GOLD IN THE PILBARA: ASSOCIATIONS AND EXTRACTABILITY

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ABSTRACT

A new method using a combination of Proton Induced X-Ray Emission (PIXE) and diagnostic leaching has been used to characterise the associations and distribution of gold in a variety of ores from the Pilbara region of Western Australia. The different ore types studied highlighted the versatility of the approach and has demonstrated its applicability to any type of ore. Characterisation of an oxide ore from a newly discovered deposit has shown how the technique can be used to gain a good initial understanding of potential metallurgical problems for a new ore. From the application of the approach to the study of two other types of refractory ores it was possible to demonstrate that in these ores the gold occurs locked within the sulphide matrix as "invisible gold" and that the form of its occurrence affects its recovery.

Keywords: Sulphide Ores, Liberation analysis

INTRODUCTION

In recent years, the gold mining industry has faced a depletion of readily extractable oxide ores and an increase of more problematic sulphide ores, which generally underlie the oxide deposits. This has made it ever more important to understand the metallurgical problems associated with these sulphide ores and develop economically viable extraction techniques. One thing that is vital in the development of an optimised processing route is a good understanding of the distribution and associations of gold.

Gold can be associated with a variety of minerals within an ore matrix in many different ways. Knowing these associations can be vital in optimisation of the extraction route. The occurrence of gold can range from large nuggets of free gold generally found in alluvial deposits to sub-micron sized particles or even gold in solid solution with the ore minerals. Ore deposits with predominantly free gold that is easily amenable to cyanide extraction have previously been defined as free-milling ores and deposits where gold is not amenable to a direct cyanide leach and requires a pre-treatment stage to liberate the gold are termed as refractory (Marsden and House 1992).

The refractory nature of gold deposits can be attributed to a number of different factors. The most common cause of metallurgical problems is the encapsulation of gold by sulphide minerals (Marsden and House 1992). This problem can often be overcome by fine grinding of the ore to liberate macroscopic gold, however, in some cases the particles of gold may be too small to be effectively liberated by fine grinding or may even be in solid solution. When this occurs gold is termed as "invisible gold", which has been defined by Boyle (1979) as colloidal or chemically bound gold that is undetectable by microscopic techniques. "Invisible gold" is generally seen in arsenopyrite or arsenic rich pyrite. A number of studies have determined the mechanism of occurrence of "invisible gold". Cook and Chryssoulis (1990) showed that "invisible gold" will only occur in pyrite once a certain bulk concentration of arsenic has been reached, while Vaughan (1995) showed that gold will be concentrated in arsenic rich rims of pyrite. It has been suggested that in arsenopyrite, depletion of Fe with gold concentration suggests Au substitutes for Fe in the sulphide matrix (Genkin et al. 1998) and in pyrite the incorporation of As into the matrix could lead to distortion of the lattice allowing the incorporation of gold (Tarnocai et al. 1997).

Knowing the distribution and association of gold within ores can help not only in identifying a processing route but also in the optimisation of an accurate assay technique. It is often assumed that a simple fire assay or aqua regia digestion will give an accurate head grade for any ore. This is not always true and optimisation of the fire assay analysis is often required, which is difficult if the true head grade is unknown. These problems are most often encountered where gold is in solid solution within a sulphide or in a gold-telluride mineral and it is for this reason that a good understanding of the

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associations and distribution of gold is essential. This information can be used to identify if gold occurs in multiple forms and if all of those forms are amenable to the assay technique being utilised. If they are not, then a new assay technique can be developed to ensure accurate head grade analysis.

The present investigation seeks to show how a combination of analytical (Proton Induced X-Ray Emission) and chemical (Diagnostic Leaching) techniques can be used to identify the distribution of gold within a given ore and hence shed light on potential metallurgical and assay problems.

PROTON INDUCED X-RAY EMISSION (PIXE)

Proton Induced X-ray Emission (PIXE) is a non-destructive, simultaneous trace multi-element analytical technique. Protons, focussed into a beam spot on the sample in a nuclear microprobe (NMP), ionise atomic electrons producing inner-shell vacancies. De-excitation of these vacancies causes the emission of characteristic X-rays for that element. A spectrum of characteristic X-rays is then developed, with each event labelled with the coordinates of the scanning beam to permit images of the elemental composition of the target mineral grain to be constructed (Johansson et al. 1995).

As a trace elemental analytical technique PIXE is very powerful with minimum detection limits (MDL) between 0.1 and 50 ppm depending on the element and host matrix (Johansson et al. 1995). This is in contrast to similar techniques such as electron microprobe analysis (EMPA), which has an achievable MDL of 50-100 ppm when great care is taken for sample preparation but is generally >500ppm (Sie et al. 1991). In addition to lower detection limits, the use of protons in PIXE rather than electrons to form the beam allows the beam to penetrate up to $30\mu m$ into the surface (Sie et al. 1991). This allows the detection of elements, which may be buried in the sample or are covered by an oxidised layer. This feature has also been used to analyse fluid inclusions in quartz in-situ to give information on the rock forming processes (Ryan et al. 2001b).

As with any X-ray spectrometry care must be taken with PIXE to allow for interferences caused by overlap of the X-ray line (Annegarn and Bauman 1990). This is especially relevant for gold analysis as the tails of the arsenic and tungsten lines overlap the gold line making analysis uncertain in matrices high in these elements.

In recent years, PIXE has been used for a wide range of investigations within the earth sciences. A number of reviews of some of these applications have been completed by Ryan (1995), Annegarn and Bauman (1990) and Sie et al. (1991). PIXE has also been used extensively for analysis of distribution of gold within sulphide ores. One example of this application was a study by Foya et al. (1999) who demonstrated "invisible gold" associated with zones of high As in the Kimberly Reefs of the Witwatersrand Basin.

DIAGNOSTIC LEACHING

Diagnostic leaching was developed by Anglo American Research Laboratories in the late 1980's to provide a way to distinguish the deportment of gold within ore. This is achieved by selective destruction by oxidative acid leach of minerals, with each stage followed by a cyanide leach to recover gold liberated. Generally it is expected that in addition to minerals destroyed at each stage approximately 10% of the next most stable mineral will also be destroyed (Lorenzen and Tumilty 1992).

As an analytical technique, diagnostic leaching is very useful in establishing the ratio of gold associated with different mineral phases within a given ore. It can be applied both to characterisation of new ores and to problem solving in well-characterised ores, where metallurgical problems are experienced. Studies of this nature have been completed by Teague et al. (1998) who used diagnostic leaching to show the behaviour of gold and gold minerals in froth flotation. Lorenzen and Tumilty (1992) used diagnostic leaching to show the effect of the addition of reagents to the performance of a gold plant. The technique has also been used to identify the refractory nature of gold ores and determine possible extraction routes (Lorenzen and van Deventer 1992; Lorenzen and van Deventer 1993).

When combined with PIXE analysis diagnostic leaching can be used to establish the bulk ratio of gold associated with each mineral phase. This information can be used to verify if gold observed in grains by PIXE is representative of the bulk sample or simply an abnormality.

MATERIALS

Three ores from the Pilbara region of Western Australia were selected for this investigation. A variety of ore types were chosen to show the versatility of using PIXE and diagnostic leaching to characterise the extractability and assay amenability of different types of gold ores. Ore 1 was an oxide ore, which

has been found to have no metallurgical processing or assay problems. Ore 2 was a sulphide ore that has shown typical characteristics of a refractory ore, with high cyanide consumption and low recoveries without pre-treatment. Ore 3 was selected as a complex sulphide ore for which there has been a history of metallurgical problems and was known to respond poorly to traditional assay techniques such as fire and aqua regia assay methods.

Preliminary head grade analysis and percentage extraction by cyanide of each ore are shown in Table 1. Head grade analysis was by commercial fire assay and cyanide amenability was based on a 24-hour agitated leach in 1000ppm NaCN.

Table 1. Fire Assay head grade and cyanide extraction of ores investigated. Percentage cyanide extraction based on fire assay head grade.

	Head Grade (g/t Au)	Cyanide Extraction (%)
Ore 1	4.69	85%
Ore 2	4.97	75%
Ore 3	5.11	26%

Ore 1

The deposit from which this ore was selected was a recent discovery that had undergone very little metallurgical characterisation. It was chosen to demonstrate how the combination of PIXE and diagnostic leaching could be used early in the characterisation of a new ore to establish if metallurgical problems were likely to be experienced. It was not expected that metallurgical problems would be identified, as it is essentially an oxide ore consisting predominantly of quartz and hematite. This mineralogy suggests that the gold should occur as free grains and that the ore should be free milling.

Ore 2

Ore 2 was chosen as a typical refractory sulphide ore. It was selected to demonstrate the effectiveness of using a combination of PIXE and diagnostic leaching to identify the association of gold within sulphide ores and to allow the selection of an effective pre-treatment stage.

Previous metallurgical and processing trials using this ore have identified a number of problems. Recovery of gold by direct cyanide leach was observed to account for only 75% of the fire assay head grade with high reagent consumption. To help overcome these problems it was hoped that diagnostic leaching could be used to identify the distribution of gold in the bulk phases along with PIXE to show how gold was associated within each of these phases.

Ore 3

Ore 3 is a complex sulphide ore, which historically has shown numerous metallurgical problems. It was chosen to show how the PIXE and diagnostic leaching techniques could be used to show the distribution of gold within a complex ore and establish a processing route based on this distribution.

This ore has been shown to respond poorly to traditional assay techniques such as aqua regia dissolution and fire assay. These techniques have consistently shown a wide variability in results suggesting that poor extraction/collection is occurring. This can be seen from Tables 1 and 2, which show very poor extraction by cyanide and a large standard deviation associated with other assay techniques.

Table 2. Assay error associated with traditional assay techniques for Ore 3. Error calculated from standard deviation from mean grade, based on a series of identical assays

	Mean Grade (g/t Au)	Standard Deviation (%)
Fire Assay (50g sample)	5.11	27%
Aqua regia (25g sample)	3.857	25%

The poor response of the ore to cyanidation (26%) suggests that the high error associated with assay is unlikely to be simply the result of a 'nugget' effect associated with coarse free gold.

This observation along with the poor response to traditional assay techniques suggests that there is a form of gold present in Ore 3 that is not amenable to direct cyanidation or consistent assay.

By using the combination of PIXE and diagnostic leaching it was hoped that the distribution of gold within this ore could be established and an accurate head grade determined. This information could

then be used to establish a reliable assay technique for use with ores of this type and an optimised processing route determined

SAMPLE PREPARATION

PIXE Analysis

Thin-sections of each ore type were prepared from hand specimens randomly chosen from ore stockpiles. Well mineralised samples were preferentially selected. To allow for the greater penetration depth of the proton beam thin-sections were cut to a thickness of ~100μm.

Areas of interest in the thin-sections were identified by optical microscopy and digitally logged for initial analysis by Electron Microprobe Analysis (EMPA). This was performed to identify areas of interest for analysis by PIXE. It was, however, also necessary to identify the major elements present using EMPA because of the difficulties faced in PIXE of identifying lighter elements ($Z < 20$). This allows PIXE to be used exclusively for trace elemental analysis and gives a more accurate overall understanding of the composition of the ore.

Diagnostic Leaching

Samples for diagnostic leaching were taken from a bulk sample of each ore. This bulk sample had been hand picked from ore stockpiles and crushed to ~850μm using a laboratory jaw crusher and laboratory hammer mill. The crushed material was then homogenised using a riffle splitter. A 2kg portion of this bulk sample was taken for the diagnostic leaching trial and ground to a P80 of 45μm using a laboratory ring mill. The sample was then split into two 1kg portions in a rotary splitter. One portion was used for the diagnostic leaching trial and the second for mineralogical evaluation.

The mineralogical evaluation consisted of quantitative X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) analysis, along with a comprehensive elemental and trace elemental analysis by acid digestion. It is necessary to have a good understanding of the mineralogy and elemental composition when undertaking diagnostic leaching because the mineral phases present dictate which oxidative acid leaches are necessary.

METHODS

Electron Microprobe Analysis (EMPA)

Electron Microprobe Analysis (EMPA) was performed using a fully automated Cameca SX50 electron microprobe equipped with four wavelength dispersive spectrometers (WDS) and an energy dispersive spectrometer (EDS). For the sulphide samples, a beam of 20 keV and 20nA was used and for oxide samples a beam of 15keV and 25nA was used. The elements analysed are presented in Table 3.

Table 3. Elements detected by EMPA

Oxide	Sulphide
Na, K, Al, Mg, Si, Ti Ca, Fe, Cr, Zn, Mn, O	S, Fe, As, Zn, Pb, Ni

It should be noted that EMPA did not analyse for Au and Ag, as the detection limit for these elements is too high. For gold it is possible to achieve a detection limit of 200ppm with increased counting times, which is still much higher than the average concentration in the ore (about 5ppm). For this reason EMPA was only used to identify the phases present and areas of interest for Nuclear Microprobe (NMP), not for trace elemental analysis.

The results of phase identification based on elemental ratios established on EMPA are shown in table 4. A number of minerals were identified that were not seen by quantitative XRD. This is consistent with low bulk concentrations of these minerals; however, they are still significant if they carry gold.

Table 4. Phases identified by EMPA

Ore 1	Ore 2	Ore 3
Quartz	Quartz	Quartz
Hematite	Pyrite	Pyrite
	Chalcopyrite	Gersdorffite
		Dolomite
		Magnesite

It was noted that for both Ores 2 and 3 appreciable arsenic (1% - 4%), was associated with some pyrite grains.

X-Ray Diffraction (XRD)

X-ray Diffraction (XRD) was performed using a Philips PW 1800 X-Ray Diffractometer. Copper Kα radiation, a graphite monochromator and a proportional detector were used to collect the diffractogram.

Quantitative analysis of each of the ore samples was performed using the "siroquant" software package.

Table 5. Mineral Phases identified by Quantitative XRD analysis.

Ore 1		Ore 2		Ore 3	
Phase	Fraction (%)	Phase	Fraction (%)	Phase	Fraction (%)
Quartz	84	Quartz	43	Quartz	27
Hematite	5	Muscovite	38	Magnesite	37
Goethite	8	Ankerite	5	Dolomite	22
		Chlorite	7	Chlorite	7
		Pyrite	5	Anorthite	5
		Calcite	2	Talc	2

No sulphide mineral phases were identified in Ore 3 using this technique. This is probably caused by the total concentration of sulphides being below the detection limit.

Proton Induced X-Ray Emission (PIXE)

PIXE analysis for this study was carried out on the CSIRO-GEMOC Nuclear Microprobe. This instrument utilises a quadrupole quintuplet lens configuration to obtain high resolution over a short length. This lens configuration allows a spot size of between ~1μm at 100pA growing to ~3μm at 20nA (Ryan et al. 1999). For this analysis, a beam current of 5nA was used with a spot size of 2μm. A 300μm Al filter was used to attenuate major elements to the hyper pure Ge detector. Dynamic analysis using the GeoPIXE II software package was used to decompose the PIXE spectrum into its elemental components to give quantitative concentration information in the form of images specific to each element (Ryan 2001). A summary of the features of the CSIRO-GEMOC Nuclear Microprobe can be found elsewhere. (Ryan et al. 1999; Ryan et al. 2001a)

Diagnostic Leaching

A set of guidelines for the design of a diagnostic leaching experiment has been demonstrated by Lorenzen (1995). These have been used in this study to establish an appropriate experimental regime. The key to the design of a successful diagnostic leaching experiment is to have a comprehensive understanding of the mineralogy of the ore to be studied. This allows the selection of the minimum number of oxidative acid leaches. Minimising the number of stages reduces experimental error. The mineralogy of each ore to be studied in this investigation was determined by quantitative XRD and appropriate oxidative leach stages determined from guidelines (Lorenzen 1995) depending on the complexity of the ore. A typical set of steps for a sulphide ore are summarised in Table 6.

The oxidative acid leach stages listed in Table 6 were used for Ores 2 and 3. Both have similar mineralogy. Diagnostic leaching for Ore 1 was not performed because the simple mineralogy of the ore and good amenability to cyanidation suggested that it was not necessary.

Table 6. Oxidative leach stages used for diagnostic leaching of Ores 2 and 3.

Step	Leach	Mineral Leached
1	Mineralogical examination	-
2	Sample preparation	-
3	Cyanide	Free Gold
4a	HCl	Pyrrhotite, Calcite, Dolomite, Galena, Goethite, Calcium Carbonate
4b	Cyanide	Free Gold
5a	H_2SO_4	Sphalerite, Labile Copper Sulphides, Labile Base metal Sulphides, Labile Pyrite
5b	Cyanide	Free Gold
6a	HNO_3	Pyrite, Arsenopyrite, Marcasite
6b	Cyanide	Free Gold
7a	HF	Silicates
7b	Cyanide	Free Gold

RESULTS

Ore 1

A typical grain analysis by PIXE for Ore 1 is shown in Figure 1. As expected the grain is predominantly Fe, consistent with it being hematite or goethite. The correlation between As and Fe suggests that As is associated with the iron oxide and the low concentration (avg. 0.8%) infers that the As is present in solid solution. The gold hotspot is correlated with Cu, Ni and Ag and has dimensions of 5μm x 12μm (plan in view), although the thickness is difficult to determine because the exact composition of the inclusion is not known. This is contrary to the postulate that gold in this ore should occur as free particles and suggests that it occurs as electrum associated with a Cu-Ni sulphide or as a more complex mineral.
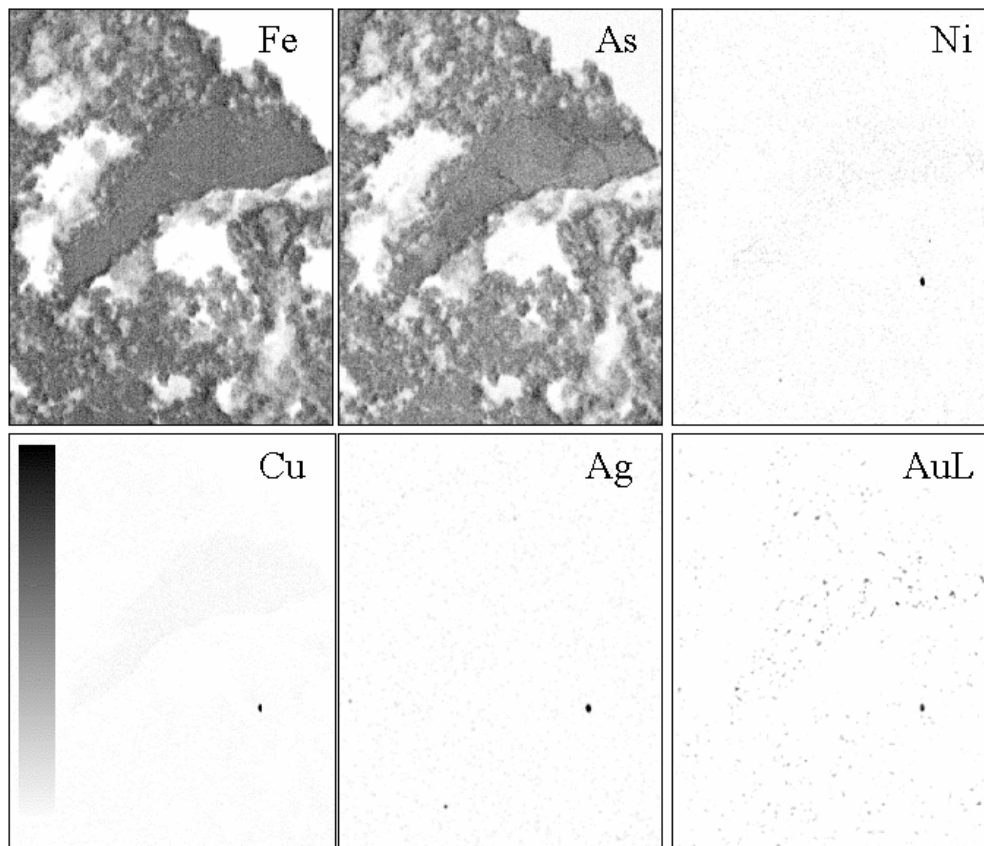
Figure 1. PIXE images of elemental distribution in hematite grain from Ore 1.
Image area is 1.0x1.0 (mm)

Table 7. Maximum concentrations of elements in PIXE image (Fig. 1)

| Fe	136%	Ni	3.31%	Cu	7.35%	Ag	0.50%	As	1.79%	Au	0.17%

The very simple mineralogical composition of Ore 1 meant that diagnostic leaching was not considered necessary for complete characterisation. Future tests will be conducted on the sulphide ore from this deposit.

Ore 2

PIXE analysis of Ore 2 was completed and typical results are shown in Figures 2a and 2b. A number of grains were analysed. In the image shown in Figure 2a, it can be seen that there are three separate grains. One grain is high in Cu and Fe, with the relative ratios of each of these elements consistent with it being chalcopyrite. The second grain, on the left of the image, is most probably As rich pyrite. The final grain is rich in Zn, As and Sb and shows considerable Ag, the composition of this grain is consistent with tetrahedrite (($Cu,Fe,Zn,Ag)_{12}Sb_4S_{13}$).

Gold is weakly distributed throughout the arsenian pyrite grain. The low concentration of gold (average. 50 ± 17ppm) is consistent with solid solution or colloidal gold, and is just above the detection limit (34ppm) for this small area. In either case it is consistent with "invisible gold" occurring in this ore. It is also interesting to note that no gold is associated with Ag or Cu in these grains. Ag occurs in the tetrahedrite grain and because of the low concentrations determined (max. 0.27%) appears to be in solid solution. Cu is concentrated mainly in the chalcopyrite grain and shows no association with gold.

Figure 2b shows a pyrite grain with As concentrated around the rim but not within the grain. This is an interesting feature because statistically significant levels of gold are not seen in the image for this grain, again consistent with "invisible gold" being associated only with As rich pyrite or arsenopyrite. The average gold content within the area of the image is 20 ppm.
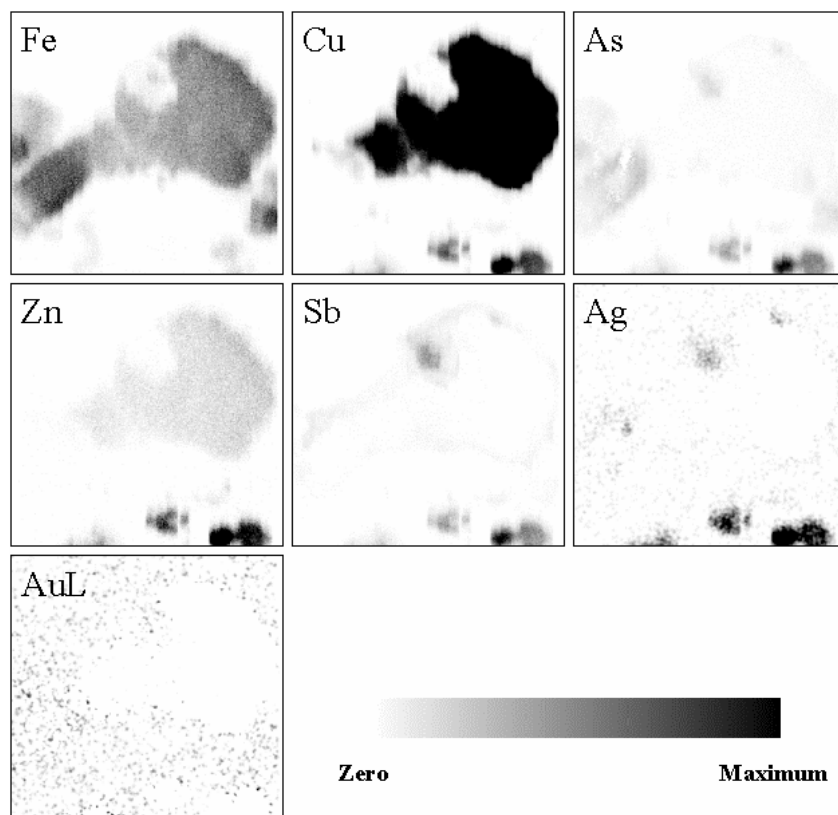
Figure 2a. Typical PIXE images of elemental distribution in grain from Ore 2.
Image area is 1.0x1.0 (mm)

Table 8. Maximum concentrations of elements in typical PIXE image (Fig. 2a) for Ore 2

Fe	62.2%	Cu	40.4%	As	2.42%	Sb	13.5%	Zn	3.88%	Ag	0.27%	Au	581ppm
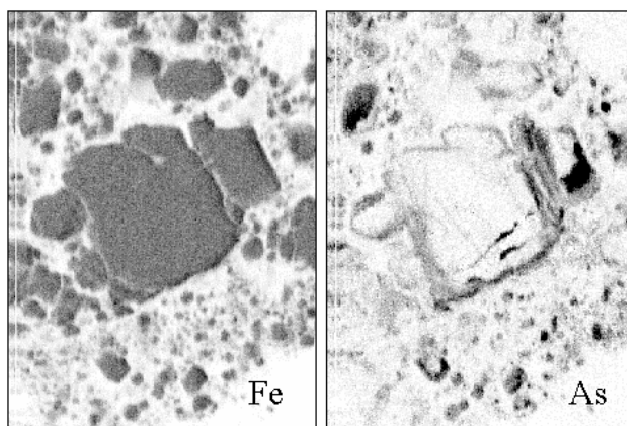
Figure 2b. PIXE image from analysis of Ore 2.
Image area is 1.0x1.0 (mm)

The results of diagnostic leaching for Ore 2 are shown in Table 9. It should immediately be noted that the calculated gold grade (7.85 g/t Au) recovered is greater than the fire assay head grade (4.97 g/t Au) for this ore. This is most probably attributable to the use of a poorly optimised fire flux used for the assay test. The distribution of gold suggests that over half is not amenable to direct cyanide leaching, demonstrating that this ore is clearly refractory. The remainder of the gold is distributed amongst the sulphide minerals. Little gold was associated with crystalline pyrite or arsenopyrite, which would have been destroyed by the nitric acid oxidative leach and showed up in this step of the diagnostic leaching test. This infers that the majority of gold is associated with amorphous base metal sulphides or amorphous pyrite. When combined with the results of PIXE it is strongly suggested that the gold is associated with amorphous pyrite.

**Table 9.** Diagnostic Leaching results for Ore 2.

Stage	Grade Recovered (g/t Au)	Cumulative Grade Recovered (g/t Au)	% Recovery (Calculated Grade)	Cumulative % Recovery (Calc. Grade)
NaCN	3.74	3.74	47.6%	47.6%
HCl	1.53	5.27	19.5%	67.1%
H_2SO_4	2.08	7.35	26.5%	93.6%
HNO_3	0.44	7.79	5.6%	99.2%
HF	0.07	7.85	0.8%	100.0%
Total		**7.85**		**100.0%**

Ore 3

The PIXE images of some typical sulphide grains for Ore 3 are shown in Figure 3. The images demonstrate a clear association of Ag with As, Ni and Sb. Unfortunately, Au could not be distinguished in the presence of the high As. This As-Ni-Sb sulphide matrix appears to be concentrated in defects in the pyrite grain suggesting that it was deposited in the ore at a later paragenetic stage. As observed in Ore 2, Ag occurs only in low concentrations consistent with it, and probably gold, being in solid solution with the sulphide matrix or present in colloidal form. This would be consistent with the postulate that molecular gold is the cause of assay problems experienced with this ore and would suggest that it is held within a Ni-As-Sb matrix.

Although coarse free gold is known to occur in this ore it was not detected by PIXE analysis. This is almost certainly a function of the small sample size analysed.
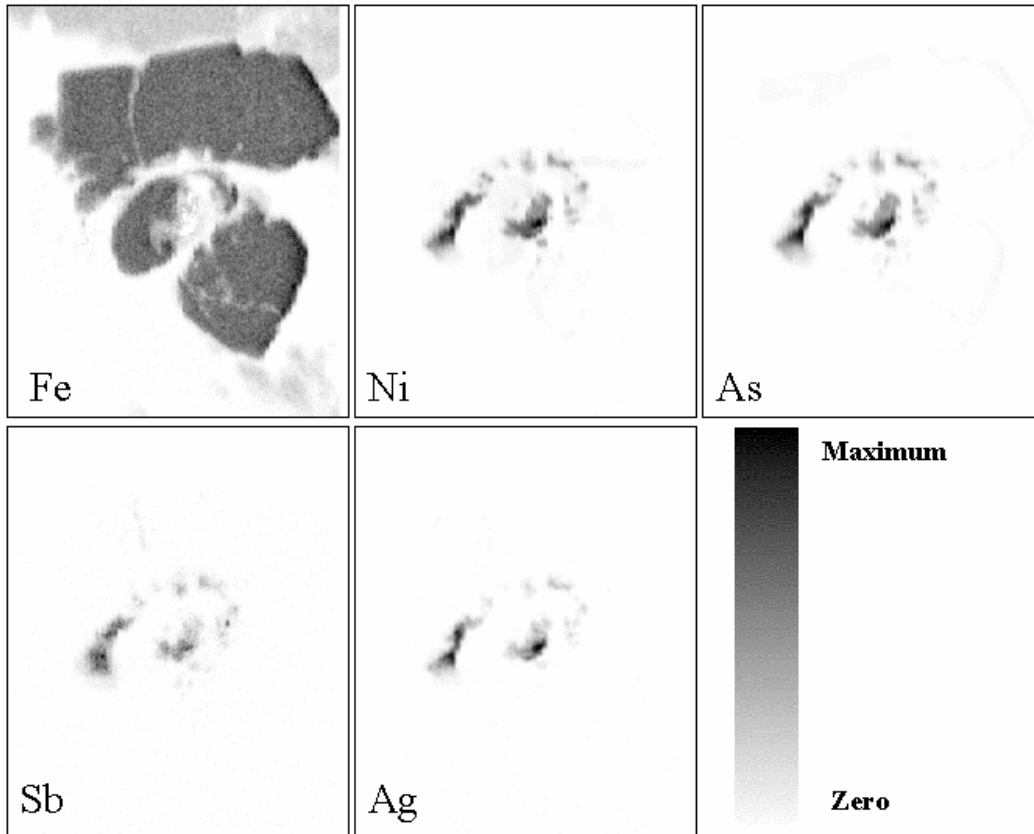
Figure 3. PIXE image of typical elemental distribution for Ore 3. Image area is 1.0 x 1.0 (mm)

Table 10. Maximum concentrations of elements in PIXE image (Fig. 3)

Fe	71.60%	As	57.10%	Ni	39.90%	Sb	5.71%	Ag	1.37%	Au	0.31%

Diagnostic leaching for Ore 3 demonstrated a very low recovery of gold by direct cyanide leach and showed that the majority of gold is locked within a sulphide matrix. The results are shown in Table 11. The recovery demonstrated in the HCl oxidative leach infers that gold is associated with galena but the elevated recovery from the HNO_3 oxidative leach demonstrates that the majority of gold is bound within a crystalline sulphide. This is consistent with the postulate that gold is associated with a Ni-As-Sb matrix, based on PIXE results. The calculated gold grade (6.62 g/t Au) is higher than the fire assay head grade (5.11 g/t Au) but is only just outside the error range (27% std. dev.). The high recovery of gold from crystalline sulphides indicates a need to optimise the fire assay technique for this ore. It would be expected that a fire assay method that had not been optimised for this sulphide ore would not liberate gold efficiently from this matrix because of poor slag formation and separation.

Table 11. Diagnostic Leaching results for Ore 3.

Stage	Grade Recovered (g/t Au)	Cumulative Grade Recovered (g/t Au)	% Recovery (Calculated Grade)	Cumulative % Recovery (Calc. Grade)
NaCN	1.33	1.33	20.03%	20.03%
HCl	1.62	2.95	24.49%	44.52%
H_2SO_4	0.78	3.72	11.73%	56.24%
HNO_3	2.83	6.55	42.74%	98.98%
HF	0.07	6.62	1.01%	100.00%
Total		**6.62**		**100.00%**

DISCUSSION

The use of PIXE analysis to show the association of Au with its host minerals and diagnostic leaching to show its bulk distribution in the three ore types under investigation demonstrates the wide range of gold associations and the importance of its distribution to leaching and recovery. This highlights the importance of understanding these factors to help develop an effective assay and processing strategy for any given ore.

It was seen for Ore 1 that it was free milling although not all gold occurred as free particles because PIXE analysis identified discrete particles of gold associated with Cu, Ni and Ag. This shows that some metallurgical problems may be encountered with this oxide ore and explains why recovery by direct cyanidation is only 85%. However, the high extraction with cyanide suggests that the majority of gold is free and that gold identified by PIXE analysis is representative of only a small proportion of the total gold. Although these results don't highlight any obvious metallurgical problems, they demonstrate how the combination of PIXE and diagnostic leaching can be used on a new ore to immediately show the distribution of gold and whether metallurgical problems should be expected. This information is vital for establishing an efficient characterisation regime and eventually in developing an effective processing route.

The results seen for Ore 2 demonstrate the existence of two forms of gold. The first form is free gold that is readily amenable to cyanide leaching and the second is associated with the sulphide matrix and is thought to be "invisible gold". The occurrence of gold in As rich pyrite grains as demonstrated by the PIXE images are consistent with the observations of Cook and Chryssoulis (1990) pointing out that there is a correlation between bulk arsenic content and "invisible gold" in pyrite. The results of the diagnostic leaching suggest that this "invisible gold" is concentrated in amorphous pyrite rather than crystalline pyrite. This is consistent with the observations of Wilson and Rucklidge (1987) who showed gold concentrations to be higher in fine-grained porous arsenian pyrite at the Owl Creek deposit, Ontario, but in contradiction to the results of Cook and Chryssoulis (1990) who observed that "invisible gold" was found in pyrite independent of textural type.

One drawback of using a combination of PIXE and diagnostic leaching is the inability of the technique to determine if "invisible gold" occurs as inclusions of metallic colloidal gold or in solid solution with the sulphide matrix. This is an important factor to consider since if gold occurs as colloidal particles, then ultra fine grinding may be used to initiate liberation, however, if the gold is in solid solution then the sulphide matrix must be destroyed before any liberation occurs. A study of the nature of "invisible gold" occurrence in pyrite carried out by Wagner et al. (1986) used ^{197}Au Mössbauer Spectroscopy to show that gold is structurally bound and bonded covalently. This method while powerful has a MDL of 100ppm, requiring concentrated samples. In another study, channelling of an MeV ion beam was used to demonstrate that a fraction of gold in arsenian pyrite from the Emperor Mine in Fiji is structurally bound (Den Besten et al. 1999).

As with Ore 2, a number of different forms of gold were identified in Ore 3. Coarse free gold is present although it comprises only a small portion (20%) of the total gold. The second form is fine gold probably associated with galena. This was liberated by the HCl oxidative leach and would be expected under optimised conditions to be amenable to cyanide leaching. The final form of gold seen to occur in Ore 3, comprising 43% of the total gold, appears to be in solid solution with a Ni-As-Sb sulphide matrix and has the same characteristics as "invisible gold". The composition of the matrix is consistent with that of gersdorffite (NiAsS), however, the inclusion of Sb and Ag suggests some tetrahedrite ((Cu,Fe,Zn,Ag)$_{12}$Sb$_4$S$_{13}$) may also be present. It has been suggested that gersdorffite may contain "invisible gold" by Cook and Chryssoulis (1990). This is an interesting result as the pyrite and arsenopyrite in this sample, which would be expected to offer a source "invisible gold", were seen to be deficient in gold by the PIXE analysis.

The results for Ore 3 highlight the effectiveness of using a combination of PIXE and diagnostic leaching to identify the associations and distribution of gold. The use of PIXE alone to show the association of gold in this ore was not satisfactory because of the high concentration of As masking the gold content. However, when combined with diagnostic leaching it was possible to show that gold was associated with a sulphide matrix and when the results of the two techniques were combined show the definite association of gold.

For both sulphide ores, where "invisible gold" was identified, it was noted that the calculated gold grade from diagnostic leaching was higher than the fire assay head grade. This highlights the need to be wary of using techniques such as fire assay and aqua regia digestion with no validation or optimisation reference. The result suggests that the fire assay technique used did not extract "invisible

gold" efficiently and that the high variability noted for Ore 3 is due to unpredictable collection from the Ni-As-Sb sulphide matrix. This need to optimise fire assay methods for sulphide ores is a well known phenomenon, however, the use of the PIXE and diagnostic leaching techniques prior to this optimisation provides information about the total gold content of the ore and the distribution of gold. This information can then be used to establish the ideal flux ratio for fire assay without the trial and error that is usually required. This process will be implemented for these two ores and the sulphide ore associated with Ore 1.

CONCLUSION

The associations and distribution of gold in three ores from the Pilbara region of Western Australia have been shown. For the first ore, it was demonstrated that some gold occurred associated with Ag, Cu and Ni, but the majority occurred as free particles. This was consistent with the postulate that the ore should be free milling but highlighted areas that may cause metallurgical problems. By using the combination of PIXE and diagnostic leaching, to characterise this newly discovered deposit it was demonstrated how these techniques could benefit a characterisation study by immediately showing the associations and distribution of gold.

The second ore studied was a refractory sulphide ore. It was shown that two forms of gold were present. Free gold and gold locked within arsenian pyrite. This gold was identified as "invisible gold" and was postulated to be the cause of unreliable assay results by fire assay.

The final ore studied was a complex refractory ore with a history of metallurgical and assay problems. Three forms of gold were identified. Free gold was shown to make up only a small portion of the total gold, with gold also present associated with galena and locked within a Ni-As-Sb sulphide matrix postulated to be gersdorffite or tetrahedrite. It was demonstrated that this last form of gold is "invisible gold" and as with the second ore is postulated to be the cause of assay unreliability.

In conclusion, this investigation has shown the effectiveness of using a combination of PIXE and diagnostic leaching to identify the associations of gold and its bulk distribution within a given ore. This information can be used to identify the cause of metallurgical and assay problems and help develop an effective processing or assay route.

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