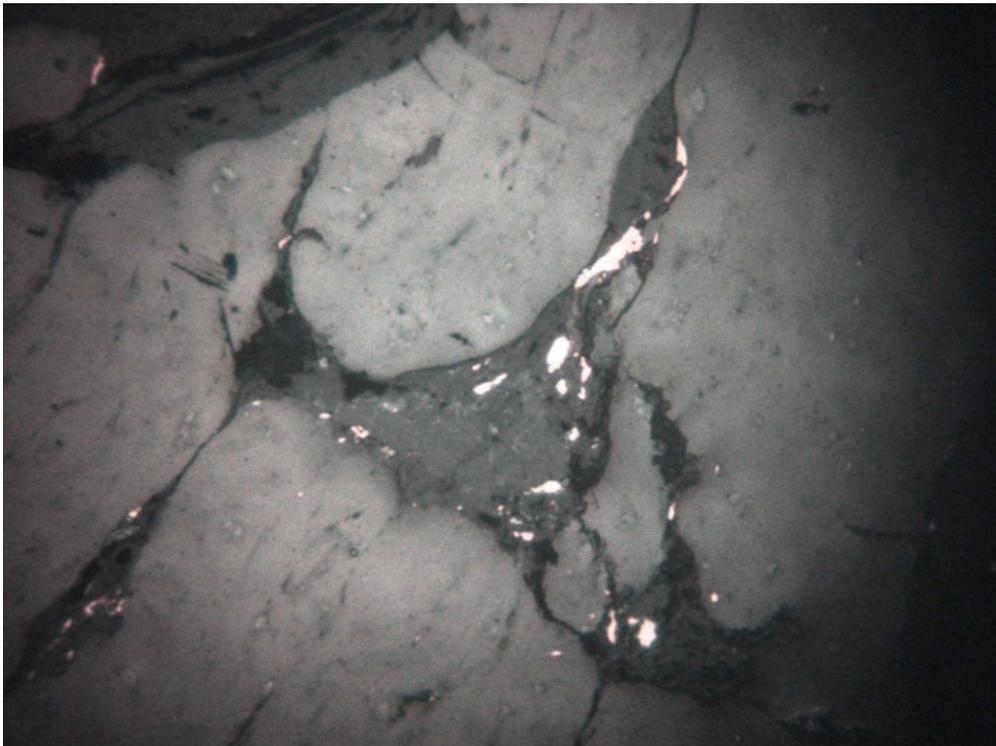


Figure 10.4. The light grey is carbon, and the rounded nature of the structure is clearly visible, as are the darker grey interstices which have a number of phases, including gold. FoV ~ 1000 μm

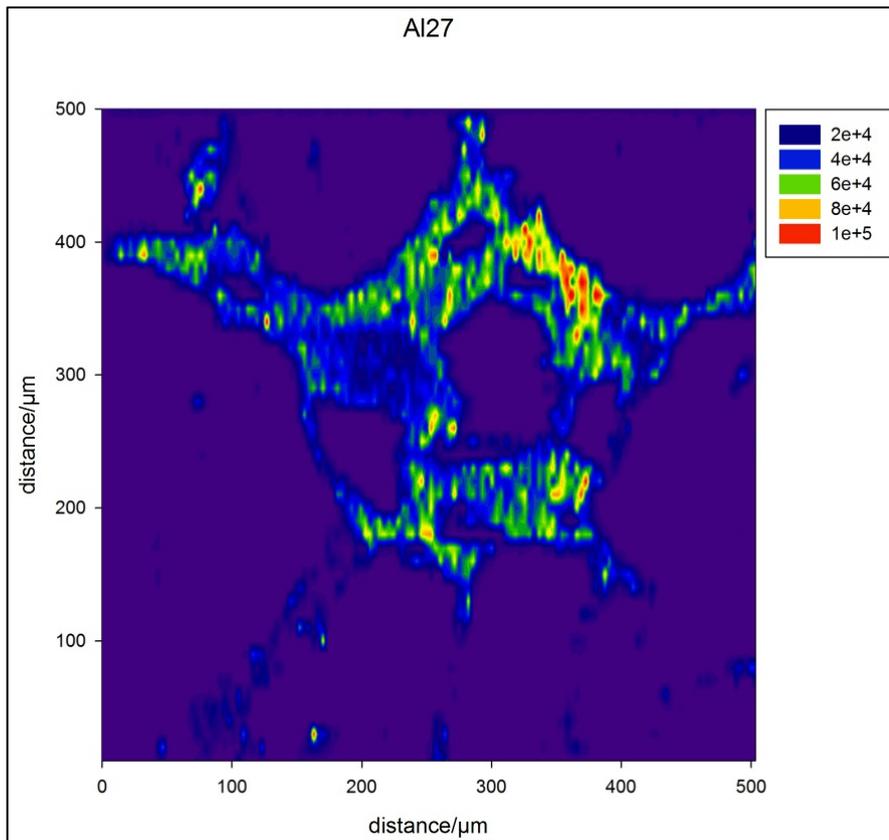


Figure 10.5. The ^{27}Al distribution within the carbon. The individual domains which are a plan view of the columns of carbon can be seen in purple. The boundaries between the columns and the interstices are visible as areas as a fill of other material. The contour values are in cps.

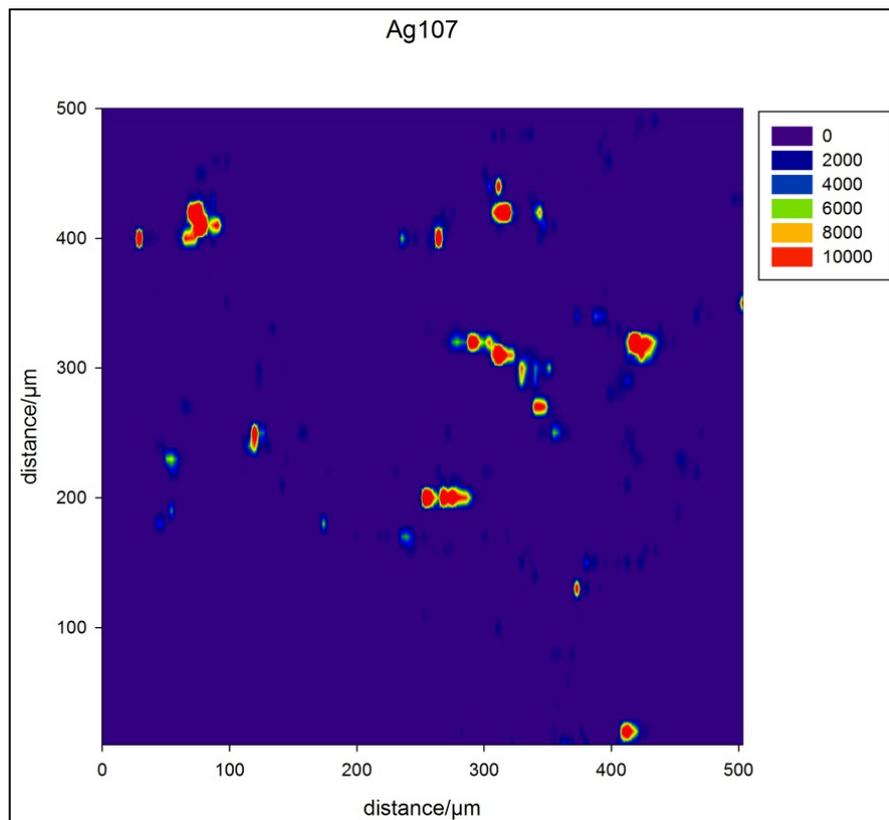


Figure 10.6. The ^{107}Ag distribution within the carbon. The distribution of the Ag is in defined spots, mainly on the surface of the carbon columns in the interstices between the columns. The contour values are in cps.

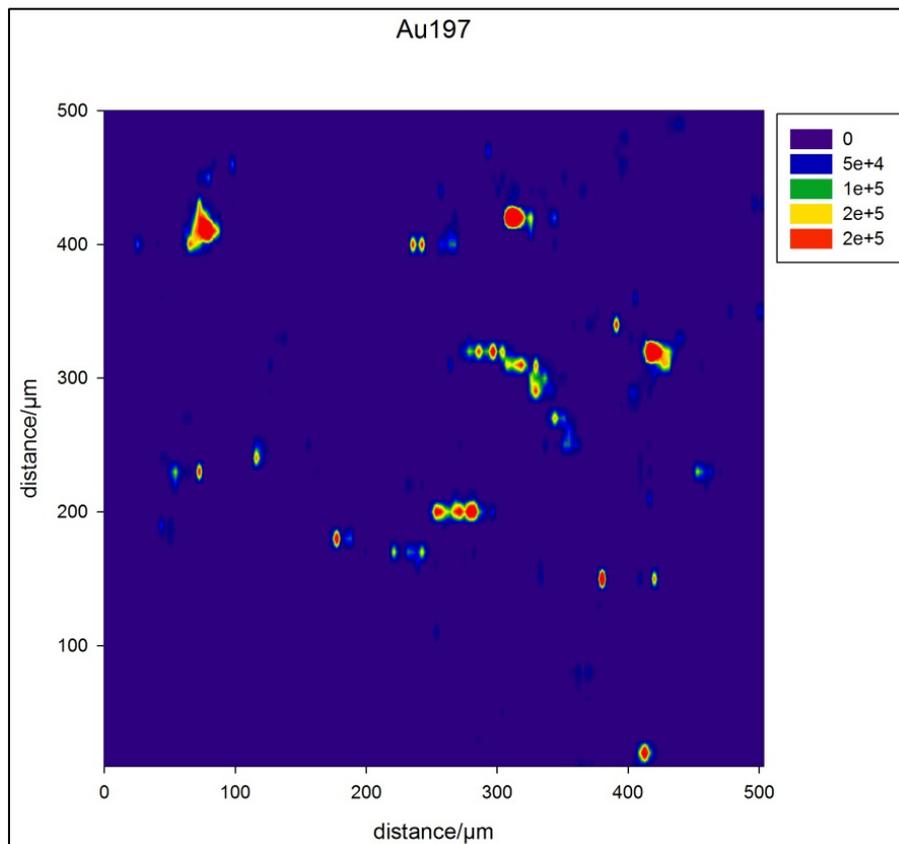


Figure 10.7. The ^{197}Au distribution within the carbon. The distribution of the Au is similar to that of the Ag. The contour values are in cps.

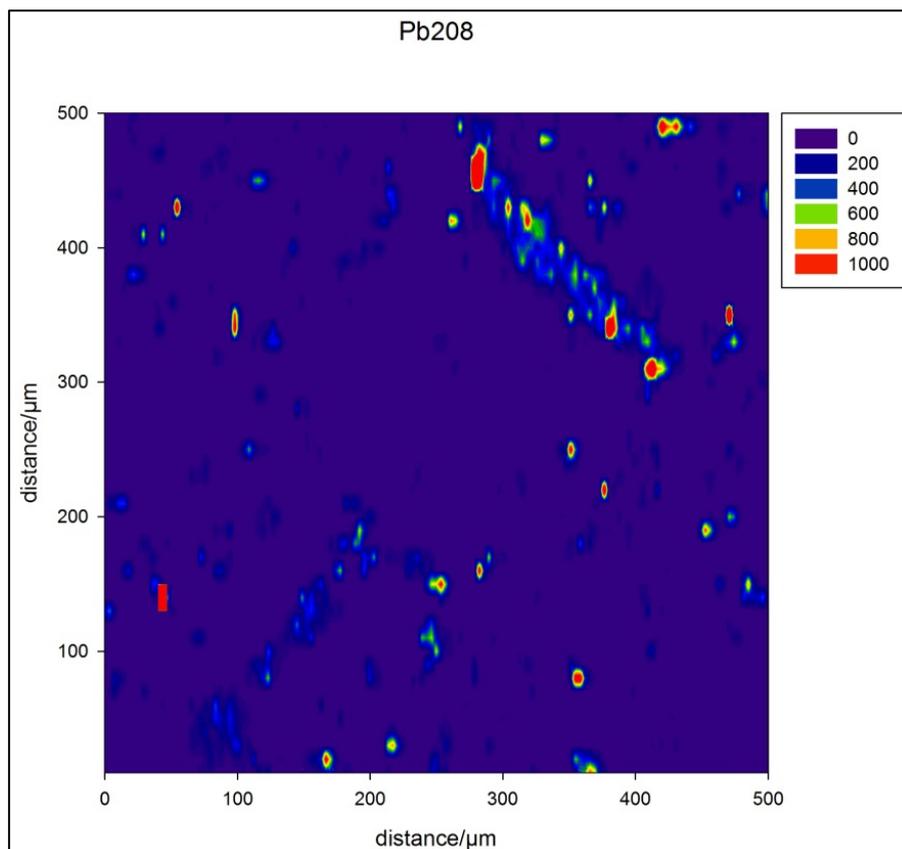


Figure 10.8. The ^{208}Pb distribution within the carbon. The distribution of the Pb is mainly in the contact zones between columns, and is similar to the U distribution. The contour values are in cps.

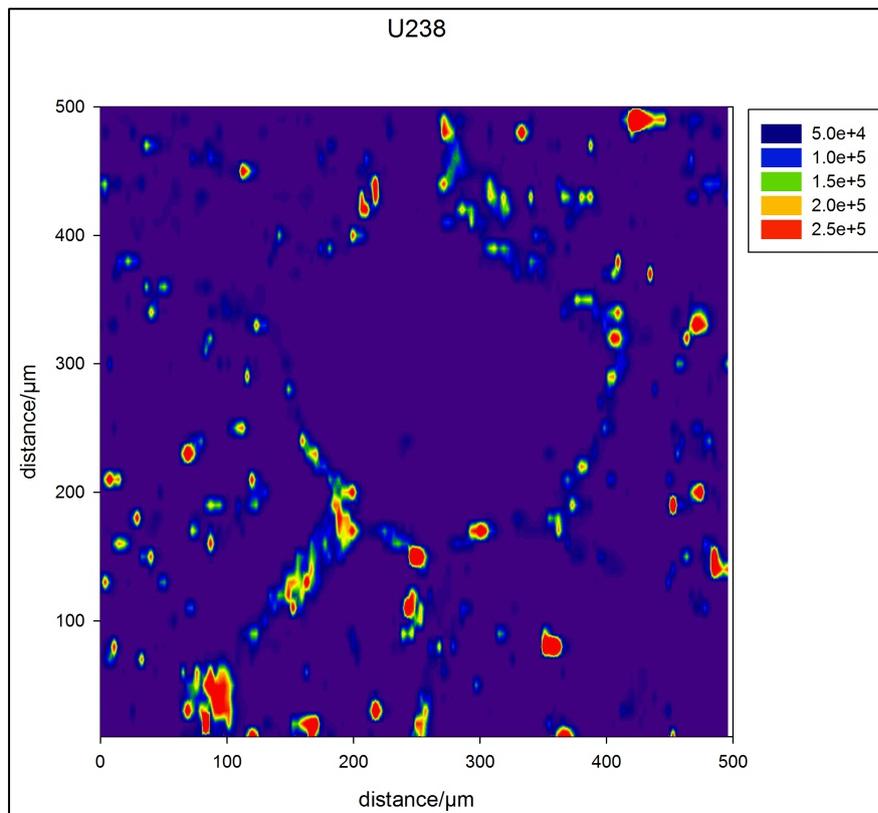


Figure 10.9. The ^{238}U distribution within the carbon. The contour values are in cps.

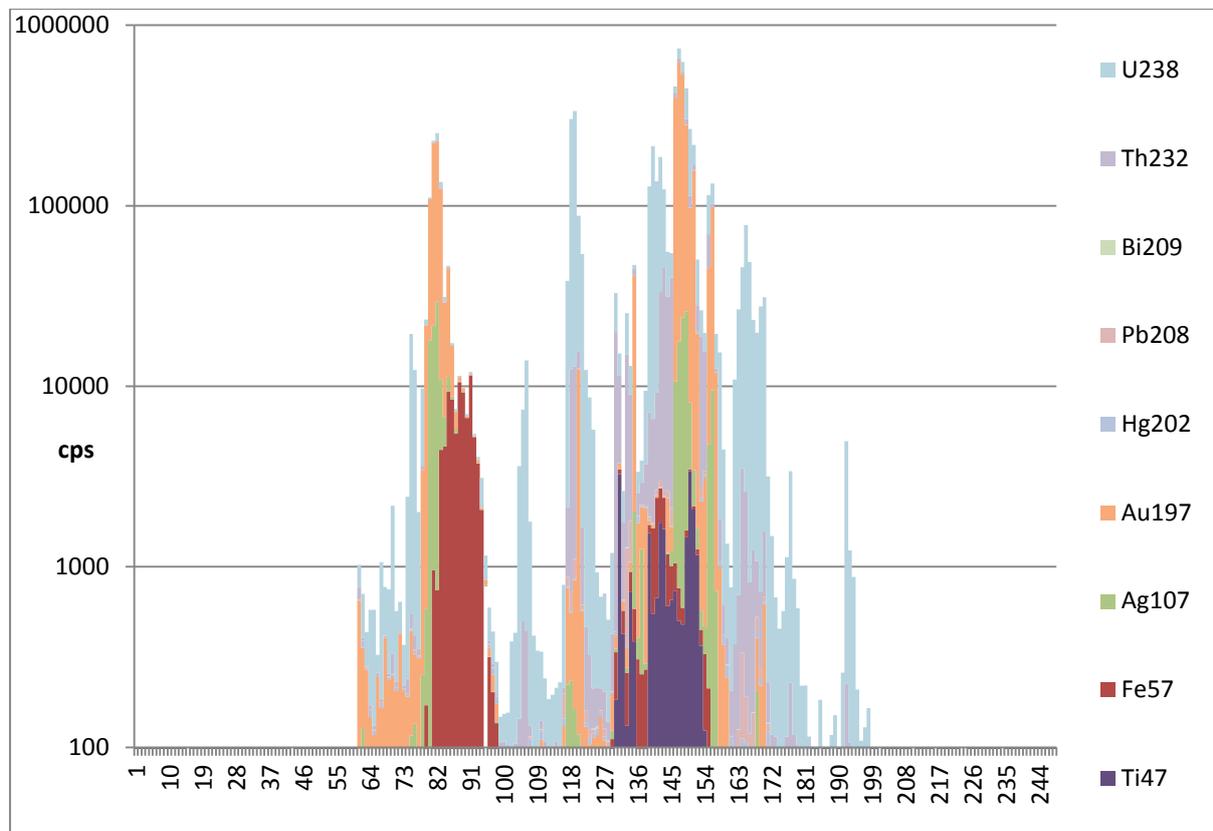


Figure 10.10. A traverse across a carbon sample with interstices in the middle. The horizontal axis shows the analysis points, from left to right, which are spaced at a distance of $\sim 2.5 \mu\text{m}$ apart. The elements plotted here give an idea of the relative proportions, with Au and U dominating. Th and Pb have a systematic relationship with U, as has Hg and Ag with Au. The Ti and Fe clusters show how various elements can overlap but do not always co-occur. The carbon matrix, shown on both sides, is almost pure C.

The distributions of Au (Fig. 10.7) and U (Fig. 10.9) in the carbon shows clearly discernible differences. The U distribution is more widespread, and appears to delineate the boundaries of the individual carbon columns. The Au has a more restricted distribution in the larger, more open interstices, as shown by the Al distribution (Fig. 10.5). In Fig. 10.4 the difference between the carbon columns and the interstices is shown, with gold grains in the latter. The distribution of the various elements detected in these carbon samples shows that they are not evenly distributed. Within the limits of the resolution of the laser ablation, there appears to be two groups of elements, one consisting mainly of Au, Ag and Hg, and the other mainly of U, Th and Pb. Other elements also show a spotty distribution, and do not appear to show any clearly observable relationships, as shown in Fig. 10.10.

The elemental distribution in the Carbon Leader, as shown in Figures 10.5 to 10.9, corresponds to a similar study by Fuchs *et al.* (2014) where micro-PIXE and micro-EBS analyses were performed on Carbon Leader Reef from the Carletonville (West Wits) goldfield. In this study, however, the carbonaceous material consisted of a seam of bitumen nodules which showed that uranium was present exclusively within the hydrocarbon nodules (unless occurring in secondary brannerite). This U was associated with high Th and low Pb, the low Pb which was attributed to a Pb-depleted uraninite generation or urano-organo complexes within the hydrocarbon structure. Fuchs *et al.* (2014) suggest “that U could have been in solution as organometallic complexes in liquid hydrocarbons and precipitated from organic matter”.

11 Discussion

In order to ascribe a geographic origin to seized, suspected stolen gold using its elemental composition as an indicator of its genesis and mode of formation, it is important to know where to begin. The single mode of origin gold deposits have been shown to be fairly simple to discriminate and identify (*e.g.* Mortensen *et al.*, 2005; Watling *et al.*, 2010), but the situation within the Witwatersrand Basin gold deposits is much more complex. It is important, therefore, to identify the different types of gold found within these deposits, as well as their ultimate origin or mode of formation, before one can use the elemental analyses with confidence.

Since the discovery of gold in the Witwatersrand Basin in 1884, there has been much discussion about its origin, and these discussions tend to veer in one of two directions - predominantly placer or predominantly hydrothermal. There is little agreement between these two positions, and the origin of the gold is thus inferred depending on which model is preferred, and which datasets are utilised. Any discussion about the origin of the gold in the Witwatersrand Basin has always elicited a fair measure on controversy, as Draper (1899) observed when responding to criticisms of his views of the origin of the gold:

“The author of the paper read at our last meeting has revived a subject which I had hoped would be allowed to rest until a geological survey of the Rand had been completed. It is a subject the discussion of which unfortunately leads to no definite results, firstly because the evidences within our reach are fragmentary and indefinite, and secondly because none of us are in a position to undertake the necessary investigations which would enable us to deal with the subject as exhaustively as its importance demands”

After almost 130 years, a lot of information and data has been collected on the Witwatersrand Basin. The origin of the gold, however, has remained a point of contention, due to the problems quoted above. The availability of samples of similar origin from the various goldfields, as collected for the gold database, and the analytical techniques now available, have hopefully advanced the level of knowledge to a position where various aspects can be identified and interpreted in the context of the entire basin.

11.1 Theories for gold mineralisation within the Witwatersrand Basin

John Ballot, a self-taught geologist, documented a variety of theories about the origin of the gold reefs, and summarized the available evidence relating to the depositional conditions, as well as what additional evidence was needed to test these various hypotheses (Ballot, 1888). Subsequently, when a lot more information was available as a result of all the mining in the Witwatersrand Basin, Louis de Launay compiled a thorough examination of the Witwatersrand reefs and their setting, and put forward the contrasting hypotheses on the origin of the gold (de Launay, 1896; 1903). He grouped these theories into three types or models:

(1) *The Placer Model*, as proposed by such authors as Ballot (1888), Schmeisser (1894), Goldmann (1895) and Becker (1897). In this model placers developed as a result of the erosion of gold-bearing veins, followed by recrystallisation of pyritic and siliceous cements by metamorphism.

(2) *The Precipitation Model*. In this model the eroded material, consisting mainly of auriferous pyrite, was dissolved in the sea-water, and then subsequently precipitated, or was precipitated from hot springs carrying dissolved gold and silica. This would have taken place along the conglomerate layers where the hot brines would have found easy passage.

(3) *The Hydrothermal Model*. This model considers that the pyritic zones were formed after the deposition of the conglomerates, and were caused by hydrothermal deposition by deep metalliferous waters which passed through spaces between the pebbles, precipitating the gold and pyrite. This model is similar to the second, but instead of being contemporaneous with the deposition of the conglomerates, was post-depositional and post-burial.

Unlike De Launay who, although he initially preferred the second model, described all three theories without a strong bias for any one of them, others were more outspoken in their preferences. Hatch (1898) stated that:

“The silicification, or more generally the mineralization, of these conglomerates is, in my opinion, the result of secondary processes of infiltration and crystallization. It is significant in this connexion that when most mineralized the conglomerates are often seamed with veins of white

quartz (as, for example, Ferreira Mine and New Rietfontein Mine); and there can be little doubt that these veins were formed in connexion with the mineralization of the conglomerates. There is no reason for ascribing a special method of origin to the gold; and I hold, therefore, that the gold has been introduced with the pyrites with which it is in intimate association, as a part of the general process of mineralization, and I cannot agree with those authors who describe the conglomerates as deposits in which the gold was either pre-existing (alluvial gold) or was introduced contemporaneously with the deposition of the pebbles and sand”.

The second of the theories outlined by De Launay, the precipitation model, soon fell away (Young, 1917), and the debate for the following century concentrated on the placer or hydrothermal models. Over 100 years later, there is still no generally accepted model for the origin of the gold mineralisation in the Witwatersrand Basin. As Saager (1968) succinctly stated:

“With certain reservations, it is possible to obtain specimens from the Witwatersrand ores which exhibit classic hydrothermal, placeristic or even sedimentary syngenetic characteristics. This means, therefore, that “proof” can be obtained for any genetical interpretation one wishes to construe on the origin of the Witwatersrand conglomerate ores.”

The placer model for the origin of the gold as detrital grains derived directly from primary deposits, mainly Archaean schist and granite-greenstone belts (Robb & Meyer, 1995; Kirk *et al.*, 2001), poses a distinct volume problem, in that the Witwatersrand deposits have yielded about 923 kg/km² Au compared to about 65 kg/km² Au in the richest known schist belts (Reimer, 1984; Phillips & Powell, 2011), although it has been proposed that the deposits which provided the gold in the Archaean were much richer than what remains (Kirk *et al.*, 2003).

The hydrothermal model accepts that all the gold, pyrite, uraninite and associated minerals, including hydrocarbon, is the result of a late-stage, basin-wide, hydrothermal fluid circulation event (Barnicoat *et al.*, 1997; Phillips & Law, 2000; Jolley *et al.*, 2004). These hydrothermal fluids deposited gold and associated minerals within the clast-supported conglomerate beds due to their high permeability.

Many studies relating to gold fineness, grain size, and morphology of the gold particles give rise to data which are difficult to reconcile with a purely detrital origin (*e.g.* Oberthür & Saager, 1986; Frimmel & Gartz, 1997). Accordingly, a number of workers have modified the placer model to allow for some contribution by the hydrothermal model. This “modified placer theory” has also been around for a long time (see Young, 1917, for a review of the early theories) and was termed as “pseudohydrothermal” by Ramdohr (1955, 1958). The modified placer model allows for post-depositional hydrothermal remobilisation during, or as a result of, tectonic or metamorphic events which have the effect of contributing to the deposition of gold, pyrite, uraninite and other associated minerals (*e.g.* Schidlofski, 1970; Oberthür, 1983; Els, 1991; Robb *et al.*, 1997; Frimmel & Minter, 2002; Agangi *et al.*, 2013). However, strong evidence for a distinct alluvial component of some gold, PGM and sulphides by means of age dating has shown that some pyrite and associated gold is dated at ~ 3 Ga (Kirk *et al.*, 2001, 2002; Malitch & Merkle, 2004), which predates the maximum age of the Central Rand Group which is ~ 2.9 Ga (Robb *et al.*, 1990).

What is not contested by anyone is that there has been hydrothermal activity within the basin and that this has had an effect on the mineralogy associated with the gold mineralisation. There is still no agreement on the origin of the hydrothermal fluids, and different episodes of extrabasinal and intrabasinal events have been postulated by various authors. Schaefer *et al.* (2010) have shown a placer origin for gold and PGE, deriving from a granite-greenstone terrain formed ~3.1 Ga that underwent hydrothermal remobilisation and deposition at ~2.2-2.5 Ga. This resulted in the textures and associations relating to the gold mineralisation, which occurred 200 to 300 Ma after deposition. Mathur *et al.* (2013) have looked at the Re-Os system in samples from both the Carbon Leader Reef as well as the Ventersdorp Contact Reef, and come to the conclusion that the modified detrital model is the best fit for their data.

“The two mineralization models have very different implications for mineral chemistry within the parageneses that occur in different parts of the CRG. Of special pertinence to efforts to discriminate between detrital and hydrothermal origins of the gold mineralization is the chemistry of the gold itself and that of the minerals that formed in association with gold, in particular phyllosilicates and sulphides. If the gold was originally detrital, some degree of variation in the composition among different populations of gold particles within the CRG may be expected to survive from the original variation present in the gold from the source region(s). The degree of preservation of such primary

heterogeneity depends upon the degree to which any later fluids present were able to remobilize gold; remobilization by hydrothermal fluids of an originally chemically heterogeneous population of gold grains would have led to a reduction in this primary heterogeneity. In contrast, a relatively low degree of chemical heterogeneity is expected from gold that was deposited during a single episode of hydrothermal circulation, if the fluids were reasonably homogeneous chemically. Gold in the Witwatersrand reefs has many and varied textural associations with a range of authigenic minerals which include chlorite, pyrite, pyrrhotite, galena and muscovite as well as altered hydrocarbon, commonly referred to in the literature as 'carbon' or 'bitumen'." (Hayward *et al.*, 2005).

11.2 Sampling and analysis of gold in this study and its difference to traditional methods

Due to the inability to accurately determine the composition of gold grains until recently, most of the mineralogical and genetic modelling for the gold in the Witwatersrand Basin gold deposits has been based on the mineralogical associations with gold, metamorphic modelling, and sedimentological, textural and structural analysis. In addition, the technology did not exist to determine the trace element composition of heterogeneous gold grains of a small size - electron microprobe analyses are limited to concentrations of at least several hundred ppm.

“Some electron microbeam analytical studies of gold grains *in situ* in thin section have been carried out on individual Witwatersrand depositional units and/or mines (Frimmel & Gartz, 1997; Frimmel *et al.*, 1993; Oberthür & Saager, 1986; Saager, 1969b), and one on individual grains from a gold concentrate from a number of mines (von Gehlen, 1983). However, most of the numerous analyses of Witwatersrand gold have been on 'bulk' samples or on gold grains isolated from their host rock by acid digestion, with consequent loss of paragenetic context (*e.g.* Reid *et al.*, 1988; Hallbauer & Utter, 1977). In other studies, the 'fineness' of the gold ($F = \text{Au} / (\text{Au} + \text{Ag}) \times 1000$) rather than the individual element concentrations was reported (Saager, 1969). The loss of textural information, reporting of only fineness values, and the effect of averaging of gold compositions leads unavoidably to oversimplification of the data on gold composition and, thus, has implications for models regarding

gold origin.” (Hayward *et al.*, 2005)

Previous work on the composition of Wits gold has been limited to NAA (Erasmus *et al.*, 1987), where a number of grains (plus included material) were collectively analysed for trace elements, and EPMA where the elements analysed for are limited to Au, Ag, Cu, Hg and Fe. Few published results are available for trace element concentrations in single gold grains, although various techniques have been discussed in this context (e.g. Antweiler & Campbell, 1977; Sie *et al.*, 1996). This paucity of data is not limited to the Witwatersrand Basin, but is a world-wide phenomenon.

The advent of ICP-MS enabled the analysis of small samples for trace elements, but the inclusions within the gold, and the heterogeneity of gold, remain a major problem. Laser-ablation coupled with time-of-flight has enabled the utilisation of ICP-MS for the analysis of small domains (from 4 μ m to 100 μ m) within a gold grain, with the determination of isotope concentrations down to ppt levels. This has provided the opportunity to analyse many gold grains for almost the entire elemental spectrum.

There have been a number of studies on the compositional variation of gold grains within the Witwatersrand Basin (e.g. Frimmel & Gartz, 1997; Hayward *et al.*, 2005) which have shown that there is a wide variation in Au, Ag and Hg concentrations between grains, but that individual grains are fairly homogeneous. These studies have also shown that gold compositions for the same reef between mines can vary greatly with regard to Au, Ag and Hg. A possible implication of this is that this variation could be used to distinguish between different source areas of the originally alluvial gold.

Unfortunately almost all of the previous studies investigating the variation in gold composition around the Witwatersrand Basin have of necessity been restricted to either a single sample (*e.g.* Minter, 1999); a single reef within a mine or goldfield (*e.g.* Oberthür, 1983; Els, 1987, 1991), or a single reef between goldfields (*e.g.* Frimmel & Gartz, 1997). For reasons of practicality, therefore, as well as enabling a large area to be investigated, the sampling described in Chapter 6 was embarked upon. This was deemed to be suitable as the reason for the study was to identify the origin of illicit gold, which is already a composite of many gold grains and possibly associated material. Similarly, the use of prills as a proxy for gold between reefs within a single mine, as described in Chapter 8, enabled a large-scale study to be done in a relatively fast and efficient manner.

In order to analyse a representative suite of gold grains from all the reefs and areas of the Witwatersrand Basin, one first needs to collect sufficient gold-containing sample material, and then extract the gold grains. This is an almost impossible task, logistically or practically, as many areas are now mined out and new samples cannot be obtained, or the area is not yet being mined and representative samples are therefore inaccessible.

Once the overview sampling and analysis was done and the variation within and between goldfields identified, analysis of actual gold grains was performed, as described in Chapter 10. These gold samples were selected on the basis of their origin and the information that they could impart in the overall understanding of the gold mineralization within the Witwatersrand Basin, and specifically in relation to the elemental and isotopic variation observed in the d'ore and prill samples.

11.3 Results of the analyses of d'ore, prill and native gold samples

As is clearly shown in the preceding chapters, there are two very distinct geochemical patterns observed within the d'ore gold produced from the three goldfields which have been investigated. These patterns correlate with the type of reef being mined – carbon-rich reefs such as the Carbon Leader Reef, Vaal Reef and Basal Reef, situated in the lower part of the Central Rand Group; and carbon-poor reefs such as the Ventersdorp Contact Reef which are in the upper part of the Central Rand Group or immediately above it.

The stratigraphic study of the prills between reefs at Driefontein mine showed that, on the basis of elemental composition, there are at least two different gold mineralisation processes discernible in the reefs, with one process dominant in the VCR (as demonstrated by the enrichment in Sn in Fig. 8.12, which can be attributed to the presence of Sn-bearing alluvial minerals) and the other dominant in the CLR (as demonstrated by the enrichment in Pd and Pt, as shown in Figs 8.11 and 8.12).

The analysis of the gold grains from the Vaal Reef has identified three populations, one consisting of gold (Au+Ag+Hg) with Cl (attributed to Cl-rich inclusions) being of an alluvial origin; the second a “dirty” gold containing traces of many elements and with a distinctive U, Th and Pb signature, in the cores of some grains; and the third a “clean” gold, consisting only of Au+Ag+Hg and without Cl.

The analyses of the carbon in the Carbon Leader Reef from Blyvooruitzicht mine in the West Wits goldfield show that the Au (+Ag) concentrations associated with the carbon are spatially separated from the U (+Th) concentrations which have associated Pb. The Pb associated with the U consists almost exclusively of radiogenic Pb. The carbon itself presents as columnar C domains which are very pure, with interstices which are impure (Fig. 10.4) and contain a variety of elements in addition to C (Fig. 10.10). This dichotomy of the distribution of U and Au in the different parts of the carbon has been recorded by Simpson & Bowles (1977) from the Carbon Leader in the West Wits goldfield. More recent elemental mapping by Depiné *et al.* (2013) and Fuchs *et al.* (2014) has shown the same distribution patterns.

11.3.1 Differences in prills between the CLR and VCR

The prill compositions of the CLR and the VCR at Driefontein indicates that the mineralisation in the two reefs has distinct differences, as shown in the various illustrations in Chapter 8. The tighter clustering of element distributions within the CLR, compared to the VCR, points to a less variable environment of mineralisation which operated in the reef. It has been shown that the Ag and Hg contents of gold grains from the CLR from the West Wits goldfield show regional variations which do not follow the sedimentological facies (Oberthür & Saager, 1986), and this has been interpreted as evidence of a regional metamorphic or hydrothermal event.

The Pt and Pd content of the prills is higher for the CLR than the VCR, whereas whole rock analyses have shown that the VCR, which has a distinct alluvial character, has a much higher PGE content than the CLR (Cousins, 1973). The gold prills are the result of the lead-collection fire assay process which has been optimised for evaluating gold grade, and so the incorporation of PGE will be dependent on the type of minerals in which they occur. It can thus be inferred that the Pt and Pd in the CLR occur in minerals which are different to those in the VCR and which result in a better collection efficiency during the fire assay process.

The Pt, Pd and Sn distributions in the prills as shown in Figures 8.11 and 8.12, show that there is a systematic relationship of Pt and Pd in the CLR, but that in the VCR there is also a strong relationship between Pt and Sn. The relationship between Pt and Sn, as discussed in Chapter 8.5, is indicative of the derivation of that Pt from PGE minerals, a number of which have Sn as a component, such as atokite (Pd,Pt)₃Sn, rustenburgite (Pt,Pd)₃Sn, paolovite (Pd,Pt)₂Sn and niggliite (Pt,Pd)Sn and are found in mafic and ultramafic rocks (Shelton *et al.*,

1981, Merkle *et al.*, 2008). The majority of PGM found in the Witwatersrand Basin are detrital in origin (Cousins, 1973), probably derived from Archaean ultramafic rocks (Malitch & Merkle, 2004). The behaviour observed in the CLR indicates that Pt and Pd in that reef could be occurring in a phase or phases which formed by a process different from the alluvial one.

11.3.2 The different types of gold grains identified by geochemistry

The analysis of the gold grains from the Vaal Reef, and the gold associated with the carbon in the Carbon Leader Reef, has revealed four distinctly different types of gold based on their composition.

The composition of the gold from the Merensky Reef is quite different from any of the gold types identified from the Witwatersrand Basin in this study, but provides valuable information about the relationships of different elements with gold. Unlike the Merensky gold, the Witwatersrand Basin populations do not contain any significant PGE content. The high Pd content of the Merensky Reef gold is attributed to crystallization in a high-temperature hydrothermal environment and the composition of the hydrothermal fluid (Merkle *et al.*, 2008).

Within the Vaal Reef, three populations of gold grains have been identified. The one population has a very clean composition, with only Au, Ag, Hg and Cl. The presence of Cl in the gold attests to the presence of Cl-rich inclusions (Moisyenko & Mironyuk, 1997; Altigani, 2013). These inclusions are the result of crystallization of the gold in boiling, Cl-rich brine, typical of epithermal vein deposition in a granite-greenstone or similar environment. These gold grains must therefore represent an alluvial component within the Vaal Reef, un-modified by subsequent post-depositional processes.

The second population contains, in addition to the Au, Ag and Hg, U and Pb associated with Bi, Fe, Cu, Co and Ni (see Fig. 10.2). This gold occurs as cores of some gold grains belonging to the third population, discussed below. There are traces of Pd in this gold as well. This population of gold shows some similarities to the Merensky gold in its element associations, and the changing abundances of trace elements from core to rim indicate crystallisation from a fluid. Unlike the Merensky gold, which formed at high temperature, and the alluvial Vaal Reef gold which formed in an boiling saline environment, the variation

in elemental concentrations from core to rim indicate growth in a relatively low-temperature environment from a fluid which has a variety of dissolved components which contains U and Pb.

The third population of gold grains identified from the Vaal Reef is quite clean, consisting of Au, Hg and Hg with only traces of a few other elements present. This gold has the same composition as that forming the rims of the gold grains which have the U-rich gold, discussed above. The formation of this gold, subsequent to the formation of the U-rich gold cores, clearly shows a change in the fluid composition from which they were formed.

The fourth population of gold, from within the carbon of the Carbon Leader Reef, consists almost exclusively of Au, Ag and Hg. All other associated elements are only associated due to proximity and size, and do not appear to have any geochemical association with the Au. Due to the small grain sizes of these grains of only a few microns, and the purity of these grains, this gold is consistent with a third mode of origin – precipitation from solution, either by adsorption onto the carbon, or as precipitation as organometallic colloids from suspension.

In a study on the Au and Ag relationship in the Basal Reef in the Welkom (Orange Free State) goldfield, Saager (1969a,b) also identified four types of gold grain, attributing to each a distinct paragenesis. It is not possible with the published information to determine whether any of the categories proposed by him are directly correlatable with those identified in this study, but it does point to there being a minimum of four types of gold, and possibly more, showing that the origin of the gold in the Witwatersrand Basin is not a simple matter, but consists of a series of events, each leaving their own distinct fingerprint.

11.4 Gold mineralisation in the Carbon Leader Reef

The Carbon Leader Reef is one of a sequence of placers formed in the West Wits goldfield, in response to periodic fluvial degradation of a series of alluvial fans spreading southward into the Witwatersrand Basin, and consists of broad, interconnecting, low-sinuosity ribbon bodies of conglomeratic and arenaceous sediments which resulted from extensive migration of belts of small braided streams (*e.g.* Vos, 1975; Buck & Minter, 1985; Frimmel & Minter, 2002).

The detrital minerals found in the CLR have a variety of origins, corresponding to predominantly Archaean granite-greenstone terrains which formerly surrounded the

Witwatersrand Basin (Wronkiewicz & Condie, 1987; Robb & Meyer, 1995). These detrital minerals were transported over relatively long distances (up to several 100 km) in a reducing environment, and deposited in active channels. In the areas between these channels microbial mats developed (Oberthür, 1983; Dyer *et al.*, 1988;). The columnar carbon layers with conspicuous gold mineralisation are the remains of these microbial mats (Spangenberg & Frimmel, 2001; Mossman *et al.*, 2008). A number of authors have posited other sources for the carbon, usually having the carbon deposited from a fluid derived from underlying shales and mudstones (*e.g.* Gray *et al.*, 1998; Parnell, 1999). These models, however, are not consistent with the features described by other authors and are contradicted by features observed during this study in the carbon seams from the CLR. Many of the features identified as proof of a fluid origin for the carbon, can be accommodated if the original source of the carbon from which the hydrocarbon fluid is derived is from *in situ* microbial mats, and this is the model which best fits the various chemical and textural features described in this study.

The gold associated with the microbial mats is often seen as platy gold on the surfaces of the columnar carbon in lacunae (Oberthür & Saager, 1986), and closer examination shows some shapes similar to that formed by bacteria and fungi, which are also formed by U-oxides, and imply that these elements were being deposited while the microbial mats were alive and growing (Hallbauer & van Warmelo, 1974; Hallbauer, 1975).

Due to its nature, gold can exist in extremely finely divided form, as flaky 'flour' or 'float' gold which may be transported for hundreds of kilometres. This has been used as an explanation for the origin of the very finely divided gold of deposits such as those found in the Witwatersrand Basin (Lindgren, 1919), where it can occur in areas of slack water or decreased flow, as shown by Minter (1999). The fine gold particles associated with the carbon, and described in Chapter 10, however, do not display the features that one would expect to see of alluvial gold.

Hallbauer (1978) records that while detrital minerals, including gold, are found concentrated on the top and in the upper portions of the carbon layers, gold and uranium occur throughout the carbon, often in vertical filaments. The antipathetic distribution of the Au and the U is very distinct, with the U occurring mainly in the columnar carbon, and most of the gold occurring in the interstices between them. This feature has previously been identified by Simpson & Bowles (1977) in the carbon seams in the Vaal and Carbon Leader reefs.

The elements which have been accumulated within the grain boundaries and interstices of the carbon follow no clear associations which can be related to mineralogical phases. The carbon, which formed originally as microbial mats growing in a shallow braided stream environment (Hallbauer, 1975; Buck & Minter, 1985), had a nodular surface upon which elements precipitated out of solution, or which were adsorbed onto the surface of the mats due to the propensity of certain elements for organic compounds.

The various domains of the different elements which are observed in the carbon are consistent with being derived from solution as colloidal precipitates, or by adsorption directly from solution onto the microbial mats. This type of chemical deposition was recorded by Kucha *et al.* (1998), who found both visible and invisible gold associated with carbon (thucolite), with the invisible gold being of small size (40 nm), non-crystalline and pure, indicating an origin from organometallic compounds.

Carbonaceous material in the Witwatersrand contains up to 10% U_3O_8 (Hallbauer, 1978). U has a relatively low toxicity compared to Au, which has a high level of cellular toxicity (Brugger *et al.*, 2013) and reduces microbial activity where it is deposited, which could result in openings where the growth rate of the microbial mats is reduced and thus precipitating Au-colloids and other elements can be deposited in these interstices.

Two types of uranium are described from the Witwatersrand (Simpson & Bowles, 1977). The one occurs as allogenic grains of similar habit to those presently being deposited in gravels in the Indus valley (Miller, 1963), from uranium derived from the Thar coalfield (Siddiqui, 2009). The other type is associated with the carbon and gold. This U was shown to be primary (syngenetic), unaffected by later remobilisation, and is attributed to the U being in solution during sedimentation and diagenesis (Pretorius, 1975; Simpson & Bowles, 1977).

A logical consequence of these observations is that a major source of the Au, Ag, U, Th and other elements associated with this colloidal-deposition in the carbon is from microbial action. Au is solubilised from alluvial gold grains in proximal alluvial deposits and soils, and released into solution as nano-particles, where it is then able to be transported as nano-particles or organometallic colloids, to be redeposited further away (Brugger *et al.*, 2013). Plyusnina *et al.* (2000) have shown that although Pt is adsorbed onto organic compounds, this process is only effective under acidic, buffered conditions and at higher temperatures, not under the conditions that would be experienced in a fluvial, braided stream environment.

The solubility of Au in near neutral to slightly acidic water can be far greater than that of Pt, with an Au/Pt solubility ratio exceeding 10^{10} (Brugger *et al.*, 2013). The combination of the higher solubility of the Au, and conditions favouring its preferential adsorption onto organic matter under the conditions prevailing during deposition, can account for the presence of Au and the other elements in the originally microbial mat carbon and the absence of PGE.

The source of the uranium within the algal mats is ascribed to the propensity of dissolved uranium (and thorium), in the presence of sulphide formation and organic material such as algae or bacteria, to form uraninite which remains stable even in the presence of oxygen, as long as there are sulphides present (Edgington *et al.*, 1996; Abdelouas *et al.*, 2000). UO_2^{2+} ions become complexed to cell wall material (Kalin *et al.*, 2005), and thus bacteria and algae can remove most dissolved U from seawater (Heide *et al.*, 1973). All U (and much of the Th) found in present-day ocean sediments is bound to organic material (Kalin *et al.*, 2005).

Elemental mapping of the carbon has shown that the U is distributed within the carbon with the gold on the outsides of the nodules. Depiné *et al.* (2013) have shown that the uraninite found within the carbon is fairly homogeneous with even distribution of a number of elements, including Au, Pb and Ce. This uraninite is very unusual in its elevated Au contents, and they state that these are “unlikely to be due to minute inclusions of native gold within the uraninite but rather due to the incorporation of Au into the uraninite structure”.

Within “pyrobitumen”, carbon nodules which have been formed from the hydrocarbon liquid generated from the breakdown of the original bacterial mat carbon, the U is evenly distributed (Fuchs *et al.* 2014) and considered to have been in solution in liquid hydrocarbons.

The presence radiogenic Pb isotopes in direct association with U found in the carbon, is a result of the in-situ radioactive decay of U and Th. The especially high values of ^{206}Pb (Rundle & Snelling, 1977), formed by the decay of ^{238}U through an intermediate daughter isotope ^{222}Rn , relative to the other isotopes, can be attributed to ^{222}Rn diffusing from the uranium would be immediately adsorbed onto the carbon where it subsequently decayed to ^{206}Pb (Zartman & Frimmel, 1999). If the Pb had been deposited with all the other elements present in the carbon, it would show a more normal Pb isotope distribution. The overall anomalous radiogenic Pb levels in the Witwatersrand Basin (Rundle & Snelling, 1977) are therefore attributed to the U mineralisation, which occurs almost entirely associated with

carbon (Simpson & Bowles, 1977; Poujol *et al.*, 1999).

Large *et al.* (2013) have shown that the detrital pyrite from the CLR is typical of diagenetic pyrite which formed in suboxic to anoxic conditions. The cores of these pyrites were dated at between 2750 and 2950 Ma, while their euhedral hydrothermal overgrowths, which were rich in radiogenic Pb, were dated at between 2100 and 2020 Ma. In a study of buckshot pyrite grains from a number of reefs from the Witwatersrand Basin, including the CLR, it was confirmed that these pyrite grains formed in the sedimentary environment during sedimentation and diagenesis (Guy *et al.*, 2014).

11.5 Gold mineralisation in the Vaal Reef

The d'ore gold from the Klerksdorp goldfield, which is derived almost exclusively from the carbon-bearing Vaal Reef, shows a very variable behaviour of the radiogenic Pb isotopes (as discussed in 7.1.2) and Au:Cu ratios, which is the opposite of that observed for most of the West Wits goldfield and portions of the Free State goldfield (see Figs 7.3, 7.7 and 7.8). The conditions which caused this decoupling could only have occurred after deposition, as the radiogenic Pb had to be produced by the decay of the various U isotopes.

The much higher Ni content in the d'ore gold from the Klerksdorp goldfield is indicative of a possible original ultramafic derivation for the source of some of the reef sediments. Toma & Murphy (1978) showed that some of the gold in the Klerksdorp goldfield is derived from original PGM deposits, associated with detrital PGM grains. The Klerksdorp d'ore gold is also enriched in Co and Pd, relative to the other two goldfields, which reinforces this origin.

The three populations of gold grains which were identified from the Vaal Reef, as described in Chapter 10.3, show the presence of two distinct genetic processes. The one population is a very clean gold containing Cl, and it is considered to be gold formed by rapid growth in boiling brine, resulting in chlorine-rich inclusions in the gold. This gold was transported from source and deposited in the alluvial environment of the placers. The second population of gold grains is very different, and shows abundant evidence of having been formed in a fluid environment containing a wide range of dissolved elements. This gold, occurring mainly as cores of gold grains, is enriched in U, Th and radiogenic lead, as well as other elements such as Co, Ni, Bi, Fe and Cu. In neither gold population is there any significant trace of any PGE. The cores are surrounded by gold which is very clean in composition, containing almost none

of the elements found in the cores, and is typical of low-temperature hydrothermal gold.

The presence of the U, Th and radiogenic Pb in the cores of these gold grains can be attributed to the dissolution of the material which was deposited from suspension as organometallic colloids and nanoparticles into the microbial mats. U and Au do not normally occur in the same compound, and often display an antipathetic behaviour (Kucha *et al.*, 1998), so the presence of the U in the cores indicates conditions of formation which were rather different to a typical hydrothermal fluid. In order to produce this U- and Au-rich fluid, conditions would have to be very reducing, and a hydrocarbon fluid would provide the right conditions for this. The width of the cores and the rapid decrease in the abundance of the U and Th outwards shows that the initial fluid composition changed rapidly, resulting in a more typical hydrothermally grown gold grain composition of fairly clean Au-Ag-Hg composition. High U values in gold grains from the Witwatersrand have been reported previously, but it was assumed that this was due to uraninite or zircon inclusions (Eugster *et al.*, 1995).

Hydrocarbon fluids were produced on a large scale within the Witwatersrand Basin, and are intimately associated with U and Au mineralisation (*e.g.* Simpson & Bowles, 1977; Gray *et al.*, 1998; Frimmel & Minter, 2002); For U to occur with Au in the cores of the gold grains, it would have to form an alloy, and there are no known naturally occurring Au-U compounds.

Gagliardi (2003) postulated the existence of stable tetragold compounds, MAu₄ (M = U, Ti, Zr, Hf, and Th). In such species gold has a valency of -1. In order for the Au to possess such a low valence state, the environment would have to be highly reducing (*e.g.* Fetzner, 1934), and the presence of organometallic compounds of U and Th would add to the reducing nature of such an environment (Grant *et al.*, 2012).

Initial formation of hydrocarbons from the breakdown of the organic compounds in the microbial mats would create a hydrocarbon-rich fluid. However, these conditions would only be of short duration, as aqueous fluids, generated by diagenesis of the surrounding sediments, would disrupt the hydrocarbon fluids, diluting them and causing their dispersion and dilution, and thereafter more normal hydrothermal conditions would prevail.

U-bearing gold was formed from Au which was within the carbon layers and therefore very finely disseminated, mainly colloidal in origin, as discussed above. The conditions for the dissolution of gold grains outside the carbon mat environment would not be as reducing as

that within it, and would have been antithetical with those required to precipitate UAu_4 . The continued existence of the Cl-rich gold grains, attributed to being of an extra-basinal alluvial origin, shows that they have survived dissolution, and the lack of such Cl enrichment in the gold surrounding the U-rich cores shows that the hydrothermal conditions were different to those that formed the alluvial grains.

These different types of gold show that within the Klerksdorp goldfield the initial geochemical conditions, which are representative of the initial depositional environment, were succeeded post-depositionally by a pervasive hydrothermal event which mobilised the elements originally deposited as chemical precipitates, and then redeposited them, forming amongst others gold grains with dirty cores, clean gold, and uraninite. After the initial highly reducing hydrocarbon fluids were diluted by aqueous fluids resulting from further diagenesis, other phases such as xenotime, pyrophyllite, uraninite, brannerite, gersdorffite, galena, chalcopyrite and pyrrhotite (England *et al.*, 2001; Oberthür, 1987; Zartman & Frimmel, 1999) were deposited.

11.6 Distribution of the two types of geochemical processes identified from the d'ore gold

The very distinct difference evidenced by the two types of d'ore composition identified within the Witwatersrand Basin suggest two very different processes and are not due to a difference in the beneficiation process. However, the differences are spatially limited, an example being the difference between Driefontein and the rest of the West Wits goldfield. A careful examination of the various physical aspects of the different mines, including the reefs mined and their geochemical variation, has shown that this difference is due predominantly to which reef was mined. The reefs towards the base of the Central Rand Group, such as the Vaal reef and the Carbon Leader reef, are also more carbon-rich, whereas the reefs towards the top, ending with the Ventersdorp Contact reef immediately above the Central Rand Group have a more alluvial or placer nature. The environments of deposition of the reefs, as well as source areas, will further add differences to their geochemical profiles.

Evidence of post-depositional mineralisation from fluids in the sediments of the Central Rand Group and the VCR is pervasive, and this has been accounted for by a variety of models, including: a hydrothermal origin for all the gold, as well as uraninite and hydrocarbon (Barnicoat *et al.*, 1997); a magmatic/hydrothermal origin linked to the emplacement of the

Bushveld Complex (Phillips & Law, 1994); or a metamorphosed, hydrothermally altered placer deposits (Frimmel & Gartz, 1997). It has also been shown that gold mobilisation and mineralisation occurred at least two times after the formation of the placer deposits by sedimentation (Frimmel, 1997).

Within the Carbon Leader Reef in the West Wits goldfield bulk rock $\delta^{18}\text{O}$ and δD values are consistent with the original detrital minerals, as well as the authigenic minerals, having a similar oxygen isotope composition, with the fluid responsible for the post-depositional mineralisation being a mixture of meteoric and metamorphic water. The finding that gold-rich and gold-poor areas of the CLR do not differ in their $\delta^{18}\text{O}$ and δD compositions excludes the contribution of significant amounts of externally derived fluids to the gold mineralisation process (Grové & Harris, 2010).

There has been much discussion about the nature and timing of these fluids. Klemd (1999) identified high-salinity CaCl_2 -rich fluids in hydrothermal quartz veins which were produced as a result of the dewatering of the sediments, and Frimmel *et al.* (1999) inferred the presence of two gold mobilising events which affected the Basin, one during early Transvaal times and the other coincident with the Vredefort impact event at around 2.02 Ga, but other hydrothermal events have also been recorded (*e.g.* Robb & Meyer, 1995; Frimmel, 1997), so a continuous but punctuated history of such events within the Witwatersrand Basin is implied over a period of almost 700 Ma.

With time and progressive diagenetic and tectonic events, it is expected that the nature of the fluids generated within the basin also change. The *in situ* generation of the hydrocarbon fluids discussed above would have to have been the very first fluid produced, with later aqueous fluids becoming saline, with the development of basinal brines (Eisenlohr *et al.*, 1994; Klemd, 1999; Seewald, 2001; Spangenberg & Frimmel, 2001).

The conditions needed for the mobilisation of the chemically precipitated colloidal material, which resulted in the formation of U-rich gold, have to exist early in the diagenetic history of the sediments, during the formation of organic fluids from the microbial mats (Spangenberg & Frimmel, 2001), when temperatures were low (Seewald, 2001), and the carbon was not yet polymerised by radiogenic activity from the U content.

Later, as pressures and temperatures rose with progressive metamorphism (Frimmel *et al.*,

1993), more water was released from the sediments producing Cl⁻ brines (Klemd, 1999; Frimmel *et al.*, 1999). Au and other dissolved materials in these brines, as a result of sudden depressurisation due to fault activation, gave rise to gold and other mineralisation, usually with the development of quartz veins (Weatherley & Henley, 2013). The various episodes of mineralisation thus triggered, culminating in the late-stage quartz veins within the Witwatersrand Basin, all gave rise to a similar suite of minerals which include bitumen nodules, gold grains (consisting almost entirely of Au, Ag and Hg, the clean gold shown in Fig. 10.1), and uraninite, as well as highly radiogenic galena (Burger *et al.*, 1962; Rundle & Snelling, 1977).

The processes discussed above are summarised schematically in Figure 11.1.

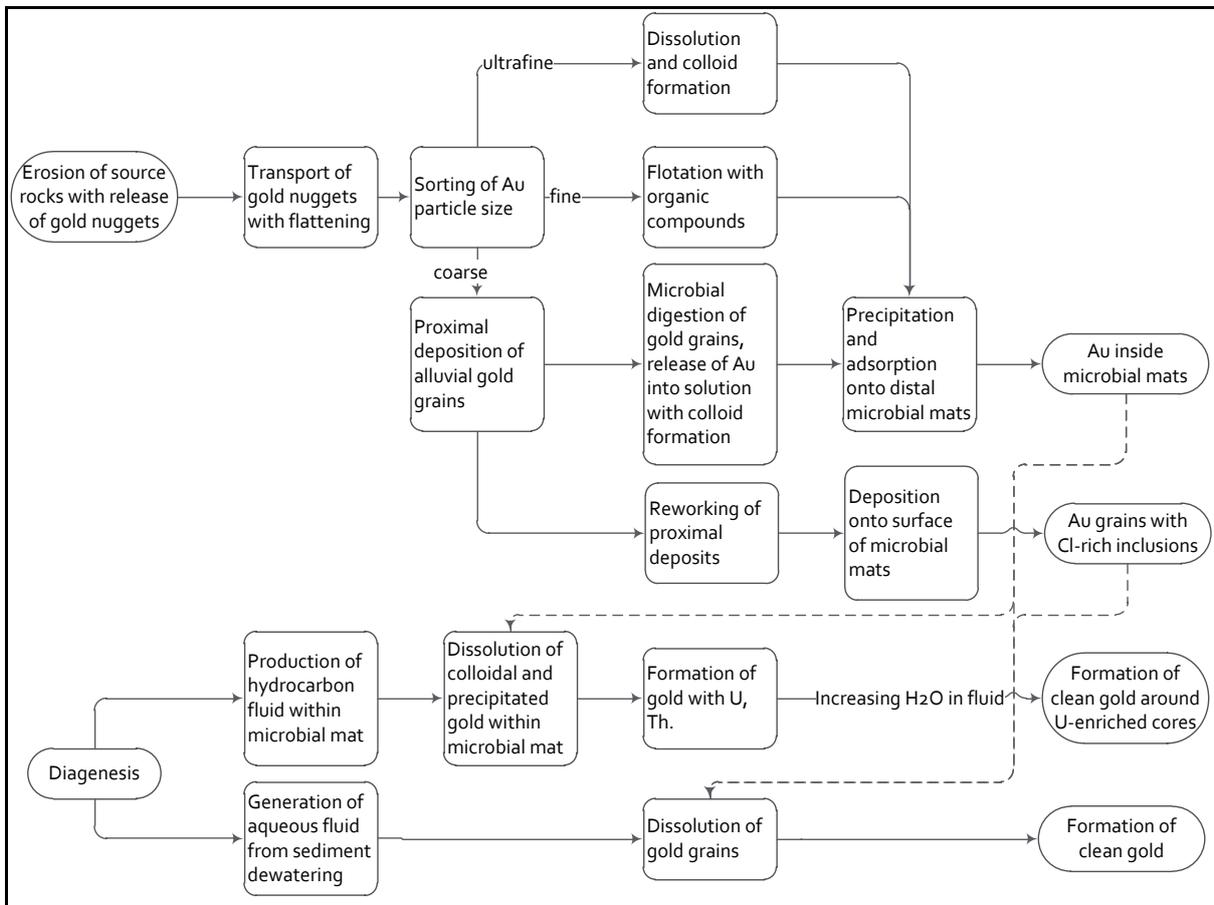


Fig. 11.1. Flowchart showing the processes involved in the production of the different types of gold composition identified in this study.

12 Conclusions

For the determination of the provenance or origin of a piece of gold which has been seized during the course of police investigation, it is essential to have a database, and more importantly one that is representative of the material in question. Whereas a geographically limited exploration project looking at alluvial gold grains to identify targets and link to ore bodies is a relatively simple matter, a database capable of the same level of success for gold which is mined and beneficiated by means of various processes will have to include samples, which are at risk of theft, from throughout the process.

Acquiring such samples for a database is a large task, and requires a coordinated effort which is usually only successful when all parties are obliged to contribute. In South Africa, where legislation has been drawn up for this specific reason, all parties wanting to mine and process gold are required to submit samples on a regular basis. This gold database, which has been accumulating samples for more than a decade, mainly from gold producers within the Witwatersrand Basin, assists in the identification of the origin of gold stolen from legal gold mines and beneficiated by alternative means.

The use of solution ICP-OES and LA-ICP-MS methods for analysing both database samples and seized illicit gold has been found to be the best way to get information on all elements present in the sample. Both natural gold as well as processed gold, both legally as well as illegally produced, are not homogeneous, and the information obtained from the small area sampled by the laser is more informative than bulk samples. The minimal sample preparation required and the speed at which the analyses are made make this a technique which can be utilised on a large scale.

From the samples in the database, which consist mainly of d'ore gold produced by the different mines, it has been shown that there are distinct elemental variations in the d'ore gold from different goldfields and gold mines within the Witwatersrand Basin. These variations are limited to those elements which are concentrated during the gold beneficiation process and thus have similar geochemical behaviour to Au, or are contained within minerals which are entrained by the process and end up being included in the d'ore gold.

The analysis of the d'ore gold from the Free State, Klerksdorp and West Wits goldfields has shown that there is a distinct enrichment in radiogenic Pb isotopes, which is attributed to the abundant U mineralisation. This enrichment can be used to distinguish illicit gold as having originated from the Witwatersrand Basin.

However, there are two distinct types of gold produced, which have geographically delineated distributions due to the specific reefs mined. One of these shows elevated concentrations of Ni, and shows that the processes accompanying mineralisation in the reefs were distinctly different. Variations in d'ore gold composition within the goldfields are seen with the elements Cu, Ni, Pb and Zn. The variation in elemental concentrations makes it possible to determine the source of d'ore gold with a high probability, but this is very dependent on having reference samples in the database.

The identification of the Au mineralisation processes within the various goldfields of the Witwatersrand Basin, based on the analysis of gold prills from the CLR and the VCR from Drifontein mine, gold grains from the Vaal Reef from the Klerksdorp goldfield, and gold within the carbon-rich CLR of Blyvooruitzicht mine, showed that the Au was deposited alluvially and precipitated from solution and colloids in suspension, independently but in the same environment as the U, associated with microbial mats.

During diagenesis, certain areas of some carbon-rich reefs in the lower portion of the Central Rand Group enjoyed conditions in which the concentration of carbon from the microbial mats was high enough to produce a hydrocarbon rich fluid or gas which was able to dissolve the metals deposited within it in a highly reducing environment, creating conditions in which Au was able to form compounds with U, which were subsequently coated with U-free Au when the reducing conditions stopped due to increasingly water-rich fluids. This mineralisation process is not consistent with a magmatic-hydrothermal Au mineralisation origin. It shows that all remobilised gold was derived from originally alluvial or chemically and biologically precipitated Au.

This remobilisation process, although widespread within the Witwatersrand Basin, did not erase the elemental variation due to the original mineralisation processes, but enhanced differences due to changes in fluid composition over time and also as the fluids ascended through the stratigraphy, redepositing dissolved elements.

Determining the origin of illicit gold based upon the data from the gold database showed that if the suspect sample had been processed from a similar material, reflecting the stage of the beneficiation process where the material was stolen, then an origin determination can be made with a high degree of certainty. However, when the material from which the suspect gold had been produced was not the same as that from which the database samples were produced, then the comparison is much more difficult, and a good understanding of the chemical and mineralogical differences and how they affect the gold composition was found to be crucial. It was shown that both natural as well as anthropogenic processes have to be understood before the data can be correctly interpreted, which means that a simple statistical method for the comparison of suspect samples to the database may not be sufficient in the majority of cases.

The increasing emphasis in the traceability of gold to ensure that it does not come from an illicit source, which has major ramifications for gold refining companies around the world, is going to make the certification of source not only a certification process, but will also require some physical record against which the origin of a shipment may be confirmed.

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References

- Abdelouas, A., Lutze, W., Gong, W., Nuttall, E.H., Strietelmeier, B.A. and Travis, B.J., (2000). Biological reduction of uranium in groundwater and subsurface soil. *Science of the Total Environment*, **250**:21-35.
- Adamson, R.J., (1972). *Gold metallurgy in South Africa*. Chamber of Mines of South Africa, Johannesburg. 452 p.
- Aeschliman, D.B., Bajic, S.J., Baldwin, D.P. and Houk, R.S., (2003). Spatially-resolved analysis of solids by laser ablation-inductively coupled plasma-mass spectrometry: trace elemental quantification without matrix-matched solid standards. *J. Anal. At. Spectrom.*, **18**:872–877.
- Aeschliman, D.B., Bajic, S.J., Baldwin, D.P. and Houk, R.S., (2004). Multivariate pattern matching of trace elements in solids by laser ablation inductively coupled plasma-mass spectrometry: source attribution and preliminary diagnosis of fractionation. *Analytical Chemistry*, **76**:3119–3125.
- Afenya, P.M., (1991). Treatment of carbonaceous refractory gold ores. *Minerals Engineering*, **4**:1043–1055.
- Agangi, A., Hofman, A. and Wohlgemuth-Ueberwasser, C.C., (2013). Pyrite zoning as a record of mineralization in the Ventersdorp Contact reef, Witwatersrand Basin, South Africa. *Economic Geology*, **108**:1243–1272.
- Altigani, M.A.H., (2013). *Mineralogical characterizations of gold ore from Barberton Greenstone Belt, South Africa*. PhD thesis, University of Pretoria, South Africa.
- Amador-Hernández, J., García-Ayuso, L.E., Fernández-Romero, J.M. and de Castro, M.L., (2000). Partial least squares regression for problem solving in precious metal analysis by laser induced breakdown spectrometry. *Journal of Analytical Atomic Spectrometry*, **15**:587–593.
- Andean Air Mail & Peruvian Times, (2012). *Peru's Illegal Gold Mining Bigger Than Drug Trade*. Andean Air Mail & Peruvian Times, May 17, 2012. <http://www.peruviantimes.com/17/perus-illegal-gold-mining-bigger-than-drug-trade/15746/> . Downloaded on 15 June 2012.
- Antweiler, J.C. and Campbell, W.L., (1977). Application of gold compositional analyses to mineral exploration in the United States. *Journal of Geochemical Exploration*, **8**:17–29.

- Ardelt, D., Polatajko, A., Primm, O. and Reijnen, M., (2013). Isotope ratio measurements with a fully simultaneous Mattauch–Herzog ICP-MS. *Analytical and Bioanalytical Chemistry*, **405**:2987–2994.
- Arehart, G.B., Chryssoulis, S.L. and Kesler, S.E., (1993). Gold and arsenic in iron sulfides from sediment-hosted disseminated gold deposits; implications for depositional processes. *Economic Geology*, **88**:171–185.
- Axelsson, M.D., Olofsson, R.S. and Rodushkin, I., (2000). Selected geological and environmental applications of laser ablation ICP-SFMS. Poster. Luleå University of Technology.
- Axelsson, M.D. and Rodushkin, I., (2001). Determination of major and trace elements in sphalerite using laser ablation double focusing sector field ICP-MS. *Journal of Geochemical Exploration*, **72**:81–89.
- Bagby, W.C. and Berger, B.R., (1985). Geologic characteristics of sediment-hosted, disseminated precious-metal deposits in the western United States. Geology and geochemistry of epithermal systems. *Reviews in Economic Geology*, **2**:169–202.
- Bailey, P.R. (1987). Application of Activated Carbon to Gold Recovery. The Extractive Metallurgy of Gold in South Africa, S. Afr. Inst. Min. Metall., Monogr. Ser. M7, **1**:379–614.
- Baker, J., Peate, D., Waight, T. and Meyzen, C., (2004). Pb isotopic analysis of standards and samples using a ^{207}Pb – ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chemical Geology*, **211**:275–303.
- Baker, J., Stos, S. and Waight, T., (2006). Lead isotope analysis of archaeological metals by multiple-collector inductively coupled plasma mass spectrometry. *Archaeometry*, **48**:45–56.
- Ballot, J., (1888). The banket formation: its probable origin and present position. Mendelssohn & Scott, Johannesburg.
- Bariyo, N., Freeman, F. and Plevin, L., (2013). Wie Blutgold aus dem Kongo auf den Weltmarkt gelangt. *The Wall Street Journal*, 15 April. Available at <http://www.wallstreetjournal.de/article/SB10001424127887324485004578424543527900854.html> [Accessed 1 May 2013].
- Barnicoat, A.C., Henderson, I.H.C., Knipe, R.J., Yardley, B.W.D., Napier, R.W., Fox, N.P.C., Kenyon, A.K., Muntingh, D.J., Strydom, D., Winkler, K.S., Lawrence, S.R., and Cornford, C., (1997). Hydrothermal gold mineralization in the Witwatersrand basin. *Nature*, **386**:820–824.

- Barton, M.M. and Miskelly, G.M., (2006). The Use and Limits of Compositional Analysis for Discrimination and Classification of Samples. *Chemistry in New Zealand.*, April 2006: 3–6.
- Becker, G.F., (1897). The Witwatersrand Banket, with short notes on other gold-bearing puddingstones. *18th Ann. Rep. U.S. Geol. Survey, Washington, D.C.*, Part 5:153–184.
- Bendall, C., Wigg-Wolf, D., Lahaye, Y., Von Kaenel, H.M. and Brey, G.P., (2009). Detecting changes of Celtic gold sources through the application of trace element and Pb isotope laser ablation analysis of Celtic gold coins. *Archaeometry*, **51**:598–625.
- Bernardin, J.E., (2000). Jewelry manufacturing with the new high carat golds. *Gold Technology*, **30**:17–21.
- Bonev, I.K., Kerestedjian, T., Atanassova, R. and Andrew, C.J., (2002). Morphogenesis and composition of native gold in the Chelopech volcanic-hosted Au-Cu epithermal deposit, Srednogorie zone, Bulgaria. *Mineralium Deposita*, **37**:614–629.
- Boulangé, B., Muller, J.P. and Sogolo, J.B., (1990). Behaviour of the rare earth elements in lateritic bauxite from syenite (Bresil). In: *Geochemistry of the Earth's surface and of mineral formation, 2nd International Symposium, July 2-8, 1990, Aix en Provence, France*, 350–351.
- Braun, J.J., Pagel, M., Muller, J.P., Bilong, P. and Michard, A. (1990). Cerium anomalies in lateritic profiles. *Geochimica et Cosmochimica Acta*, **54**:781–796.
- Braun, J.J., Viers, J., Dupré, B., Polve, M., Ndam, J. and Muller, J.P. (1998). Solid/Liquid REE Fractionation in the Lateritic System of Goyoum, East Cameroon: The Implication for the Present Dynamics of the Soil Covers of the Humid Tropical Regions. *Geochimica et Cosmochimica Acta*, **62**:273–299.
- Broeders, A.P.A., (2003). Forensic Evidence and International Courts and Tribunals - Why bother, given the present state of play in forensics? Paper presented at the 17th Conference of the International Society for the Reform of Criminal Law, The Hague, Netherlands, August 24-28, 2003.
- Broekman, B.R., Carter, L.A.E. and Dunne, R.C., (1987). *Flotation. The Extractive Metallurgy of Gold in South Africa*, Monograph Series M7, **1**:235-275.
- Brown, S.M., Johnson, C.A., Watling, R.J. and Premo, W.R. (2003). Constraints on the composition of ore fluids and implications for mineralising events at the Cleo gold deposit, Eastern Goldfields Province, Western Australia. *Australian Journal of Earth Sciences*, **50**:19–38.

- Brugger, J., Etschmann, B., Grosse, C., Plumridge, C., Kaminski, J., Paterson, D., Shar, S.S., Ta, C., Howard, D.L., de Jonge, M.D., Ball, A.S., Reith, F., (2013). Can biological toxicity drive the contrasting behavior of platinum and gold in surface environments? *Chemical Geology*, **343**:99–110.
- BSR, (2010). Conflict minerals and the Democratic Republic of Congo. www.BSR.org, May 2010.
- Buck, S.G. and Minter, W.E.L., (1985). Placer formation by fluvial degradation of an alluvial fan sequence: the Proterozoic Carbon Leader Placer, Witwatersrand Supergroup, South Africa. *J. Geol. Soc. London*, **142**:757–764.
- Bugoi, R., Constantinescu, B., Constantin, F., Catana, D., Plostinaru, D. and Sasianu, A., (1999). Archaeometrical Studies of Greek and Roman Silver Coins. *Journal of Radioanalytical and Nuclear Chemistry*, **242**:777–781.
- Burger, A.J., Nicolaysen, L.O. and de Villiers, J.W.L., (1962). Lead isotopic compositions of galenas from the Witwatersrand and Orange Free State, and their relation to the Witwatersrand and Dominion Reef uraninites. *Geochimica et Cosmochimica Acta*, **26**: 25–59.
- Butler, O.T., Cairns, W., Cook, J.M. and Davidson, C.M., (2011). Atomic spectrometry update. Environmental analysis. *Journal of Analytical Atomic Spectrometry*, **26**:250–286.
- Cabri, L.J., (1988). *The role of mineralogy in gold metallurgy*. CANMET, Rep. MSI 8E-51.
- Cabri, L.J., Chryssoulis, S.L., De Villiers, J.P.R., Laflamme, J.H.G. and Buseck, P.R., (1989). The nature of "invisible" gold in arsenopyrite. *Canadian Mineralogist*, **27**:353–362.
- Chapman, R.J. and Mortensen, J.K. (2006). Application of microchemical characterization of placer gold grains to exploration for epithermal gold mineralization in regions of poor exposure. *Journal of Geochemical Exploration*, **91**:1–26.
- Chapman, R.J., Leake, R.C., Moles, N.R., Earls, G., Cooper, C., Harrington, K. and Berzins, R. (2000). The application of microchemical analysis of alluvial gold grains to the understanding of complex local and regional gold mineralization: a case study in the Irish and Scottish Caledonides. *Economic Geology*, **95**:1753–1773.
- Chen, Z., Doherty, W., Gregoire, D.C. and Harris, D., (1997). Application of laser microprobe inductively coupled plasma mass spectrometry for trace metal fingerprinting of native gold. *Geol. Surv. Can., Current Res.* **1997-D**:57–62.
- Coetzee, B. and Horn, R., (2007). *Theft of precious metals from South African mines and refineries*. ISS Monograph Series, No 133, May 2007, 122p

- Cole, S.A., (2009). Forensics without uniqueness, conclusions without individualization: the new epistemology of forensic identification. *Law, Probability and Risk*, 8: 233–255.
- Corti, C.W., (1999). Metallurgy of microalloyed 24 carat golds. *Gold Bulletin*, 32: 39–47.
- Cousins, C.A., (1973). Platinoids in the Witwatersrand system. *Journal of the South African Institute of Mining and Metallurgy*, 73:184–199.
- Cretu, C., van der Lingen, E. and Glaner, L., (2000). Hard 22 carat gold alloy. *Gold Technology*, 29:25–28.
- Cuvelier, J., (2011). *Kenya's role in the trade of gold from eastern DRC*. IPIS, Antwerp, www.ipisresearch.be, 9 pp.
- Dai, X., Simons, A. and Breuer, P., (2012). A review of copper cyanide recovery technologies for the cyanidation of copper containing gold ores. *Minerals Engineering*, 25:1–13.
- Dalpé, C., Hudon, P., Ballantyne, D.J., Williams, D. and Marcotte, D., (2010). Trace Element Analysis of Rough Diamond by LA-ICP-MS: A Case of Source Discrimination? *Journal of Forensic Sciences*, 55:1443–1456.
- de la Rey, J.H., (2007). *The fact-finding process and the burden of proof during litigation*. Magister Legum thesis, University of Pretoria.
- de Launay, L., (1896). *Les Mines d'Or du Transvaal*. Librairie Polytechnique, Baudry et Cie, Paris, 540 pp.
- de Launay, L., (1903). *Les Richesses Minérales de l'Afrique*. Librairie Polytechnique Ch. Béranger, Paris, 395 pp.
- de Wit, M.J. and Thiar, C., (2005). Metallogenic fingerprints of Archaean cratons. In: McDonald, I., Boyce, A.J., Butler, I.B., Herrington, R.J. & Polya, D.A. (eds), *Mineral Deposits and Earth Evolution*. Geological Society, London, Special Publications, 248:59–70.
- Deconinck, I., Latkoczy, C., Günther, D., Govaert, F. and Vanhaecke, F., (2006). Capabilities of laser ablation—inductively coupled plasma mass spectrometry for (trace) element analysis of car paints for forensic purposes. *J. Anal. At. Spectrom.*, 21:279–287.
- Demaske, B.J., Zhakhovsky, V.V., Inogamov, N.A. and Oleynik, I.I., (2010). Ablation and spallation of gold films irradiated by ultrashort laser pulses. *Physical Review B*, 82:064–113.
- Department of Minerals and Energy, (2006). *South Africa's Mineral Industry 2005/2006*. 23rd ed. Pretoria, 173 p.

- Depiné, M., Frimmel, H.E., Emsbo, P., Koenig, A.E. and Kern, M., (2013). Trace element distribution in uraninite from Mesoarchaeon Witwatersrand conglomerates (South Africa) supports placer model and magmatogenic source. *Mineralium Deposita*, **48**:423–435.
- Diamantatos, A., (1977). An integrated scheme for the recovery of the six platinum-group metals and gold after lead fusion and perchloric acid parting and a comparison with the lead cupellation, tin, and nickel sulphide collection schemes. *Analytica Chimica Acta*, **94**:49–55.
- Dixon, R.D., Ueckermann, H., Espach, H.J., De Jager, L.L. & Roberts, R.J., (2007). Combatting the illegal gold trade using chemical profiling. *Proceedings of the American Academy of Forensic Sciences*, Volume XIII, p 44.
- Dodd-Frank Wall Street Reform and Consumer Protection Act, (2010). Dodd-Frank Section 1502. 111th Congress Public Law 203.
- Donovan, D.R., (2014). Mineral smuggling in Central Africa. *Africa Conflict Monthly Monitor*, 62–66.
- Douglas, J.K.E. and Moir, A.T., (1961). A review of South African gold recovery practice. *7th Commonwealth Mining and Metallurgical Congress*, **3**:971–1003.
- Draper, D., (1899). Notes on Mr Bleloch's paper, entitled "On Rand Conglomerates". *Transactions of the Geological Society of South Africa*, **5**:3-15.
- Dyer, B.D., Krumbein, W.E. & Mossman, D.J. (1988). Nature and origin of stratiform kerogen seams in lower Proterozoic Witwatersrand-type paleoplacers – the case for biogenicity. *Geomicrobiology Journal*, **6**:33–47.
- Edgington, D.N., Robbins, J.A., Colman, S.M., Orlandini, K.A. and Gustin, M.P., (1996). Uranium-series disequilibrium, sedimentation, diatom frustules, and paleoclimate change in Lake Baikal. *Earth and Planetary Science Letters* **142**:29–42.
- Ehrke, H.U., Hombourger, C. and Outrequin, M., (2013). Quantitative analysis with the CAMECA SXFIVE FE at high lateral resolution. Applications to Geochronology and Mineralogy. In EGU General Assembly Conference Abstracts (Vol. 15, p. 3250).
- Eisenlohr, B.N., Tompkins, L.A., Cathles, L.M., Barley, M.E. & Groves, D.I., (1994). Mississippi Valley-type deposits: products of brine expulsion by eustatically induced hydrocarbon generation? An example from northwestern Australia. *Geology*, **22**:315–318.
- Els, B.G., (1987). *The auriferous Middelvllei reef depositional system, West Wits Line, Witwatersrand Supergroup*. Unpub. PhD thesis, Rand Afrikaans University, 329 p.

- Els, B.G., (1991). Placer formation during progradational fluvial degradation: the Late Archaean Middelvlei gold placer, Witwatersrand, South Africa. *Economic Geology*, **86**:29–45.
- ENFSI, (2008). *CIP Project*. Report of the CIP Forensic Review Board. 23 April 2008. The Hague, The Netherlands. The CIP project report can also be accessed at <http://www.enfsi.eu/page.php?uid=96>
- England, G.L., Rasmussen, B., McNaughton, N.J., Fletcher, I.R., Groves, I.D. and Krapez, B. (2001). SHRIMP U-Pb ages of diagenetic and hydrothermal xenotime from the Archaean Witwatersrand Supergroup of South Africa. *Terra Nova*, **13**:360–367.
- Erasmus, C.S., Sellschop, J.P.F. and Watterson, J.I.W., (1987). New evidence on the composition of mineral grains of native gold. *Nuclear Geophysics*, **1**:1–23.
- Eugster, O., Niedermann, S., Thalmann, C., Frei, R., Kramers, J., Krähenbühl, U., Liu, Y.Z., Hofmann, B., Boer, R.H., Reimold, W.U. and Bruno, L., (1995). Noble gases, K, U, Th, and Pb in native gold. *Journal of Geophysical Research: Solid Earth*, **100(B12)**:24677–24689.
- Farah, D., (2002). Al Qaeda's Road Paved With Gold. Secret Shipments Traced Through a Lax System In United Arab Emirates. Washington Post Foreign Service. Sunday, February 17, 2002; Page A01.
- Feather, C.E., (1976). Mineralogy of platinum group minerals in the Witwatersrand, South Africa. *Economic Geology*, **71**:1399–1428.
- Feather, C.E., (1977). *Mineralogical considerations in the recovery of platinum group minerals from Witwatersrand mimics gravity concentrates*. Internal report, Anglo American Research Laboratories, 11pp.
- Feather, C.E. and Koen, G.M., (1975). The mineralogy of the Witwatersrand Reefs. *Minerals Sci. Engng*, **7**:189–224.
- Fetzer, W.G., (1934). Transportation of gold by organic solutions. *Economic Geology*, **29**:599–604.
- Fleming, C.A., (1992). Hydrometallurgy of precious metals recovery. *Hydrometallurgy*, **30**: 127–162.
- Fleming, C. and Cromberge, G., (1984). The Extraction of Gold From Cyanide Solutions by Strong- and Weak-Base Anion-Exchange Resins. *Journal of the South African Institute of Mining and Metallurgy*, **84**:125–137.

- Foya, S.N., Reimold, W.U., Przybylowicz, W.J. and Gibson, R.L., (1999). PIXE microanalysis of gold-pyrite associations from the Kimberley Reefs, Witwatersrand basin, South Africa. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **158**:588-592.
- Frimmel, H.E. and Minter, W.E.L., (2002). Recent developments concerning the geological history and genesis of the Witwatersrand gold deposits, South Africa. In: Goldfarb, R. and Nielsen, R.L., (editors) *Global Exploration 2002 - Integrated Methods for Discovery*. Littleton, Soc. Econ.Geol., Special Publ., **9**:17–45.
- Frimmel, H.E., (1997). Detrital origin of hydrothermal Witwatersrand gold—a review. *Terra Nova*, **9**:192–197.
- Frimmel, H.E. and Gartz, V.H., (1997). Witwatersrand gold particle chemistry matches model of metamorphosed, hydrothermally altered placer deposits. *Mineralium Deposita*, **32**:523–530.
- Frimmel, H.E., Le Roex, A.P., Knight, J. and Minter, W.E.L., (1993). A case study of the postdepositional alteration of the Witwatersrand Basal reef gold placer. *Economic Geology*, **88**:249–265.
- Frimmel, H.E., Hallbauer, D.K. and Gartz, V.H., (1999). Gold mobilizing fluids in the Witwatersrand Basin: composition and possible sources. *Mineralogy and Petrology*, **66**:55–81.
- Fryer, B.J., Jackson, S.E. and Longerich, H.P., (1995). The design, operation and role of the laser-ablation microprobe coupled with an inductively coupled plasma-mass spectrometer (LAM-ICP-MS) in the earth sciences. *Canadian Mineralogist*, **33**:303–303.
- Fuchs, S., Przybylowicz, W.J. and Williams-Jones, A.E., (2014). Elemental imaging of organic matter and associated metals in ore deposits using micro PIXE and micro-EBS. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **318**:157–162.
- Gäbler, H.E., Melcher, F., Graupner, T., Bahr, A., Sitnikova, M.A., Henjes-Kunst, F., Oberthür, T., Brätz, H. and Gerdes, A., (2011). Speeding Up the Analytical Workflow for Coltan Fingerprinting by an Integrated Mineral Liberation Analysis/LA-ICP-MS Approach. *Geostandards and Geoanalytical Research*, **35**:431–448.
- Gagliardi, L., (2003). When does gold behave as a halogen? Predicted uranium tetraauride and other MAu₄ tetrahedral species, (M= Ti, Zr, Hf, Th). *Journal of the American Chemical Society*, **125**:7504–7505.

- Gao, S., Liu, X., Yuan, H., Hattendorf, B., Günther, D., Chen, L. and Hu, S., (2002). Determination of Forty Two Major and Trace Elements in USGS and NIST SRM Glasses by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. *Geostandards Newsletter*, **26**:181–196.
- García-Sánchez, A., Contreras, F., bAdams, M., & Santos, F., (2006). Atmospheric mercury emissions from polluted gold mining areas (Venezuela). *Environmental geochemistry and health*, **28**:529–540.
- Gastrow, P., (2001). *Theft from South-African Mines and Refineries B The illicit market for gold and platinum*. ISS Monograph Series, No 54, April 2001, 72p.
- Gauert, C.D.K., Brauns, M., Batchelor, D. and Simon, R., (2011). Gold provenance of the Black Reef conglomerate, West and East Rand, South Africa. Abstract, SGA biennial conference, Antofagasta, Chile. 3p
- George, M.W., (2007). Gold. *U.S. Geological Survey, Mineral Commodity Summaries, January 2007*. U.S. Department of the Interior.
- George, M.W., (2013). *Gold – 2011*. U.S. Geological Survey 2011 Minerals Yearbook, U.S. Department of the Interior.
- Gibbs, A.K., Barron, C.N. and Tabcart, F., (1993). *The geology of the Guiana Shield*. New York: Oxford University Press.
- Gießmann, U. and Greb, U., (1994). High resolution ICP-MS—a new concept for elemental mass spectrometry. *Fresenius' journal of analytical chemistry*, **350**:186–193.
- Goldfarb, R.J., Groves, D.I. and Gardoll, S., (2001). Orogenic gold and geologic time: a global synthesis. *Ore Geology Reviews*, **18**:1–75.
- Goldmann, C.S., (1895). *South African Mines, their Position, Results and Developments, together with an Account of Diamond, Land and Kindred Concerns, with co-operation of Joseph Kitchin*. Effingham Wilson and Co., London, Johannesburg. 3 volumes: Volume 1: Rand Mining Companies, Volume 2: Miscellaneous Companies, Vol. 3: Maps and Plans.
- Grant, D.J., Stewart, T.J., Bau, R., Miller, K.A., Mason, S.A., Gutmann, M., McIntyre, G.J., Gagliardi, L. and Evans, W.J., (2012). Uranium and Thorium Hydride Complexes as Multielectron Reductants: A Combined Neutron Diffraction and Quantum Chemical Study. *Inorganic Chemistry*, **51**:3613–3624.
- Graton, L.C., (1930). Hydrothermal origin of the Rand gold deposits; Part 1, Testimony of the conglomerates. *Economic Geology*, **25**(3 Suppl):1–185.

- Gray, G.J., Lawrence, S.R., Kenyon, K. & Cornford, C., (1998). Nature and origin of 'carbon' in the Archaean Witwatersrand Basin, South Africa. *Journal of the Geological Society*, **155**:39–59.
- Greffié, C., Benedetti, M.F., Parron, C., and Amouric, M. (1996). Gold and iron oxide associations under supergene conditions - an experimental approach. *Geochimica et Cosmochimica Acta*, **60**:1531–1542.
- Grigorova, B., Anderson, S., de Bruyn, J., Smith, W., Stülpner, K. and Barzev, A., (1998). The AARL gold fingerprinting technology. *Gold Bulletin*, **31**:26–29.
- Grové, D. and Harris, C., (2010). O-and H-isotope study of the Carbon Leader reef at the Tau Tona and Savuka mines (Western Deep Levels), South Africa: Implications for the origin and evolution of Witwatersrand Basin fluids. *South African Journal of Geology*, **113**:73–86.
- Groves, D.I., Goldfarb, R.J., Gebre-Mariam, M., Hagemann, S.G. and Robert, F., (1998). Orogenic gold deposits: a proposed classification in the context of their crustal distribution and relationship to other gold deposit types. *Ore geology reviews*, **13**:7–27.
- Guerra, M.F., Calligaro, T. and Perea, A., (2007). The treasure of Guarrazar: tracing the gold supplies in the visigothic Iberian Peninsula. *Archaeometry*, **49**:53–74.
- Guerra, M.F., Radtke, M., Reiche, I., Riesemeier, H. and Strub, E., (2008). Analysis of trace elements in gold alloys by SR-XRF at high energy at the BAMline. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **266**:2334–2338.
- Gumiński, C. (1989). Classification of simple amalgams. *Journal of Materials Science*, **24**:3285–3288.
- Gumiński, C. (1990a). The Hg-Pd (mercury-palladium) system. *Journal of Phase Equilibria*, **11**:22–26.
- Gumiński, C. (1990b). The Hg-Pt (mercury-platinum) system. *Journal of Phase Equilibria*, **11**:26–32.
- Günther, D. and Hattendorf, B., (2005). Solid sample analysis using laser ablation inductively coupled plasma mass spectrometry. *Trends in Analytical Chemistry*, **24**:255–265.
- Gusmano, G., Montanari, R., Montesperelli, G., Tata, M.E., Bemporad, E., Valente, M., Kaciulis, S. and Mattogno, G., (2001). Influence of Si, Ni and Co additions on gold alloy for investment cast process. *Journal of Alloys and Compounds*, **325**: 252–258.

- Guy, B.M., Ono, S., Gutzmer, J., Lin, Y. and Beukes, N.J., (2014). Sulfur sources of sedimentary “buckshot” pyrite in the auriferous conglomerates of the Mesoarchean Witwatersrand and Ventersdorp Supergroups, Kaapvaal Craton, South Africa. *Mineralium Deposita*, DOI:10.1007/s00126-014-0518-3, 1–25.
- Haffty, J., Riley, L.B. and Goss, W.D., (1977). *A Manual on Fire Assaying and Determination of the Noble Metals in Geological Materials*. U.S. Geological Survey Bulletin 1445.
- Haken, J., (2011). Transnational Crime. In: *The Developing World*. Global Financial Integrity, Center for International Policy, Washington, 51–54.
- Hall, G.E.M. and Pelchat, J.C., (1994). Analysis of geological materials for gold, platinum and palladium at low ppb levels by fire assay-ICP mass spectrometry. *Chemical Geology*, **115**:61–72.
- Hallbauer, D.K., (1975). The plant origin of Witwatersrand carbon. *Minerals Science and Engineering*, **7**:111–131.
- Hallbauer, D.K., (1978). Witwatersrand Gold Deposits. Their genesis in the light of morphological studies. *Gold Bulletin*, **11**:18–23.
- Hallbauer, D.K. and Barton, J.M., (1987). The fossil gold placers of the Witwatersrand. *Gold Bulletin*, **20**:68–79.
- Hallbauer, D.K. and Utter, T., (1977). Geochemical and morphological characteristics of gold particles from recent river deposits and the fossil placers of the Witwatersrand. *Mineralium Deposita*, **12**:293–306.
- Hallbauer, D.K. and van Warmelo, K.T., (1974). Fossilized plants in thucholite from Precambrian rocks of the Witwatersrand, South Africa. *Precambrian Research*, **1**:199–212.
- Harrington, K.J., Land, D.P., Pollock, E.M., Springer, F.A. and Howitt, D.G., (2006). *Forensic applications of LA-ICP-MS: elemental profiling and evaluation of homogeneity in soda-lime container glass*. Downloaded from <http://projects.nfstc.org/trace/docs/final/Harrington.pdf> on 3 July 2012.
- Harris, D.C., (1990). The mineralogy of gold and its relevance to gold recoveries. *Mineralium Deposita*, **25**:S3–S7.
- Hatch, F.H., (1898). A Geological Survey of the Witwatersrand and other Districts in the Southern Transvaal. *Quarterly Journal of the Geological Society*, **54**:73–100

- Hayward, C.L., Reimold, W.U., Gibson, R.L. and Robb, L.J., (2005). Gold mineralization within the Witwatersrand Basin, South Africa: evidence for a modified placer origin, and the role of the Vredefort impact event. In: McDonald, I., Boyce, A.J., Butler, I.B., Herrington, R.J. & Polya, D.A., (eds). *Mineral Deposits and Earth Evolution*. Geological Society, London, Special Publications, **248**:31–58.
- Healy, R. E. and Petruk, W. (1990). Petrology of Au-Ag-Hg alloy and "invisible" gold in the Trout Lake massive sulfide deposit, Flin Flon, Manitoba. *The Canadian Mineralogist*, **28**:189–206.
- Hedenquist, J.W. and Lowenstern, J.B., (1994). The role of magmas in the formation of hydrothermal ore deposits. *Nature*, **370**:519–527.
- Heide, E.A., Wagener, K., Paschke, M. and Wald, M., (1973). Extraction of uranium from sea water by cultured algae. *Naturwissenschaften*, **60**: 431.
- Henley, K.J., (1975). Gold-ore mineralogy and its relation to metallurgical treatment. *Minerals Sci. Engng*, **7**:289–312.
- Hobbs, A. and Almirall, J.R., (2003). Trace elemental analysis of automotive paints by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Journal of Analytical and Bioanalytical Chemistry*, **376**:1265–1271.
- Holden, N.E., (2004). Table of the Isotopes. *In* D.R. Lide (ed). *CRC Handbook of Chemistry and Physics* (85th ed.). CRC Press.
- Horn, I., Guillong, M. and Günther, D., (2001). Wavelength dependant ablation rates for metals and silicate glasses using homogenized laser beam profiles—implications for LA-ICP-MS. *Applied surface science*, **182**:91–102.
- Horscroft, F.D.M., Mossman, D.J., Reimer, T.O. and Hennigh, Q., (2011) Witwatersrand metallogenesis: the case for (modified) syngeneses. *in* *Microbial Mats in Siliciclastic Depositional Systems Through Time*, SEPM Special Publication No. 101, 75–95.
- Inman, K. and Rudin, N., (2002). The origin of evidence. *Forensic Science International*, **126**:11–16.
- Jackson, J.A. and Bates, R.L. (eds) (1997). *Glossary of Geology*. 4th ed. American Geological Institute, 769 p.
- Jochum, K.P., Stoll, B., Herwig, K. and Willbold, M., (2007). Validation of LA-ICP-MS trace element analysis of geological glasses using a new solid-state 193 nm Nd:YAG laser and matrix-matched calibration. *J. Anal. At. Spectrom.*, **22**:112–121.

- Jolley, S. J., Freeman, S. R., Barnicoat, A. C., Phillips, G. M., Knipe, R. J., Pather, A., Fox, N.P.C., Strydom, D., Birch, M.T.G., Henderson, I.H.C. and Rowland, T. W., (2004). Structural controls on Witwatersrand gold mineralisation. *Journal of Structural Geology*, **26**:1067–1086.
- Jolley, S.J., Henderson, I.H.C., Barnicoat, A.C. and Fox, N.P.C., (1999). Thrust-fracture network and hydrothermal gold mineralization: Witwatersrand Basin, South Africa. Geological Society, London, Special Publications, **155**:153–165.
- Junk, S.A., (2001). Ancient artefacts and modern analytical techniques—Usefulness of laser ablation ICP-MS demonstrated with ancient gold coins. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **181**:723–727.
- Kaasa, S.O., Peterson, T., Morris, E.K. and Thompson, W.C., (2007). Statistical inference and forensic evidence: Evaluating a bullet lead match. *Law and human behavior*, **31**:433–447.
- Kalin, M., Wheeler, W.N. and Meinrath, G., (2005). The removal of uranium from mining waste water using algal/microbial biomass. *Journal of environmental radioactivity*, **78**:151–177.
- Keegan, E., Richter, S., Kelly, I., Wong, H., Gadd, P., Kuehn, H. and Alonso-Munoz, A., (2008). The provenance of Australian uranium ore concentrates by elemental and isotopic analysis. *Applied Geochemistry*, **23**:765–777.
- Kirk, J., Ruiz, J., Chesley, J. and Titley, S. (2003). The Origin of Gold in South Africa. *American Scientist*, **91**:534–541.
- Kirk, J., Ruiz, J., Chesley, J., Titley, S. and Walshe, J., (2001). A detrital model for the origin of gold and sulfides in the Witwatersrand basin based on Re-Os isotopes. *Geochimica et Cosmochimica Acta*, **65**:2149–2159.
- Kirk, J., Ruiz, J., Chesley, J., Walshe, J. and England, G., (2002). A major Archean, gold- and crust-forming event in the Kaapvaal Craton, South Africa. *Science*, **297**:1856–1858.
- Klemm, R., (1999). A comparison of fluids causing post depositional hydrothermal alteration in Archaean basement granitoids and the Witwatersrand Basin. *Mineralogy and Petrology*, **66**:111–122.
- Knight, J.B., Mortensen, J.K. and Morison, S.R. (1999). Lode and placer gold composition in the Klondike District, Yukon Territory, Canada; implications for the nature and genesis of Klondike placer and lode gold deposits. *Economic Geology*, **94**:649–664.

- Koch, J. and Günther, D., (2011). Review of the State-of-the-Art of Laser Ablation Inductively Coupled Plasma Mass Spectrometry. *Applied Spectroscopy*, **65**:155A–162A.
- Koshima, H. and Onishi, H. (1986). Adsorption of metal ions on activated carbon from aqueous solutions at pH 1–13. *Talanta*, **33**:391–395.
- Kucha, H., Plimer, I.R. and Stumpfl, E.F., (1998). Geochemistry and mineralogy of gold and PGE's in mesothermal and epithermal deposits and their bearing on the metal recovery. *Fizykochemiczne Problemy Mineralurgii / Physicochemical Problems of Mineral Processing (Poland)*, **32**:7–30.
- Large, R.R., Meffre, S., Burnett, R., Guy, B., Bull, S., Gilbert, S., Goemann, K. and Danyushevsky, L., (2013). Evidence for an intrabasinal source and multiple concentration processes in the formation of the Carbon Leader Reef, Witwatersrand Supergroup, South Africa. *Economic Geology*, **108**:1215–1241.
- Laxen, P.A., Becker, G.S.M. and Rubin, R., (1979). Developments in the application of carbon-in-pulp to the recovery of gold from South African ores. *Journal of The South African Institute Of Mining And Metallurgy*, **79**:315–326.
- Laxen, P.A., Becker, G.S.M. and Rubin, R., (1994). Developments in the application of carbon-in-pulp to the recovery of gold from South African ores. *Journal of the South African Institute of Mining and Metallurgy*, **94**:189–203.
- Leach, A.M. and Hieftje, G.M., (2000). Methods for shot-to-shot normalization in laser ablation with an inductively coupled plasma time-of-flight mass spectrometer. *Journal of Analytical Atomic Spectrometry*, **15**:1121-1124.
- Leach, A.M. and Hieftje, G.M., (2001). Standardless semiquantitative analysis of metals using single-shot laser ablation inductively coupled plasma time-of-flight mass spectrometry. *Analytical chemistry*, **73**:2959–2967.
- Leach, A.M. and Hieftje, G.M., (2002). Identification of alloys using single shot laser ablation inductively coupled plasma time-of-flight mass spectrometry. *Journal of Analytical Atomic Spectrometry*, **17**:852–857.
- Leake, R.C., Chapman, R.J., Bland, D.J., Condliffe, E. and Styles, M.T., (1997). Microchemical Characterization of Alluvial Gold from Scotland. *Transactions of the Institution of Mining and Metallurgy, Section B - Applied Earth Science*, **106**: B85-B98.
- Letfullin, R.R., Joenathan, C., George, T.F. and Zharov, V.P., (2006). Laser-induced explosion of gold nanoparticles: potential role for nanophotothermolysis of cancer. *Nanomedicine*, **1**:473–480.

- Levey, F.C., Cortie, M.B. and Cornish, L.A., (2002). Hardness and colour trends along the 76 wt.% Au (18.2 carat) line of the Au–Cu–Al system. *Scripta Materialia*, **47**:95–100.
- Lindgren, W., (1919). *Mineral Deposits*. 2nd ed. New York: McGraw-Hill.
- Lloyd, P.J.D., (1978). Maximizing the recovery of gold from Witwatersrand ores. *Minerals Science and Engineering*, **10**: 208–221.
- Logan, M., (2004). Making Mining Work: Bringing poverty-stricken, small-scale miners into the formal private sector. Mining Policy Research Initiative.
- Lublinski, J., Griebeler, M. and Farivar, C., (2010). Coltan mines to be 'fingerprinted,' German scientists say. Downloaded from <http://www.dw.de/coltan-mines-to-be-fingerprinted-german-scientists-say/a-5907446> on 2013-06-11.
- MacKenzie, D.J. and Craw, D., (2005). The mercury and silver contents of gold in quartz vein deposits, Otago Schist, New Zealand. *New Zealand journal of geology and geophysics*, **48**:265–278.
- Malitch, K.N., Kostoyanov, A.I. and Merkle, R.K.W., (2000). Mineral composition and osmium isotopes of PGE mineralization of Eastern Witwatersrand (South Africa). *Geology of Ore Deposits*, **42**:253–266.
- Malitch, K.N., & Merkle, R.K., (2004). Ru–Os–Ir–Pt and Pt–Fe alloys from the Evander Goldfield, Witwatersrand Basin, South Africa: detrital origin inferred from compositional and osmium-isotope data. *The Canadian Mineralogist*, **42**:631–650.
- Marsden, J.O. and House, C.I., (2006). *The chemistry of gold extraction*. 2nd edition. Society for Mining, Metallurgy and Exploration, Inc., Colorado.
- Martinón-Torres, M. and Rehren, T., (2005). Alchemy, chemistry and metallurgy in Renaissance Europe: a wider context for fire-assay remains. *Historical metallurgy*, **39**:14–28.
- Marucco, A., (2004). Low-energy ED-XRF spectrometry application in gold assaying. *Nuclear Instruments and Methods in Physics Research B*, **213**:486–490.
- Mathur, R., Gauert, C., Ruiz, J. and Linton, P., (2013). Evidence for mixing of Re–Os isotopes at < 2.7 Ga and support of a remobilized placer model in Witwatersrand sulfides and native Au. *Ore deposits and the role of the lithospheric mantle, Lithos*, Volumes **164–167**:65–73.
- McCandless, T.E., Baker, M.E. and Ruiz, J. (1997). Trace Element Analysis of Natural Gold by Laser Ablation ICP-MS: A Combined External/Internal Standardisation Approach. *Geostandards Newsletter*, **21**:271–278.

- McDougall, G.J., Hancock, R.D., Nicol, M.J., Wellington, O.L. and Copperthwaite, R.G., (1980). The mechanism of the adsorption of gold cyanide on activated carbon. *J. S. Afr. Inst. Min. Metall.*, **80**:344–356.
- McInnes, M., Greenough, J.D., Fryer, B.J. and Wells, R., (2008). Trace elements in native gold by solution ICP-MS and their use in mineral exploration: A British Columbia example. *Applied Geochemistry*, **23**:1076–1085.
- Menéndez, F., (1997). A Geochemical Model of Metal and Mineral Distributions in a Deeply Weathered Profile, Chocó 6 Concession, Bolivar State, Venezuela. M.Sc. thesis, Colorado School of Mines.
- Merkle, R.K.W. and Dixon, R.D., (2006). Possibilities and limitations of trace element characterization (fingerprinting) of precious materials. *IMA2006, Kobe, Japan, 23 – 28 July, Program and Abstracts*. Abstract 016–01.
- Merkle, R.K.W., Dixon, R.D. and Kijko, A., (2004). Trace Element Characterization of Gold and Platinum-group Element Deposits and Products in South Africa. In: Pecchio, M., Andrade, F.R.D., D'Angostino, L.Z., Kahn, H., Sant 'Agostino, L.M. and Tassinari, M.M.M.L., (editors) *Applied Mineralogy: Developments in Science and Technology*. International Council for Applied Mineralogy do Brasil, São Paulo, 901–904.
- Merkle, R.K.W., Grote, W. and Graser, P., (2008). Compositional and textural peculiarities of gold-rich alloys from the Merensky Reef. *S. A. Journal Geology*, **111**:177–186.
- Merkle, R.K.W., Espach, H., Ueckermann, H., Dixon, R.D. and De Jager, L.L., (2001). Gold Characterisation by Laser Ablation ICP-MS. *Colloquium Spectroscopicum Internationale CSI XXXII, Pretoria 8 – 13 July 2001, Volume of Abstracts*, P6–6.
- Miller, J.M., (1963). Uraninite-bearing placer deposits in the Indus alluvium near Hazro, Pakistan. Rep. No. 254 Geol. Surv. G.B. Atomic Energy Division (unpublished).
- Mineral and Petroleum Resources Development Act, (2002). *Act No. 28 of 2002*. Pretoria: Government Printer.
- Minerals Act, (1991). *Act No. 50 of 1991*. Pretoria: Government Printer
- Mining Rights Act, (1967). *Act No. 20 of 1967*. Pretoria: Government Printer
- Minter, W.E.L., (1999). Irrefutable detrital origin of Witwatersrand gold and evidence of aeolian signatures. *Economic Geology*, **94**:665–670.
- Minter, W.E.L., Goedhart, M., Knight, J. and Frimmel, H.E., (1993). Morphology of Witwatersrand gold grains from the Basal Reef; evidence for their detrital origin. *Economic Geology*, **88**:237–248.

- Moisyenko, V. and Mironyuk, A., (1997). Composition peculiarities of inclusions in native gold and ore quartz of the Russian Far East deposits. *In: Energy and Mineral Resources for the 21st Century: Geology of Mineral Deposits: Mineral Economics: Proceedings of the 30th International Geological Congress, Beijing, China, 4-14 August 1996, Vol. 9, pp. 405-408. VSP, Utrecht, The Netherlands.*
- Monteiro, S., Hobbs, A., French, T. and Almirall, J.R., (2003). Elemental profiling of glass fragments by ICP-MS as evidence of association: analysis of a case. *Journal of Forensic Sciences*, **48**:1101–1107.
- Morrison, G.W., Rose, W.J. and Jaireth, S., (1991). Geological and geochemical controls on the silver content (fineness) of gold in gold-silver deposits. *Ore Geology Reviews*, **6**:333–364.
- Mortensen, J.K., Chapman, R., LeBarge, W. and Jackson, L., (2005). Application of placer and lode gold geochemistry to gold exploration in western Yukon. *In: Yukon Exploration and Geology 2004, D.S. Emond, L.L. Lewis and G.D. Bradshaw (eds.), Yukon Geological Survey, p. 205–212.*
- Mossman, D.J., Minter, W.E.L., Dutkiewicz, A., Hallbauer, D.K., George, S.C., Hennigh, Q., Reimer, T.O. and Horscroft, F.D., (2008). The indigenous origin of Witwatersrand “carbon”. *Precambrian Research*, **164**:173–186.
- Müller, J. and Frimmel, H.E., (2010). Numerical analysis of historic gold production cycles and implications for future sub-cycles. *Open Geology Journal*, **4**:29–34.
- Natal Mines Act, (1899). Act No. 43 of 1899. Durban: Government Printer.
- National Research Council (US), (2004). Forensic Analysis: Weighing Bullet Lead Evidence. Committee on Scientific Assessment of Bullet Lead Elemental Composition Comparison. 90–94.
- Negron, F.A., (2010). Business Plan. Colombia – alluvial gold recovery. Areas in Chocó, Colombia. Downloaded from <http://www.apmrlc.com>.
- Nicolaysen, L.O., Burger, A.Z. and Liebenberg, W.R., (1962). Evidence for the extreme age of certain minerals from the Dominion Reef conglomerates and the underlying granite in the Western Transvaal. *Geochim Cosmochim Acta*, **26**:15–23.
- Oberthür, T., (1983). *Metallogenetische Überlegungen zur Bildung des Carbon Leader Reef, Carletonville Goldfield, Witwatersrand, Südafrika*. Ph.D. thesis: Cologne, Germany, University of Cologne, 241 p.

- Oberthür, T., (1987). Mineralogy and geochemistry of phosphate minerals and brannerite from the Proterozoic Carbon Leader Reef gold and uranium placer deposit, Witwatersrand, South Africa. In: Friedrich, G. et. al. (Eds.) *Uranium Mineralization: New Aspects on Geology, Mineralogy, Geochemistry and Exploration Methods*, Monograph Series on Mineral Deposits, **27**:129–142.
- Oberthür, T. and Saager, R., (1986). Silver and mercury in gold particles from the Proterozoic Witwatersrand placer deposits of South Africa: metallogenic and geochemical implications. *Econ. Geol.*, **81**:20–31.
- Ohta, A. and Kawabe, I. (2001). REE(III) adsorption onto Mn dioxide (δ -MnO₂) and Fe oxyhydroxide: Ce(III) oxidation by δ -MnO₂. *Geochimica et Cosmochimica Acta*, **65**:695–703.
- Ott, D., (2002). Optimising gold alloys for the manufacturing process. *Gold Technology*, **34**: 37–44.
- Outridge, P.M., Doherty, W. and Gregoire, D.C., (1998). Determination of Trace Elemental Signatures in Placer Gold by Laser-Ablation Inductively-Coupled Plasma-Mass Spectrometry as a Potential Aid for Gold Exploration. *Journal of Geochemical Exploration*, **60**:229–240.
- Page, M., Taylor, J. and Blenkin, M., (2011). Uniqueness in the forensic identification sciences – fact or fiction? *Forensic Science International*, **206**:12–18.
- Parnell, J., (1999). Petrographic evidence for emplacement of carbon into Witwatersrand conglomerates under high fluid pressure. *Journal of Sedimentary Research*, **69**:164–170.
- Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R. and Chenery, S.P., (1997). A Compilation of New and Published Major and Trace Element Data for NIST SRM 610 and NIST SRM 612 Glass Reference Materials. *Geostand. Newsl.*, **21**:115–144.
- Penman, D.W., (1987). *Gravity Concentration*. South African Institute of Mining and Metallurgy, The Extractive Metallurgy of Gold in South Africa., 1:219-234.
- Penny, G., (2001). *Fingerprinting gold using laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS): an exploration tool*. Unpubl. B.Sc. Honors Thesis, Memorial Univ. Newfoundland.
- Phillips, G.N. and Law, J.D., (1994). Metamorphism of the Witwatersrand gold fields: a review. *Ore Geology Reviews*, **9**:1–31.
- Phillips, G.N. and Law, J.D.M., (2000). Witwatersrand gold fields: Geology, genesis and exploration. *Society of Economic Geologists Reviews Series*, **13**:439–500.

- Phillips, G.N. and Powell, R., (2011). Origin of Witwatersrand gold: a metamorphic devolatilisation-hydrothermal replacement model. *Applied Earth Science*, **120**:112–129.
- Plyusnina, L.P., Kyz'mina, T.V., Likhoidov, G.G. and Narnov, G.A., (2000). Experimental modeling of platinum sorption on organic matter. *Applied Geochemistry*, **15**:777-784.
- Poujol, M., Robb, L.J., and Respaut, J.P., (1999). U-Pb and Pb-Pb isotopic studies relating to the origin of gold mineralization in the Evander goldfield, Witwatersrand basin, South Africa. *Precambrian Research*, **95**:167–185.
- Precious and Base Metals Act, (1908). Act No. 35 of 1908. Pretoria: Government Printer
- Precious Metals Act, (2005). Act 37 of 2005. Government Gazette, 28764:2–28. 21 April, 2005.
- Pretorius, D.A., (1975). The depositional environment of the Witwatersrand gold fields. A chronological review of speculations and observations. *Miner. Sci. Eng.*, **7**:18–47.
- Precious Metals Regulations, (2007). Government Gazette, 30061:9 July 2007.
- Pryor, E.J., (1965). *Mineral Processing*. 3rd edition. Applied Science Publishers Limited, London. 844 p.
- Ramdohr, P., (1955). Neue Beobachtungen an Erzen des Witwatersrandes in Südafrika und ihre genetische Bedeutung. *Abh. Deutsch. Akad. Wiss. Berlin Kl. Math. Allg. Nat.*, **5**: 43p.
- Ramdohr, P., (1958). New observations on the ores of the Witwatersrand in South Africa and their genetic significance. *Transactions of the Geological Society of South Africa, Annexure*, **61**:1–50.
- Rand Refinery, (2012). Integrated annual report 2012. Johannesburg.
- Rapson, W.S., (1990). The metallurgy of the coloured carat gold alloys. *Gold Bulletin*, **23**:125–131.
- Raub, C.J. and Ott, D., (1983). Gold casting alloys. The effect of zinc additions on their behaviour. *Gold Bulletin*, **16**: 46–51.
- Raub, C.J. and Ott, D., (1986). Developments in modern gold jewellery alloys. Gold 100. South African Institute of Mining and Metallurgy, Johannesburg, 3. Proceedings of the Symposium on the Industrial Uses of Gold, 65–72.
- Reddi, G.S. and Rao, C.R.M., (1999). Analytical techniques for the determination of precious metals in geological and related materials. *Analyst*, **124**:1531–1540.
- Reed, S.J.B., (2005). *Electron microprobe analysis and scanning electron microscopy in geology*. 2nd ed. Cambridge University Press.

- Reid, A.M., le Roex, A.P., and Minter, W.E.L., (1988). Composition of gold grains in the Vaal Placer, Klerksdorp, South Africa. *Mineralium Deposita*, **23**:211–217.
- Reimer, T.O., (1984). Alternative model for the derivation of gold in the Witwatersrand Supergroup. *Journal of the Geological Society*, **141**:263–271.
- Robb, L.J., Charlesworth, E.G., Drennan, G.R., Gibson, R.L., and Tongu, E.L., (1997). Tectono-metamorphic setting and paragenetic sequence of Au-U mineralisation in the Archaean Witwatersrand basin, South Africa. *Australian Journal of Earth Sciences*, **44**:353–371.
- Robb, L.J., Davis, D.W., and Kamo, S.L., (1990). U-Pb ages on single detrital zircon grains from the Witwatersrand basin, South Africa: Constraints on the age of sedimentation and on the evolution of granites adjacent to the basin. *The Journal of Geology*, **98**:311–328.
- Robb, L.J. and Meyer, F.M., (1995). The Witwatersrand Basin, South Africa: Geological framework and mineralization processes. *Ore Geology Reviews*, **10**:67–94.
- Robb, L.J. and Robb, V.M., (1998). Gold in the Witwatersrand Basin. In: Wilson, M.G.C. & Anhaeusser, C.R., (editors): *The Mineral Resources of South Africa*. Handbook, Council for Geoscience, **16**:294–349.
- Rowe, M.C., Wolff, J.A. and Cornelius, S., (2010). Analysis of Fine-Scale Feldspar Zoning and Groundmass by FE-EMPA: An Example from the Jemez Mountains Volcanic Field, New Mexico. In AGU Fall Meeting Abstracts (Vol. 1, p. 2203).
- Rundle, C.C. and Snelling, N.J., (1977). The geochronology of uraniferous minerals in the Witwatersrand Triad: An interpretation of new and existing U Pb age data on rocks and minerals from the Dominion reef, Witwatersrand and Ventersdorp supergroups. *Phil. Trans. R. Soc. A*, **286**:567–583.
- S v Abrahams 1979 (1) SA 203 (A)
- S v Janse van Rensburg and Another (A 689/2007) [2008] ZAWCHC 40; 2009 (2) SACR 216 (C) (24 July 2008)
- Saager, R., (1968). Newly observed ore-minerals from the Basal Reef in the Orange free State Goldfield in South Africa. University of the Witwatersrand, Economic Geology Research Unit, Information Circular **42**, 17 p.
- Saager, R., (1969a). The relationship of silver and gold in the basal reef of the Witwatersrand System, South Africa. University of the Witwatersrand, Economic Geology Research Unit, Information Circular **52**, 17 p.
- Saager, R., (1969b). The relationship of silver and gold in the basal reef of the Witwatersrand System, South Africa. *Mineralium Deposita*, **4**:93–113.

- Saks, M.J. and Koehler, J.J., (2005). The coming paradigm shift in forensic identification science. *Science*, **309**:892–895.
- Samusikov, V.P., (2002). Relationships between Ag and Au in Au-Ag natural system. *Russian Geology and Geophysics*, **43**:746–753.
- Sanborn, M. and Telmer, K. (2003). The spatial resolution of LA-ICP-MS line scans across heterogeneous materials such as fish otoliths and zoned minerals. *Journal of Analytical Atomic Spectrometry*, **18**:1231–1237.
- Savu-Krohn, C., Rantitsch, G., Auer, P., Melcher, F., and Graupner, T. (2011). Geochemical Fingerprinting of Coltan Ores by Machine Learning on Uneven Datasets. *Natural Resources Research*, **20**:177–191.
- Schaefer, B. F., Pearson, D. G., Rogers, N. W., and Barnicoat, A. C. (2010). Re–Os isotope and PGE constraints on the timing and origin of gold mineralisation in the Witwatersrand Basin. *Chemical Geology*, **276**:88–94.
- Schidlowski, M. (1970). Untersuchungen zur Metallogeneese im südwestlichen Witwatersrand-Becken (Oranje-Freistaat-Goldfeld, Südafrika). Bundesanstalt für Bodenforschung, Hannover. *Beihefte zum Geologischen Jahrbuch*, **85**:1–80
- Schmeisser, K., (1894). *Über Vorkommen und Gewinnung der nutzbaren Mineralien in der südafrikanische Republik (Transvaal) unter besondere Berücksichtigung des Goldbergbaues*. D. Reimer, Berlin, 151 pp.
- Schmidt, C.W.H. and Rademeyer, H., (2006). *Bewysreg*. Butterworths, Durban.
- Seewald, J.S., (2001). Model for the origin of carboxylic acids in basinal brines. *Geochimica et Cosmochimica Acta*, **65**:3779–3789.
- Shelton, K.L., Merewether, P.A. and Skinner, B.J., (1981). Phases and phase relations in the system Pd-Pt-Sn. *The Canadian Mineralogist*, **19**:599–605.
- Shikazono, N. and Shimizu, M. (1988). *Electrum: chemical composition, mode of occurrence, and depositional environment*. University Museum, University of Tokyo.
- Siddiqui, I., (2009). Enrichment and distribution of uranium in Thar coalfield, Sindh, Pakistan. *Sindh Univ. Res. Jour. (Sci. Ser.)*, **41**:27–34
- Sie, S.H., Murao, S. and Suter, G.F., (1996). Trace-Element Distribution in Native Gold. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **109**:633–638.
- Simmons, S.F. and Brown, K. L., (2006). Gold in magmatic hydrothermal solutions and the rapid formation of a giant ore deposit. *Science*, **314**:288–291.

- Simon, G., Huang, H., Penner-Hahn, J.E., Kesler, S.E. and Kao, L.S., (1999). Oxidation state of gold and arsenic in gold-bearing arsenian pyrite. *American Mineralogist*, **84**:1071–1079.
- Simpson, P.R. & Bowles, J.F.W., (1977). Uranium mineralization of the Witwatersrand and Dominion Reef systems. *Philosophical Transactions for the Royal Society of London. Series A, Mathematical and Physical Sciences*, **286**:527–548.
- Smith, T., (2008). *Materials Profiling: Identification of Source within a Legal Context*. Unpublished thesis, University of Pretoria.
- Spangenberg, J.E. and Frimmel, H.E., (2001). Basin-internal derivation of hydrocarbons in the Witwatersrand Basin, South Africa: Evidence from bulk and molecular $\delta^{13}\text{C}$ data. *Chemical Geology*, **173**:339–355.
- Stange, W., (1999). The process design of gold leaching and carbon-in-pulp circuits. *The Journal of The South African Institute of Mining and Metallurgy*, **99**:13–26
- Stoddard, E., (2013). South Africa mining to shed jobs in troubled times. Reuters, Cape Town, Wed Feb 6, 2013 12:24pm EST. Downloaded from <http://www.reuters.com/article/2013/02/06/us-africa-mining-jobs-idUSBRE9150Z820130206>
- Stoney, D.A., (1991). What made us ever think we could individualize using statistics? *Journal of the Forensic Science Society*, **31**:197–199.
- Sylvester, P.J., (2008). Matrix effects in laser ablation-ICP-MS. Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues. *Mineralogical Association of Canada, Short Courses*, **40**:67–78.
- Tanner, S.D., Baranov, V.I. and Bandura, D.R., (2002). Reaction cells and collision cells for ICP-MS: a tutorial review. *Spectrochimica Acta Part B: Atomic Spectroscopy*, **57**:1361-1452.
- Tanner, M. and Günther, D., (2009). Short transient signals, a challenge for inductively coupled plasma mass spectrometry, a review. *Analytica Chimica Acta*, **633**:19–28.
- Teal, L. and Benavides, A., (2010). History and Geologic Overview of the Yanacocha Mining District, Cajamarca, Peru. *Economic Geology*, **105**:1173–1190.
- The Precious Minerals Act, (1898). *Act No. 31 of 1898*. Cape Town: Government Printer
- Thornber, M.R. and Wildman, J.E. (1979). Supergene alteration of sulphides, IV. Laboratory study of the weathering of nickel ores. *Chemical Geology*, **24**:97–110.
- Tistl, M., (1994). Geochemistry of Platinum-Group Elements of the Zoned Ultramafic Alto Condoto Complex, Northwest Colombia. *Economic Geology*, **89**:158–167.

- Tistl, M., Burgath, K.P., Höhndorf, A., Kreuzer, H., Muñoz, R. and Salinas, R., (1994). Origin and emplacement of Tertiary ultramafic complexes in northwest Colombia: Evidence from geochemistry and K-Ar, Sm-Nd and Rb-Sr isotopes. *Earth and Planetary Science Letters*, **126**:41–59.
- Toma, S.A. and Murphy, S., (1978). Exsolution of gold from detrital platinum-group metal grains in Witwatersrand auriferous conglomerates. *The Canadian Mineralogist*, **16**: 641–650.
- Trejos, T., Montero, S. and Almirall, J.R., (2003). Analysis and comparison of glass fragments by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ICP-MS. *Analytical and Bioanalytical Chemistry*, **376**:1255–1264.
- United Nations, (2000). *Kimberley Process Certification Scheme*. United Nations General Assembly Resolution 55/56
- Utter, T., (1980). Rounding of ore particles from the Witwatersrand gold and uranium deposit (South Africa) as an indicator of their detrital origin. *Journal of Sedimentary Research*, **50**:71–76.
- Valeton, I., Schumann, A., Vinx, R., and Wieneke, M. (1997). Supergene alteration since the upper Cretaceous on alkaline igneous and metasomatic rocks of the Pocos de Caldas ring complex, Minas Gerais, Brazil. *Applied Geochemistry*, **12**:133–154.
- van der Schyff, E., (2012). South African mineral law: A historical overview of the State's regulatory power regarding the exploitation of minerals. *New Contree*, **64**:131–153.
- van der Weijden, C.H. and van der Weijden, R.D., (1995). Mobility of major, minor and some redox-sensitive trace elements and rare-earth elements during weathering of four granitoids in central Portugal. *Chemical Geology*, **125**:149–167.
- van Heuzen, A. A. (1991). Analysis of solids by laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) - I. Matching with a glass matrix. *Spectrochim. Acta, Part B*, **46**:1803–1817.
- Veiga, M.M. (1997). Mercury in artisanal gold mining in Latin America: Facts, fantasies and solutions. In UNIDO-Expert Group Meeting-Introducing New Technologies for Abatement of Global Mercury Pollution Deriving from Artisanal Gold Mining, Vienna, Austria.
- von Gehlen, K., (1983). Silver and mercury in single gold grains from the Witwatersrand and Barberton, South Africa. *Mineralium Deposita*, **18**:529–534.
- von Rahden, H.V.R., (1963). A detailed mineralogical investigation of the Ventersdorp Contact reef at Ventersdorp. Unpublished M.Sc. thesis, University of the Witwatersrand, Johannesburg.

- von Rahden, H.V.R., (1965). Apparent fineness values of gold from two Witwatersrand gold mines. *Economic Geology*, **60**:980–997.
- Vorobyev, A.Y. and Guo, C., (2005). Enhanced absorptance of gold following multipulse femtosecond laser ablation. *Physical Review B*, **72**:195422.
- Vos, R.G., (1975). An alluvial plain and lacustrine model for the Precambrian Witwatersrand deposits of South Africa. *Journal of Sedimentary Research*, **45**:480–493.
- Ward, J.H.W. & Wilson, M.G.C., (1998). Gold outside the Witwatersrand basin. In: Wilson, M.G.C. and Anhaeusser, C.R., (editors) *The Mineral Resources of South Africa*. Council for Geosciences, 350–386.
- Watling, R.J., (1998). Sourcing the provenance of cannabis crops using inter-element association patterns ‘fingerprinting’ and laser ablation inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.*, **13**:917–926.
- Watling, R.J., Herbert, H.K., Delev, D. and Abell, I.D., (1994). Gold fingerprinting by laser ablation inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*; **49**:205–219.
- Watling, R.J., Scadding, C.J. and Dixon, R.D., (2010). Chapter 88A : Gold - identifying its provenance. In: Freckelton, I. & Selby, H., (eds), *Expert Evidence*, Thomson Reuters, Australia.
- Weatherley, D.K. and Henley, R.W., (2013). Flash vaporization during earthquakes evidenced by gold deposits. *Nature Geoscience*, **6**:294–298.
- White, D., (2005). *Curse of Africa's precious metal haunts miners*. Financial Times, 1st June 2005.
- Wiltche, H. and Günther, D., (2011). Capabilities of femtosecond laser ablation ICP-MS for the major, minor, and trace element analysis of high alloyed steels and super alloys. *Anal. Bioanal. Chem.*, **399**:2167–2174.
- Winter, L. S., (2008). *The genesis of ‘giant’ copper-zinc-gold-silver volcanogenic massive sulphide deposits at Tambogrande, Perú : age, tectonic setting, paleomorphology, litho geochemistry, and radiogenic isotopes*. Unpublished Ph.D thesis, University of British Columbia (Vancouver), 260pp.
- Woodhead, J.D., Hellstrom, J., Hergt, J.M., Greig, A. and Maas, R., (2007). Isotopic and elemental imaging of geological materials by laser ablation inductively coupled plasma-mass spectrometry. *Geostandards and Geoanalytical Research*, 31:331-343.
- World Gold Council, (2011). *World Gold Council Standard: Conflict-Free Gold*. 16 June 2011, version 5.3. 40pp.

- World Gold Council, (2013). Numbers and facts. Downloaded on 2013-06-10 from http://www.gold.org/about_gold/story_of_gold/numbers_and_facts/.
- Wronkiewicz, J.D. and Condie, C.K., (1987). Geochemistry of Archaean shales from the Witwatersrand Supergroup, South Africa: source area weathering and provenance. *Geochimica et Cosmochimica Acta*, **51**:2401–2416.
- Young, R.B., (1917). *The Banket. A study of the auriferous conglomerates of the Witwatersrand and the associated rocks*. London, Gurney & Jackson, 125pp.
- Young, G.J.C., (1987). Cyanidation. The Extractive Metallurgy of Gold in South Africa, S. Afr. Inst. Min. Metall., Monogr. Ser. M7, 1:277-330.
- Youngson, J.H., Wopereis, P., Kerr, L.C., & Craw, D. (2002). Au-Ag-Hg and Au-Ag alloys in Nokomai and Nevis valley placers, northern Southland and Central Otago, New Zealand, and their implications for placer-source relationships. *New Zealand Journal of Geology and Geophysics*, **45**:53–69.
- Zartman, R.E. & Frimmel, H.E., (1999). Rn-generated ^{206}Pb in hydrothermal sulphide minerals and bitumen from the Ventersdorp Contact Reef, South Africa. *Mineralogy and Petrology*, **66**:171–191.
- Zhou, Z., Zhou, K., Hou, X. and Luo, H., (2005). Arc/spark optical emission spectrometry: Principles, instrumentation, and recent applications. *Applied Spectroscopy Reviews*, **40**:165–185.

Appendix A.

Table of compositions of some Rand Refinery alloy compositions in production in 2002, from data supplied by Rand Refinery. These compositions show whether the Cu and Zn were added in the form of a brass alloy, and if so the percentage of the brass in the alloy.

The colours of the alloys are shown in the last column – white gold (W), yellow gold (Y) and red gold (R).

It can be seen that the majority of the alloys consist of different combinations of only four elements – Au, Ag, Cu and Zn. Speciality alloys have other elements added for specific purposes, the majority of these alloys having Pd or Ni added to produce white gold alloys.

ALLOY	AU	AG	70/30 BRASS	CU	IN	ZN	PD	SI	NI	CO	SB	CR	MN	AL	TOTAL	COLOUR
09OB307W1	37.56	1.80	41.34	35.69		12.40			12.55						100.00	W
09RJ	37.56	3.00		59.44											100.00	R
09DDI	37.56	3.06	45.80	45.64		13.74									100.00	Y
09H	37.56	5.44	11.68	53.50		3.50									100.00	Y
09DD	37.56	11.90	36.67	37.54		11.00		2.00							100.00	Y
09G	37.56	12.36	11.68	46.58		3.50									100.00	Y
09SC	37.56	12.50	28.47	41.40		8.54									100.00	Y
09NEJ	37.56	13.75	29.25	39.92		8.78									100.00	Y
09AA	37.56	15.00	30.00	38.44		9.00									100.00	Y
09WJ	37.56	50.44					12.00								100.00	W
09WA12B1	37.56	53.00	3.93	2.75	2.19	4.50									100.00	W
09LX	37.56	53.32	2.50	1.75		7.37									100.00	W
09CW	37.56	55.44				5.00			2.00						100.00	W
09AAH	37.56	57.73		4.71											100.00	Y
09MW	37.56	57.94		4.50											100.00	W
09VSW	37.56	62.44													100.00	W
09WB1482W	37.56		31.80	43.10		9.54			9.80						100.00	W
09SF928CH	37.56		61.80	43.90		18.54									100.00	W
10CW	41.72	52.28				4.00		2.00							100.00	W
14RJ	58.56	3.00		38.44											100.00	R
14AGC	58.56	4.00	20.47	31.30		6.141									100.00	Y
14HG	58.56	25.53		15.91											100.00	Y
14J	58.56	31.14		10.30											100.00	Y
14WJ	58.56	31.44					10.00								100.00	W
14AR	58.56	35.04		6.40											100.00	Y
14LX	58.56	35.38	1.66	1.162		4.90									100.00	W
16J2	70.00	14.00	5.00	14.50		1.50									100.00	Y
16J1	70.00	16.00	6.70	11.99		2.01									100.00	Y
18HD	75.10	1.00		10.40			2.00					2.00	9.00	0.50	100.00	W
18SW	75.10	7.90					17.00								100.00	W
18C	75.10	8.90		16.00											100.00	Y
18ALL	75.10	10.60	6.46	4.52		2.45	7.32								100.00	W
18WJ	75.10	11.40					13.50								100.00	W
18BS	75.10	13.00		11.90											100.00	Y
SP18SWA	75.10	14.90					10.00								100.00	W
18ALO	75.10	15.88		9.02											100.00	Y
18CJM	75.10	16.00	4.50	7.55		1.35									100.00	Y
18J	75.10	16.85		8.05											100.00	Y
18BS2	75.10	19.00		5.90											100.00	Y
18WA12B1	75.10	21.12	1.58	1.11	0.88	1.79									100.00	Y
18LX	75.10	21.27	1.00	0.70		2.93									100.00	W
18WN	75.10		13.57	14.86		4.07			5.97						100.00	W
20J	83.40	10.30	3.34	5.30		1.00									100.00	Y
22F	91.70	1.20		7.10											100.00	Y
22B	91.70	6.10		2.20											100.00	Y
22E	91.70	8.30													100.00	Y
22A	91.70			8.30											100.00	Y
22J	91.72	2.40		5.88											100.00	Y
22HD	91.72	5.78								2.50					100.00	Y
24HD	99.50									0.20	0.30				100.00	Y
SF-AG		92.50	7.50	5.25		2.25									100.00	W

Appendix B.

A table of ICP-OES analyses is provided for d'ore gold from the gold database which were used in Chapter 7 to look at the variation in d'ore gold composition within the Witwaterrand Basin in the West Wits, Klerksdorp and Free State goldfields.

All values are in percent. Where the element was not detected (below detection limits) a blank was left. If a zero value is present, it indicates that the element was detected but at levels lower than 0.005 %.

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
VRO 1 to 7 shafts		89.84			0.01	0.14	2.70	1.71	0.13		0.16	0.03	0.83	0.16								0.00	0.00	95.72	4.28
VRO 1 to 7 shafts		89.11			0.01	0.14	2.92	2.22	0.23		0.30	0.01	1.02	0.22								0.01	0.00	96.20	3.80
VRO 1 to 7 shafts		89.64				0.09	2.91	1.82	0.21		0.28		0.89	0.21									0.00	96.07	3.93
VRO 1 to 7 shafts		91.58					3.34	0.22			0.01		0.38	0.12									0.00	95.65	4.35
VRO 1 to 7 shafts		89.40			0.00		3.50	0.25			0.01		0.46	0.15									0.01	93.78	6.22
VRO 1 to 7 shafts		89.39			0.00		3.51	0.27			0.01		0.48	0.14									0.01	93.81	6.19
VRO 1 to 7 shafts	0.30	86.24			0.15		1.61	5.27			0.03		0.58	0.26		0.02							0.01	94.48	5.52
VRO 1 to 7 shafts		87.04				0.04	1.79	0.62			0.12		0.62	0.09									0.00	90.32	9.68
VRO 1 to 7 shafts		85.76			0.00	0.08	1.86	1.06			0.22		0.80	0.10									0.00	89.89	10.11
VRO 1 to 7 shafts		85.28			0.00	0.10	1.91	1.29			0.29		0.89	0.11								0.00	0.00	89.86	10.14
VRO 1 to 7 shafts		83.54			0.00	0.18	1.87	1.42			0.32		0.89	0.11								0.00	0.00	88.34	11.66
VRO 1 to 7 shafts		85.59			0.00	0.02	2.29	1.43			0.38		1.47	0.20									0.00	91.38	8.62
VRO 1 to 7 shafts		84.72			0.00	0.02	2.27	1.56			0.43		1.52	0.19									0.00	90.72	9.28
VRO 1 to 7 shafts		84.19			0.00	0.02	2.27	1.58			0.44		1.54	0.19									0.00	90.24	9.76
VRO 1 to 7 shafts		85.21			0.00	0.02	2.36	1.61			0.45		1.60	0.21									0.00	91.48	8.52
VRO 1 to 7 shafts		87.70					2.25	0.50			0.04		0.62	0.11									0.00	91.24	8.76
VRO 1 to 7 shafts		86.85					2.38	1.16			0.11		0.96	0.15									0.01	91.61	8.39
VRO 1 to 7 shafts		85.63				0.01	2.40	1.68			0.16		1.16	0.17									0.01	91.22	8.78
VRO 1 to 7 shafts		85.32				0.01	2.46	1.94			0.19		1.30	0.18									0.01	91.41	8.59
VRO 1 to 7 shafts		85.14				0.01	2.45	1.95			0.19	0.01	1.30	0.18									0.01	91.25	8.75
VRO 1 to 7 shafts		85.16				0.01	2.43	1.93			0.19		1.31	0.17									0.01	91.20	8.80
VRO 1 to 7 shafts		83.91			0.00	0.03	2.42	1.59			0.09		1.34	0.17									0.01	89.57	10.43
VRO 1 to 7 shafts		83.27			0.00	0.05	2.52	2.41			0.15		1.68	0.20									0.01	90.29	9.71
VRO 1 to 7 shafts		82.95			0.00		3.68	0.24			0.02		1.19	0.23									0.01	88.31	11.69
VRO 1 to 7 shafts		83.27			0.00		3.84	0.31			0.03		1.39	0.25									0.01	89.09	10.91
VRO 1 to 7 shafts		82.83			0.00		3.88	0.35			0.03		1.48	0.26									0.00	88.82	11.18
VRO 1 to 7 shafts		82.27					6.28	0.02			0.00		0.55	0.10										89.21	10.79
VRO 1 to 7 shafts		85.61					6.52	0.02			0.00		0.64	0.14										92.93	7.07
VRO 1 to 7 shafts		90.95					4.45	0.03			0.00		0.26	0.02										95.72	4.28
VRO 1 to 7 shafts		90.60					4.91	0.04			0.00		0.40	0.03										95.99	4.01
VRO 1 to 7 shafts		89.98					5.56	0.06			0.00		0.59	0.05										96.24	3.76
VRO 1 to 7 shafts		89.07					5.47	0.05			0.00		0.57	0.05										95.21	4.79
Great Noligwa		87.32					2.15	0.04			0.00		2.02	0.07									0.01	91.61	8.39

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Great Noligwa		87.67		0.00			2.18	0.06			0.00		2.42	0.08									0.01	92.43	7.57
Great Noligwa		87.15		0.00			2.23	0.10			0.00		3.03	0.09									0.01	92.61	7.39
Great Noligwa		86.94		0.00			2.30	0.11			0.00		3.28	0.11									0.01	92.75	7.25
Great Noligwa		86.18		0.00			2.35	0.11			0.00		3.70	0.14									0.02	92.50	7.50
Great Noligwa		85.98		0.00			2.29	0.10			0.00		3.60	0.12									0.01	92.11	7.89
Great Noligwa		84.67			0.00	0.06	3.16	2.58			0.19		4.04	0.13									0.02	94.86	5.14
Great Noligwa		82.49		0.00	0.01	0.09	3.13	3.26			0.23		4.84	0.14								0.00	0.02	94.20	5.80
Great Noligwa		81.94		0.00	0.01	0.10	3.11	3.57			0.25		5.22	0.13								0.00	0.02	94.35	5.65
Great Noligwa		81.88		0.00	0.01	0.13	3.12	4.05			0.27		5.98	0.14								0.00	0.02	95.61	4.39
Great Noligwa		83.78		0.00	0.01	0.11	3.20	3.84			0.28		5.35	0.16								0.00	0.02	96.75	3.25
Great Noligwa		83.46					1.89	0.26			0.04		2.75	0.13					0.02				0.03	88.58	11.42
Great Noligwa		83.68					1.90	0.31			0.04		2.80	0.14					0.03				0.03	88.92	11.08
Great Noligwa		84.37					1.88	0.32			0.04		2.71	0.12					0.02				0.03	89.49	10.51
Great Noligwa		84.19					1.89	0.33			0.04		2.77	0.13					0.02				0.03	89.40	10.60
Great Noligwa		83.95					1.90	0.32			0.03		2.82	0.14					0.03				0.03	89.22	10.78
Great Noligwa		84.00					1.89	0.31			0.03		2.77	0.13					0.02				0.03	89.18	10.82
Great Noligwa		84.70					1.90	0.32			0.03		2.78	0.13					0.02				0.03	89.91	10.09
Great Noligwa		82.78					2.80	0.49			0.07		3.82	0.15					0.02				0.02	90.14	9.86
Great Noligwa		82.40					2.81	0.54			0.06		4.02	0.16					0.02				0.02	90.04	9.96
Great Noligwa		82.22			0.00		2.82	0.63			0.10		4.15	0.14	0.01				0.02				0.03	90.11	9.89
Great Noligwa	0.02	80.71			0.00		2.28	0.58			0.09		4.49	0.17	0.01				0.01				0.03	88.40	11.60
Great Noligwa	0.02	80.83			0.00		2.28	0.54			0.09		4.07	0.17	0.01				0.02				0.03	88.06	11.94
Great Noligwa	0.02	80.91			0.00		2.28	0.53			0.09		3.99	0.18	0.01				0.02				0.03	88.05	11.95
Great Noligwa	0.02	80.72			0.00		2.28	0.53			0.09		3.96	0.18	0.01				0.02				0.03	87.83	12.17
Great Noligwa	0.03	78.25			0.00		2.21	0.73			0.10		5.61	0.17	0.01				0.01				0.02	87.15	12.85
Great Noligwa	0.02	80.93			0.00		2.28	0.49			0.09		3.73	0.17	0.01				0.02				0.03	87.77	12.23
Great Noligwa		85.07					2.28	0.05			0.00		1.63	0.03	0.01				0.01				0.00	89.08	10.92
Great Noligwa		83.13					2.37	0.05			0.00		2.84	0.05	0.01				0.01				0.00	88.47	11.53
Great Noligwa		81.93					2.47	0.05			0.00		3.98	0.07	0.01				0.02				0.00	88.53	11.47
Great Noligwa		81.20					2.52	0.04			0.00		4.78	0.08	0.01				0.02				0.01	88.67	11.33
Great Noligwa		80.18					2.52	0.04			0.00		5.05	0.08	0.01				0.02				0.00	87.92	12.08
Great Noligwa		80.21					2.51	0.04			0.00		4.97	0.08	0.01				0.02				0.00	87.85	12.15
Great Noligwa		79.89			0.01		6.14	0.50			0.02		6.98	0.14	0.01				0.03				0.03	93.74	6.26

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Great Noligwa		79.87			0.01		6.13	0.49			0.02		6.97	0.13	0.01				0.03				0.03	93.70	6.30
Great Noligwa		79.97			0.01		6.13	0.49			0.02		6.96	0.14					0.03				0.03	93.77	6.23
Great Noligwa		77.03					5.94	0.10			0.00		8.08	0.09	0.01				0.03				0.01	91.29	8.71
Great Noligwa		76.50					5.90	0.09			0.00		8.13	0.09	0.01				0.03				0.02	90.77	9.23
Great Noligwa		76.24			0.00		5.87	0.08			0.00		8.11	0.09	0.01				0.03				0.01	90.44	9.56
Great Noligwa		76.00			0.00		5.86	0.08			0.00		8.10	0.09	0.01				0.03				0.01	90.18	9.82
Great Noligwa		75.86			0.00		5.84	0.07			0.00		8.06	0.08	0.01				0.03				0.01	89.97	10.03
Great Noligwa		75.91			0.01	0.01	3.94	1.84			0.11		8.13	0.22					0.03				0.13	90.32	9.68
Great Noligwa		75.97			0.01	0.01	3.91	1.87			0.12		8.07	0.22					0.03				0.13	90.33	9.67
Great Noligwa		75.82			0.01	0.01	3.90	1.86			0.11		8.04	0.22					0.03				0.13	90.14	9.86
Great Noligwa		75.72			0.01	0.01	3.90	1.86			0.11		8.01	0.22					0.03				0.13	90.00	10.00
Great Noligwa		83.41			0.00		4.41	0.23			0.00		3.65	0.16				0.04	0.01				0.00	91.91	8.09
Great Noligwa		85.05					3.16	0.12			0.01		1.94	0.07									0.01	90.37	9.63
Great Noligwa		84.56					3.19	0.17			0.01		2.19	0.08									0.01	90.22	9.78
Great Noligwa		85.82					3.22	0.17			0.01		2.22	0.09									0.01	91.54	8.46
Great Noligwa		85.77					3.22	0.18			0.01		2.26	0.07									0.02	91.53	8.47
Great Noligwa		84.82					4.22	0.03			0.00		1.42	0.08									0.00	90.58	9.42
Great Noligwa		85.14					4.26	0.03			0.00		1.47	0.09									0.01	91.01	8.99
Great Noligwa		85.21					4.27	0.02			0.00		1.49	0.08									0.00	91.08	8.92
Great Noligwa		85.26					4.28	0.02			0.00		1.50	0.09									0.00	91.16	8.84
Great Noligwa		85.53					5.15	0.55			0.01		1.56	0.06									0.02	92.87	7.13
Great Noligwa		84.77					5.37	0.64			0.01		1.82	0.08									0.02	92.72	7.28
Great Noligwa		84.57					5.38	0.65			0.01		1.88	0.08									0.02	92.60	7.40
Tau Lekoa	0.01	76.92			0.01		4.91	1.36			0.27		8.21	0.17									0.02	91.88	8.12
Tau Lekoa		77.10			0.01		4.91	1.38			0.28		8.17	0.17									0.02	92.04	7.96
Tau Lekoa		76.78			0.01		4.91	1.32			0.28		7.87	0.17									0.02	91.36	8.64
Tau Lekoa		82.56			0.00	0.17	4.17	2.61			1.89		3.65	0.14									0.01	95.20	4.80
Tau Lekoa		83.51			0.00	0.17	4.21	2.54			1.92		3.46	0.15									0.01	95.98	4.02
Tau Lekoa		80.70			0.01		3.79	0.66			0.11		6.48	0.16									0.01	91.91	8.09
Tau Lekoa		79.42			0.01		3.80	0.81			0.13		7.33	0.18									0.01	91.69	8.31
Tau Lekoa		79.44			0.01		3.81	0.90			0.14		7.68	0.19									0.01	92.19	7.81
Tau Lekoa		82.72			0.00	0.03	3.91	1.36			0.59		3.69	0.13									0.01	92.43	7.57
Tau Lekoa		82.53			0.00	0.03	3.90	1.38			0.60		3.69	0.13									0.01	92.27	7.73

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder	
Tau Lekoa		76.26			0.00		4.60	0.11			0.01		5.38	0.14									0.00	86.51	13.49	
Tau Lekoa		74.74			0.00		4.62	0.11			0.01		6.25	0.15										0.00	85.88	14.12
Tau Lekoa		72.75			0.00		4.58	0.11			0.01		6.83	0.18										0.00	84.46	15.54
Tau Lekoa	0.02	73.20			0.02		6.75	0.16			0.00		9.72	0.31									0.07	90.24	9.76	
Tau Lekoa	0.03	73.01			0.02		6.77	0.15			0.00		9.89	0.33									0.06	90.25	9.75	
Tau Lekoa		76.86			0.02	0.11	5.74	3.04			0.65		7.11	0.24									0.04	93.80	6.20	
Tau Lekoa		78.48			0.01	0.01	5.29	0.87			0.10		6.03	0.13									0.02	90.94	9.06	
Tau Lekoa		78.46			0.01	0.01	5.23	0.86			0.10		5.82	0.12									0.02	90.64	9.36	
Tau Lekoa		72.04			0.02	0.14	7.92	3.24			0.79		5.68	0.10									0.01	89.94	10.06	
Tau Lekoa		71.56			0.01	0.14	8.03	2.86			0.82		4.83	0.10									0.01	88.37	11.63	
Tau Lekoa		83.21					7.15	0.06			0.00		1.76	0.03									0.00	92.21	7.79	
Tau Lekoa		82.69					7.38	0.05			0.00		2.04	0.04									0.00	92.21	7.79	
Tau Lekoa		85.04					7.48	0.12			0.01		2.31	0.06									0.00	95.02	4.98	
Tau Lekoa		84.41					7.68	0.12			0.01		2.52	0.07									0.00	94.82	5.18	
Tau Lekoa		82.95			0.01	0.03	7.48	1.56	0.13		0.16		3.82	0.07									0.01	96.22	3.78	
Tau Lekoa		83.56			0.01	0.03	7.50	1.64	0.14		0.17	0.05	3.99	0.09									0.01	97.18	2.82	
Tau Lekoa	0.02	86.77			0.01	0.01	3.47	1.28			0.14	0.07	2.48	0.10									0.01	94.36	5.64	
Kopanang		83.40					2.95	0.03			0.00		6.37	0.20									0.00	92.95	7.05	
Kopanang		83.37					2.97	0.03			0.00		7.15	0.21									0.01	93.73	6.27	
Kopanang		83.01			0.00		3.02	0.02			0.00		7.67	0.24									0.00	93.96	6.04	
Kopanang		84.29			0.00		3.03	0.03			0.00		7.52	0.22									0.00	95.10	4.90	
Kopanang		85.86			0.00		3.09	0.02			0.00		7.72	0.22									0.00	96.92	3.08	
Kopanang	0.02	81.88		0.00	0.01		3.22	0.11			0.00		12.91	0.33									0.02	98.51	1.49	
Kopanang	0.02	77.16			0.01		3.05	0.11			0.00		12.15	0.30									0.02	92.81	7.19	
Kopanang	0.02	77.98			0.01		3.07	0.10			0.00		12.40	0.32									0.02	93.93	6.07	
Kopanang		79.70					3.33	0.03			0.00		8.39	0.26									0.00	91.71	8.29	
Kopanang		77.91					3.32	0.03			0.00		9.79	0.29									0.00	91.34	8.66	
Kopanang		76.69					3.33	0.03			0.00		11.23	0.32									0.00	91.60	8.40	
Kopanang		76.82					3.35	0.03			0.00		11.51	0.32									0.00	92.02	7.98	
Kopanang		77.16			0.00		3.35	0.02			0.00		11.40	0.32									0.00	92.27	7.73	
Kopanang		77.11			0.00		3.77	0.04			0.00		9.95	0.26									0.01	91.15	8.85	
Kopanang		76.86			0.00		3.76	0.04			0.00		10.08	0.26									0.00	91.01	8.99	
Kopanang	0.02	76.75			0.00		3.76	0.03			0.00		10.25	0.27									0.00	91.10	8.90	

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Kopanang	0.02	78.35			0.01		3.28	0.11			0.00		8.52	0.25									0.00	90.54	9.46
Kopanang	0.02	77.81			0.01		3.26	0.09			0.00		8.50	0.25									0.00	89.93	10.07
Kopanang	0.02	78.17			0.01		3.26	0.09			0.00		8.49	0.25									0.00	90.28	9.72
Kopanang	0.02	79.10			0.01		3.30	0.08			0.00		8.63	0.27									0.00	91.41	8.59
Kopanang	0.02	68.86			0.02		6.37	0.18			0.00		14.87	0.32									0.01	90.66	9.34
Kopanang	0.02	69.68			0.02		6.45	0.22			0.00		15.21	0.31									0.01	91.92	8.08
Kopanang		76.72			0.01		6.93	0.03			0.00		9.29	0.23									0.00	93.21	6.79
Kopanang		76.27			0.01		6.90	0.03					9.44	0.24									0.00	92.88	7.12
Kopanang		79.71			0.02		3.70	0.76			0.17		8.86	0.43									0.03	93.68	6.32
Kopanang		78.99			0.02		3.67	0.81			0.20		8.77	0.43									0.03	92.92	7.08
Kopanang		78.63			0.02		3.64	0.80			0.20		8.67	0.41									0.03	92.40	7.60
Kopanang		78.49			0.01	0.01	3.93	0.31			0.03		7.17	0.22									0.03	90.20	9.80
Kopanang	0.02	78.28			0.01	0.01	3.93	0.36			0.04		7.26	0.23									0.03	90.16	9.84
Kopanang		77.99			0.01		3.92	0.40			0.04		7.30	0.23									0.03	89.92	10.08
Kopanang		78.39			0.02		3.65	0.83			0.19		8.70	0.42									0.03	92.22	7.78
Kopanang	0.09	84.11			0.02	0.01	3.82	1.36			0.04		2.77	0.45	0.02								0.01	92.70	7.30
Kopanang		82.44			0.00		5.21	0.07			0.01		3.15	0.15									0.00	91.03	8.97
Kopanang		80.97			0.00		5.52	0.08			0.01		4.00	0.20									0.00	90.79	9.21
Kopanang		80.71			0.00		5.64	0.08			0.01		4.30	0.20									0.01	90.95	9.05
Kopanang		82.84					7.25	0.14			0.01		2.79	0.15									0.01	93.18	6.82
Kopanang		81.30			0.00		8.02	0.19			0.01		3.76	0.21									0.01	93.51	6.49
Kopanang		84.28			0.00		5.61	0.47			0.04		3.11	0.27									0.05	93.82	6.18
Kopanang		84.14			0.00		5.55	0.47	0.04		0.04		3.07	0.26									0.05	93.63	6.37
Deelkraal		77.54					11.76	0.00					0.00	0.14				0.01					0.08	89.52	10.48
Deelkraal		77.98		0.00			11.58	0.00					0.01	0.46									0.23	90.26	9.74
Deelkraal	0.02	70.91		0.00			15.82	0.00					0.02	1.86									0.90	89.53	10.47
Deelkraal		82.35					6.87	0.01					0.00	0.03									0.01	89.27	10.73
Driefontein		90.11				0.01	0.71	0.36					0.79	0.10									0.00	92.08	7.92
Driefontein		89.78				0.01	0.70	0.33					0.78	0.08									0.00	91.69	8.31
Driefontein		89.17				0.01	0.56	0.38					0.92	0.13									0.02	91.18	8.82
Driefontein		86.36					2.53	0.01					1.61	0.06				0.02					0.00	90.60	9.40
Driefontein		85.99					2.53	0.01					1.66	0.06				0.03					0.00	90.28	9.72
Driefontein		89.64					0.55	0.44					0.36	0.16									0.03	91.18	8.82

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Driefontein		89.32					0.55	0.61					0.41	0.16									0.03	91.09	8.91
Driefontein		87.08				0.01	0.42	0.41			0.00		0.97	0.16									0.03	89.08	10.92
Driefontein		85.23				0.01	0.92	0.22					1.33	0.07									0.00	87.77	12.23
Driefontein		85.71				0.01	0.90	0.18					1.30	0.07									0.00	88.16	11.84
Driefontein		85.06				0.01	0.89	0.15					1.28	0.07									0.00	87.46	12.54
Driefontein		84.73					1.51	0.01					1.06	0.04				0.02					0.00	87.35	12.65
Driefontein		84.41					1.49	0.00					0.87	0.05				0.02					0.00	86.85	13.15
Driefontein		86.69				0.01	0.51	0.51			0.00		0.65	0.18									0.03	88.57	11.43
Driefontein		86.10		0.00		0.02	0.65	0.23					1.24	0.09									0.00	88.34	11.66
Driefontein		87.00		0.00		0.02	0.67	0.23					1.27	0.09									0.00	89.30	10.70
Driefontein		87.57				0.02	0.66	0.21					1.25	0.08									0.00	89.80	10.20
Driefontein		87.30					0.60	0.27					0.65	0.13									0.02	88.96	11.04
Driefontein		84.00				0.01	0.48	0.40			0.00		1.31	0.11									0.01	86.32	13.68
Driefontein		83.50				0.01	0.48	0.42			0.00		1.32	0.10									0.01	85.83	14.17
Driefontein		83.98					0.93	0.02					3.00	0.08									0.00	88.02	11.98
Driefontein		84.59					0.92	0.02					2.78	0.07									0.00	88.39	11.61
Driefontein		85.53			0.00		1.22	0.87			0.00		0.74	0.06									0.01	88.43	11.57
Driefontein		84.82					1.63	0.15			0.00		0.53	0.03									0.01	87.16	12.84
Driefontein		84.67					5.15	0.04					0.62	0.08									0.01	90.57	9.43
Driefontein		85.00					2.02	0.07					1.28	0.11									0.02	88.50	11.50
Driefontein		84.39					1.49	0.05			0.00		0.93	0.06									0.00	86.92	13.08
Driefontein		84.73			0.01		2.57	0.32			0.00		1.00	0.25									0.01	88.89	11.11
Driefontein		88.56					2.86	0.05			0.00		0.18	0.02									0.00	91.69	8.31
Driefontein		88.65					2.19	0.04			0.00		0.23	0.01									0.00	91.12	8.88
Kloof		88.18				0.01	0.31	0.05					0.07	0.12									0.02	88.75	11.25
Kloof		87.06				0.01	0.25	0.13			0.00		0.07	0.11									0.02	87.64	12.36
Kloof		87.43				0.01	0.24	0.14			0.00		0.08	0.08									0.01	87.99	12.01
Kloof		91.54				0.01	0.31	0.15			0.00		0.05	0.13									0.01	92.20	7.80
Kloof		91.84				0.02	0.36	0.30			0.00		0.08	0.10									0.01	92.72	7.28
Kloof		91.88				0.01	0.59	0.18			0.00		0.11	0.09									0.03	92.89	7.11
Kloof		92.49				0.03	0.47	0.34			0.00		0.15	0.09									0.02	93.60	6.40
Kloof		90.98				0.01	0.22	0.18			0.00		0.03	0.20									0.00	91.64	8.36
Kloof		94.88				0.02	0.16	0.21			0.00	0.00	0.02	0.06									0.00	95.35	4.65

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Kloof		88.69				0.02	0.32	0.11			0.00		0.03	0.07									0.00	89.26	10.74
Kloof		89.86		0.00		0.00	0.25	0.03			0.00		0.02	0.06									0.00	90.24	9.76
Kloof		87.84		0.00		0.01	0.23	0.13			0.00	0.00	0.02	0.09									0.00	88.33	11.67
Kloof		91.68				0.02	0.24	0.19			0.00		0.03	0.06									0.00	92.23	7.77
Kloof		91.28				0.01	0.20	0.07			0.00		0.02	0.06									0.00	91.64	8.36
Kloof		87.90				0.04	0.17	0.24			0.00	0.00	0.03	0.08									0.00	88.47	11.53
Kloof		90.35				0.02	0.15	0.16			0.00		0.04	0.05									0.00	90.78	9.22
Kloof		89.07				0.02	0.19	0.12			0.00	0.00	0.03	0.05									0.00	89.48	10.52
Kloof		90.30		0.00		0.02	0.35	0.34			0.00	0.00	0.16	0.10									0.01	91.28	8.72
Kloof		89.91				0.02	0.28	0.32			0.00		0.12	0.08									0.01	90.74	9.26
Kloof		88.74				0.10	0.57	0.52			0.00	0.00	0.32	0.06								0.00	0.01	90.33	9.67
Kloof		89.75		0.00		0.01	0.37	0.18			0.00	0.00	0.10	0.06									0.01	90.50	9.50
Kloof		88.93				0.08	0.32	0.69			0.00	0.00	0.15	0.07								0.00	0.01	90.24	9.76
Kloof		89.30				0.02	0.23	0.25			0.00	0.00	0.10	0.12									0.01	90.04	9.96
Kloof		89.94		0.00		0.03	0.16	0.27			0.00		0.09	0.12									0.00	90.62	9.38
Kloof		88.29				0.02	0.13	0.29			0.00		0.11	0.10									0.00	88.93	11.07
Kloof		88.69				0.02	0.20	0.25			0.00		0.14	0.08									0.01	89.39	10.61
Kloof		85.91				0.06	0.15	0.42			0.00	0.00	0.13	0.12								0.00	0.01	86.80	13.20
Leeudoorn		89.84					0.22	0.06			0.00		0.15	0.18									0.01	90.46	9.54
Leeudoorn		90.49					0.26	0.08			0.00		0.15	0.20									0.01	91.19	8.81
Leeudoorn		92.25					0.27	0.05					0.15	0.18									0.01	92.91	7.09
Libanon		84.30					9.72	0.01					0.01	0.06	0.01								0.00	94.11	5.89
Libanon	0.01	76.82		0.00			12.04	0.12					0.35	2.41	0.01		0.01						0.06	91.84	8.16
Libanon		81.81					6.41	0.08					0.23	1.40									0.02	89.96	10.04
Libanon		81.13				0.01	11.06	0.26					0.33	0.21									0.13	93.13	6.87
Libanon		84.00					4.22	0.67			0.00		0.22	0.11								0.00	0.04	89.26	10.74
Libanon		81.82					6.19	0.40			0.00		0.32	0.19									0.06	88.98	11.02
Mponeng		85.35					3.49	0.00					0.16	0.22									0.03	89.26	10.74
Mponeng		84.88					3.48	0.00					0.16	0.22									0.03	88.77	11.23
Mponeng		85.09					3.45	0.01					0.14	0.19									0.03	88.91	11.09
Mponeng		85.98					3.39	0.00					0.01	0.01									0.00	89.39	10.61
Mponeng		83.02					4.59	0.00					0.08	0.06									0.01	87.74	12.26
Mponeng		83.23					4.43	0.00					0.05	0.03									0.00	87.75	12.25

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Mponeng		84.00					4.17	0.00					0.00	0.01									0.00	88.18	11.82
Mponeng		84.44					4.06	0.00					0.00	0.01									0.00	88.51	11.49
Mponeng		84.62					2.84	0.00					0.11	0.44									0.01	88.03	11.97
Mponeng		84.49					2.94	0.00					0.15	0.56				0.01					0.01	88.17	11.83
Mponeng		85.33					2.45	0.00					0.09	0.59									0.01	88.47	11.53
Mponeng		84.97					2.46	0.00					0.10	0.62									0.01	88.17	11.83
Mponeng		77.45					13.22	0.00					0.02	0.01									0.00	90.69	9.31
Savuka		89.70					1.13	0.02					0.06	0.11									0.02	91.04	8.96
Savuka		88.81					1.12	0.02					0.07	0.11									0.02	90.15	9.85
Savuka		87.49					0.88	0.04			0.00		0.08	0.16									0.03	88.70	11.30
Savuka		87.88					0.94	0.05			0.00		0.09	0.18									0.03	89.18	10.82
Savuka		88.10					0.61	0.02					0.10	0.46									0.01	89.31	10.69
Savuka		88.38					0.60	0.03			0.00		0.11	0.46									0.01	89.59	10.41
Savuka		84.23					2.70	0.04					0.31	0.31									0.04	87.63	12.37
Beatrix		86.94					0.04	0.05					0.00	1.06										88.09	11.91
Beatrix		88.65					0.08	0.01					0.00	0.74										89.48	10.52
Beatrix		87.73					0.13	0.03			0.00		0.00	0.60										88.49	11.51
Beatrix		89.06					0.13	0.02					0.00	0.60										89.81	10.19
Beatrix		88.65					0.15	0.08			0.00		0.00	1.08									0.00	89.96	10.04
Beatrix		88.77				0.00	0.16	0.05			0.00		0.04	0.72										89.75	10.25
Beatrix		87.86					0.58	0.08					0.03	1.05									0.00	89.60	10.40
Beatrix		85.08					1.74	0.01					0.12	0.55									0.00	87.50	12.50
Beatrix		86.20					2.55	0.01					0.07	0.00										88.83	11.17
Beatrix		86.83					2.97	0.01					0.09	0.01										89.91	10.09
Beatrix		88.75					3.43	0.01					0.13	0.02										92.33	7.67
Beatrix		86.09					3.54	0.01					0.15	0.02										89.80	10.20
Beatrix		87.84					3.88	0.01					0.19	0.03										91.96	8.04
Beatrix		86.39					3.96	0.01					0.12	0.02										90.50	9.50
Beatrix		86.63					4.12	0.01					0.25	0.03										91.03	8.97
Beatrix		84.99					4.20	0.01					0.13	0.01										89.34	10.66
Beatrix		82.36					4.41	0.00					0.13	0.00										86.90	13.10
Beatrix		85.31					4.44	0.00					0.34	0.06										90.14	9.86
Beatrix		86.33					4.58	0.03					0.11	0.00								0.00		91.04	8.96

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder
Beatrix		86.28					4.66	0.02					0.20	0.02	0.01								0.00	91.18	8.82
Beatrix		84.50					4.78	0.00					0.74	0.15										90.16	9.84
Beatrix		84.51					5.11	0.01					0.45	0.17										90.25	9.75
Beatrix		85.46					5.16	0.03					0.27	0.02	0.01									90.95	9.05
Beatrix		85.89					5.34	0.04					0.19	0.00										91.47	8.53
Beatrix		84.17					5.50	0.02					0.01	0.00										89.70	10.30
Beatrix		85.25					5.70	0.01					0.01	0.00										90.97	9.03
Beatrix		84.70					5.70	0.01					0.01	0.00										90.42	9.58
Beatrix		84.66					5.76	0.01					0.01	0.01										90.44	9.56
Beatrix		84.47					6.14	0.13			0.00		0.16	0.00										90.90	9.10
Beatrix		83.44					6.17	0.08					0.22	0.00										89.91	10.09
Beatrix		85.67					6.19	0.08					0.30	0.01								0.00		92.25	7.75
Beatrix		84.92					6.34	0.08			0.00		0.33	0.01									0.00	91.68	8.32
Beatrix		84.08					6.37	0.01					0.29	0.05	0.02								0.00	90.82	9.18
Beatrix		79.96					6.37	0.10					0.95	0.00	0.01								0.00	87.39	12.61
Beatrix		84.14					6.47	0.14			0.00		0.46	0.01										91.21	8.79
Beatrix		83.66					6.53	0.12			0.00		0.52	0.00										90.83	9.17
Beatrix		82.07				0.00	6.79	0.22			0.00		0.60	0.01										89.69	10.31
Beatrix		82.76					6.80	0.14					0.15	0.00										89.84	10.16
Beatrix		82.86				0.00	6.84	0.21			0.00		0.68	0.01									0.00	90.60	9.40
Beatrix		82.96					6.95	0.01					0.07	0.00										89.99	10.01
Beatrix		82.73				0.01	7.00	0.25			0.00		0.76	0.01										90.75	9.25
Beatrix		83.61					7.15	0.16					0.39	0.01									0.00	91.32	8.68
Beatrix		82.46				0.01	7.17	0.29			0.00		0.76	0.01										90.70	9.30
Beatrix		83.38					7.26	0.02					0.03	0.01										90.71	9.29
Beatrix		79.21		0.00		0.01	7.38	0.28			0.00		0.47	0.07									0.00	87.43	12.57
Beatrix		83.36					7.42	0.01					0.45	0.11										91.35	8.65
Beatrix		78.90				0.03	7.55	0.63			0.00		0.65	0.08									0.00	87.84	12.16
Beatrix		82.65					7.59	0.09			0.00		0.47	0.02									0.00	90.83	9.17
Beatrix		82.61					7.61	0.18					0.47	0.02									0.00	90.88	9.12
Beatrix		83.24					7.62	0.01					0.43	0.09									0.00	91.39	8.61
Beatrix		82.20					7.62	0.01					0.85	0.15										90.83	9.17
Beatrix		79.49				0.00	7.64	0.03			0.00		0.70	0.25									0.00	88.13	11.87

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder	
Beatrix		78.61				0.03	7.70	0.80			0.00		0.76	0.11									0.00	88.02	11.98	
Beatrix		82.52					7.71	0.19					0.50	0.01										0.00	90.93	9.07
Beatrix		77.90				0.05	7.77	1.11			0.00		0.88	0.13										0.00	87.84	12.16
Beatrix		78.79				0.05	7.86	1.11			0.00		0.89	0.13										0.00	88.84	11.16
Beatrix		82.82					7.87	0.13			0.00		0.58	0.02										0.00	91.42	8.58
Beatrix		83.41					7.93	0.14			0.00		0.58	0.02										0.00	92.09	7.91
Beatrix		82.86					7.93	0.01					0.04	0.01											90.86	9.14
Beatrix		83.18					8.01	0.15			0.00		0.63	0.03										0.00	92.00	8.00
Beatrix		81.30				0.05	8.07	1.05			0.00		0.86	0.08										0.00	91.42	8.58
Beatrix		84.11					8.48	0.00					0.18	0.01											92.79	7.21
Beatrix		83.03					9.08	0.02					0.48	0.10											92.71	7.29
Beatrix		83.22					9.09	0.02					0.47	0.11									0.00	92.92	7.08	
Beatrix		80.09					10.04	0.01					0.27	0.00											90.41	9.59
Beatrix		79.37					10.95	0.02					0.40	0.00											90.74	9.26
Beatrix		78.45					12.54	0.01					0.50	0.01											91.51	8.49
Oryx		86.35					1.49	0.00					0.22	0.17											88.23	11.77
Oryx		88.06					1.50	0.01					0.14	0.11											89.82	10.18
Oryx		90.40					1.62	0.02					0.15	0.09											92.27	7.73
Oryx		86.36				0.10	1.74	1.51			0.01		0.56	0.09									0.00	90.36	9.64	
Oryx		86.70				0.11	1.75	1.65			0.01		0.57	0.09									0.00	90.88	9.12	
Oryx		86.69				0.11	1.76	1.65			0.01		0.58	0.09									0.00	90.90	9.10	
Oryx		86.45					1.88	0.01					0.18	0.12											88.64	11.36
Oryx		85.69					1.88	0.02					0.20	0.13											87.93	12.07
Oryx		85.77					1.89	0.02					0.21	0.13											88.02	11.98
Oryx		85.33					1.90	0.00					0.26	0.11											87.60	12.40
Oryx		85.62					1.95	0.02					0.22	0.15											87.95	12.05
Oryx		85.68					1.96	0.03			0.00		0.22	0.15											88.05	11.95
Oryx		83.64				0.03	2.14	1.05			0.00		0.36	0.07											87.30	12.70
Oryx		86.84				0.03	2.15	0.97					0.35	0.09									0.00	90.43	9.57	
Oryx		88.50					2.16	0.00					0.15	0.13											90.95	9.05
Oryx		90.63				0.03	2.20	0.25					0.26	0.08									0.00	93.44	6.56	
Oryx		89.64				0.04	2.27	0.32					0.30	0.08									0.00	92.65	7.35	
Oryx		88.01				0.01	2.30	0.30					0.17	0.03											90.83	9.17

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder	
Oryx		88.11				0.03	2.36	0.27			0.00		0.32	0.10										91.18	8.82	
Oryx		89.47				0.04	2.38	0.28					0.36	0.21										0.00	92.75	7.25
Oryx		89.60				0.04	2.40	0.28					0.36	0.22										0.00	92.90	7.10
Oryx		86.57				0.02	2.43	0.45			0.00		0.22	0.03											89.73	10.27
Oryx		88.60				0.03	2.48	0.27					0.32	0.08											91.78	8.22
Oryx		86.91				0.02	2.48	0.48			0.00		0.23	0.03											90.14	9.86
Oryx		85.79				0.02	2.48	0.26					0.39	0.08										0.00	89.03	10.97
Oryx		83.87				0.02	2.51	0.40			0.00		0.40	0.06										0.00	87.26	12.74
Oryx		83.14				0.06	2.54	0.94			0.00		0.37	0.09											87.15	12.85
Oryx		82.43				0.07	2.55	0.98			0.00		0.38	0.09											86.49	13.51
Oryx		86.00				0.04	2.60	0.38					0.48	0.10											89.60	10.40
Oryx		85.40				0.04	2.61	0.38					0.49	0.10											89.01	10.99
Oryx		85.81				0.03	2.62	0.37					0.48	0.11										0.00	89.42	10.58
Oryx		83.54				0.04	2.67	0.60			0.00		0.51	0.06										0.00	87.43	12.57
Oryx		88.58				0.02	2.75	0.75			0.00		0.72	0.14											92.96	7.04
Oryx		88.23				0.02	2.76	0.80			0.00		0.72	0.15											92.68	7.32
Oryx		88.32				0.04	2.78	0.53			0.00		0.60	0.22											92.48	7.52
Oryx		88.11				0.04	2.80	0.58			0.00		0.63	0.22											92.38	7.62
Oryx		86.59				0.09	2.92	0.53			0.00		0.50	0.07							0.00	0.00			90.69	9.31
Oryx		86.19				0.07	2.92	0.47			0.00		0.37	0.06											90.08	9.92
Oryx		84.18				0.01	3.36	0.30					0.28	0.09											88.22	11.78
Oryx		83.56				0.01	3.38	0.31					0.28	0.10											87.64	12.36
Oryx		83.83				0.01	3.44	0.37					0.31	0.09											88.05	11.95
Oryx		89.81				0.03	4.95	0.62			0.00		0.53	0.09											96.03	3.97
Oryx		88.89				0.03	5.24	0.71					0.62	0.09										0.00	95.58	4.42
St Helena		88.01				0.00	3.53	0.01					0.10	0.64										0.02	92.30	7.70
St Helena		87.49					3.85	0.01					0.05	0.33										0.01	91.74	8.26
St Helena		84.32					4.12	0.00					0.01	0.63										0.00	89.08	10.92
St Helena		84.31					5.15	0.00					0.00	0.43										0.00	89.89	10.11
St Helena		83.45					5.16	0.00					0.00	0.45										0.00	89.07	10.93
St Helena		79.92			0.00	0.00	6.58	0.19			0.00		0.24	3.52										0.25	90.70	9.30
St Helena		80.36			0.00	0.00	6.61	0.20			0.00		0.24	3.50										0.25	91.17	8.83
St Helena	0.01	83.42		0.00		0.01	6.73	0.33			0.06		0.07	1.53										0.13	92.29	7.71

PROVENANCE OF ILLICIT GOLD WITH EMPHASIS ON THE WITWATERSRAND BASIN

Gold mines	As	Au	Ca	Cd	Co	Cr	Cu	Fe	Ir	Mg	Mn	Mo	Ni	Pb	Pd	Pt	Sb	Se	Sn	Ti	Tl	V	Zn	Total	Remainder	
St Helena		81.61				0.00	7.02	0.00					0.01	0.61										0.00	89.26	10.74
St Helena	0.00	82.89					7.09	0.00					0.01	0.58										0.00	90.58	9.42
St Helena		84.65					7.16	0.01					0.08	0.69										0.03	92.62	7.38
St Helena		83.03			0.00	0.01	7.20	0.47			0.06		0.04	0.73										0.17	91.72	8.28
St Helena		82.21				0.00	7.32	0.13			0.04		0.02	1.67										0.08	91.46	8.54
St Helena		78.07			0.00	0.00	8.43	0.71			0.01		0.30	3.23										0.29	91.05	8.95
St Helena		78.48			0.00	0.00	8.50	0.73			0.01		0.31	3.33										0.30	91.65	8.35
St Helena		81.62				0.00	8.74	0.10			0.03		0.02	1.17										0.08	91.76	8.24
St Helena	0.01	78.55		0.00			10.44	0.00					0.02	1.61										0.01	90.63	9.37
St Helena	0.01	79.00		0.00			10.44	0.01					0.02	1.57										0.01	91.05	8.95
St Helena		79.06					11.21	0.01			0.00		0.02	0.83										0.02	91.14	8.86