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FURTHER ASPECTS OF THE CHEMISTRY OF GOLD IN SOME WESTERN AUSTRALIAN SOILS

D.J. Gray and M.J. Lintern

CRC LEME OPEN FILE REPORT 34

September 1998

(CSIRO Division of Exploration Geoscience Report 391R, 1993. Second impression 1998)









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RESEARCH ARISING FROM CSIRO/AMIRA REGOLITH GEOCHEMISTRY PROJECTS 1987-1993

In 1987, CSIRO commenced a series of multi-client research projects in regolith geology and geochemistry which were sponsored by companies in the Australian mining industry, through the Australian Mineral Industries Research Association Limited (AMIRA). The initial research program, "Exploration for concealed gold deposits, Yilgarn Block, Western Australia" (1987-1993) had the aim of developing improved geological, geochemical and geophysical methods for mineral exploration that would facilitate the location of blind, buried or deeply weathered gold deposits. The program included the following projects:

P240: Laterite geochemistry for detecting concealed mineral deposits (1987-1991). Leader: Dr R.E. Smith. Its scope was development of methods for sampling and interpretation of multi-element laterite geochemistry data and application of multi-element techniques to gold and polymetallic mineral exploration in weathered terrain. The project emphasised viewing laterite geochemical dispersion patterns in their regolith-landform context at local and district scales. It was supported by 30 companies.

P241: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1987-1991). Leader: Dr C.R.M. Butt.

The project investigated the distribution of ore and indicator elements in the regolith. It included studies of the mineralogical and geochemical characteristics of weathered ore deposits and wall rocks, and the chemical controls on element dispersion and concentration during regolith evolution. This was to increase the effectiveness of geochemical exploration in weathered terrain through improved understanding of weathering processes. It was supported by 26 companies.

These projects represented "an opportunity for the mineral industry to participate in a multi-disciplinary program of geoscience research aimed at developing new geological, geochemical and geophysical methods for exploration in deeply weathered Archaean terrains". This initiative recognised the unique opportunities, created by exploration and open-cut mining, to conduct detailed studies of the weathered zone, with particular emphasis on the near-surface expression of gold mineralisation. The skills of existing and specially recruited research staff from the Floreat Park and North Ryde laboratories (of the then Divisions of Minerals and Geochemistry, and Mineral Physics and Mineralogy, subsequently Exploration Geoscience and later Exploration and Mining) were integrated to form a task force with expertise in geology, mineralogy, geochemistry and geophysics. Several staff participated in more than one project. Following completion of the original projects, two continuation projects were developed.

P240A: Geochemical exploration in complex lateritic environments of the Yilgarn Craton, Western Australia (1991-1993). Leaders: Drs R.E. Smith and R.R. Anand.

The approach of viewing geochemical dispersion within a well-controlled and well-understood regolith-landform and bedrock framework at detailed and district scales continued. In this extension, focus was particularly on areas of transported cover and on more complex lateritic environments typified by the Kalgoorlie regional study. This was supported by 17 companies.

P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration. Leader: Dr. C.R.M. Butt.

The significance of gold mobilisation under present-day conditions, particularly the important relationship with pedogenic carbonate, was investigated further. In addition, attention was focussed on the recognition of primary lithologies from their weathered equivalents. This project was supported by 14 companies.

Although the confidentiality periods of the research reports have expired, the last in December 1994, they have not been made public until now. Publishing the reports through the CRC LEME Report Series is seen as an appropriate means of doing this. By making available the results of the research and the authors' interpretations, it is hoped that the reports will provide source data for future research and be useful for teaching. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authorisation to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian Mineral Industry.

This report (CRC LEME Open File Report 34) is a first revision of CSIRO, Division of Exploration Geoscience Restricted Report 391R, first issued in 1993, which formed part of the CSIRO/AMIRA Project P241A.

Copies of this publication can be obtained from:

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PREFACE

Soil sampling is extensively employed in modern-day Au exploration. A major part of the activity of the Weathering Processes group has been to examine the distribution of Au in soils, with regard to improving soil sampling techniques. This report details studies on the chemistry of Au in soils and regolith of the Yilgarn, with the goal of understanding how Au is associated with its constituents. This subject is important for our understanding of the mechanisms of the formation of Au anomalies in soil and deciding how to use soil most effectively as an exploration medium. Specifically, the study:

- (i) demonstrates the high solubility of Au in some soil horizons;
- (ii) confirms and expands on previous limited observations, that, contrary to expectations, Au in pedogenic carbonate is highly soluble;
- (iii) confirms the lesser solubility of Au in Fe oxide dominated soils;
- (iv) indicates that extractable Au is correlated with the concentration of pedogenic carbonate, and that this correlation can be observed even in "complex" profiles where Au appears to be associated with differing phases at differing depths;
- (v) suggests that Au distribution in soils is partly controlled by physical rather than chemical factors: specifically that the Au/carbonate association is due to Au being precipitated via evaporative processes.

This investigation is complementary to other investigations of Au chemistry and studies of the nature and surface expression of Au mineralization, and expands our understanding of the nature and exploration potential of soil Au anomalies. Together they address many of the principal objectives of the Project.

C.R.M. Butt, Project Leader. June, 1993

ABSTRACT

Understanding of the soil chemistry of Au is important for the development and modification of sampling and analysis of soils for exploration. Gold chemistry in a range of soils and regolith materials from the southern Yilgarn, W.A. was investigated by selective extraction, primarily using an iodide reagent or deionized water. On the basis of these results, a number of different classes were delineated:

- (i) unweathered rock and saprolite low Au solubility;
- (ii) laterite and other Fe oxide-dominated regolith moderate Au solubility, with significant readsorption of any dissolved Au;
- (iii) Mn oxide-dominated regolith very high Au solubility when pulverized;
- (iv) carbonate high Au solubility even without pulverizing;
- (v) organic-rich low Au solubility, possibly due to readsorption of dissolved Au;
- (vi) hardpan high Au solubility when pulverized.

The very high solubility of Au in Mn-rich regolith suggests that Mn can act to mobilize Au, which is consistent with previous investigations indicating an important role for Mn in dissolution of Au in chloride-rich groundwaters.

Results for carbonate-rich soils from various sites across the southern Yilgarn craton indicate highly consistent Au behaviour. In general, about 30 - 50% of the total Au is dissolved in iodide reagent. Indeed, the inherent Au solubility is even higher (up to 100%), with the reduction in observed solubility being due to readsorption of some of the dissolved Au by surfaces (such as Fe oxides) exposed by grinding. Commonly, Au solubility is as high, or higher, in coarsely ground material as compared with finely pulverized material. These results indicate that Au in these carbonate soils is highly soluble and commonly found on mineral surfaces or otherwise available to solution. Iodide-soluble Au is consistently found to be correlated with friable carbonate, even where other phases occur, such as Au associated with Fe oxides or contained in carbonate concretions. These results suggest that Au is behaving as a soluble element (like Ca or Mg) in soils and is precipitating in response to similar factors.

Pedogenic carbonate forms in soil as a result of evaporative processes, with the carbonate coating the surfaces of other minerals. Gold may be highly mobile in soil, as a result of biologically generated ligands and may be taken up by plants. As plant material is deposited on the ground surface, Auorganic complexes are formed that then percolate down the soil profile. Once these complexes reach the carbonate horizon, they will be immobilized, not necessarily by chemical means, but because these horizons are an evaporative zone. Therefore, the primary controls on Au distribution in soil with pedogenic carbonate may be biological and physical, rather than purely chemical, as first expected. Gold in such soils is in a highly dynamic state, which may explain why Au mobilization processes may give rise to enrichments, even in geologically recent overburden, that reflect underlying mineralization.

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1 INTRODUCTION

Soil sampling is extensively employed in modern-day Au exploration. A major component of AMIRA Research Projects P241 and P241A has been to examine the distribution of Au in soils, so as to improve soil sampling and interpretation techniques. Soils are commonly the most convenient and inexpensive medium to collect for Au exploration. However, several problems have been encountered in investigating their characteristics:

- (i) Soils are generally highly weathered, and most minerals of interest are fine grained, commonly poorly crystalline and/or of varying chemical composition. The most chemically active phases, such as fine hydrated Fe or Mn oxides or organic matter, are generally difficult to investigate by techniques such as thin-section studies, X-ray diffraction or electron microprobe.
- (ii) Complex biological reactions within the soil may be important controls on element mobilities. This is because biological processes may control the pH/Eh characteristics of a soil, produce ligands (such as cyanide, amino acids, sulphur compounds or humic/fulvic acids), and/or create sites for sorption (such as solid organic matter, oxides precipitated via biological reactions, or cell walls). These factors may be of particular importance to Au, due to its very high affinity for organically derived ligands (Gray, 1988) such as those mentioned above. These biological reactions are extremely complex and very difficult to model.
- (iii) Soil waters are difficult to separate. In addition, soils within the Yilgarn block are commonly very dry. It is possible that major chemical redistributions occur during periods of higher water content, *i.e.*, after rain, but it is usually impracticable to sample soils during such periods.
- (iv) The overwhelming proportion of Au in natural soils occurs as sub-micron particles. These are not able to be isolated and physically examined with optical or electron microscopic techniques. Research in these projects suggests that some Au may occur as chemical complexes, e.g., with organic matter.

In general, the distribution and chemistry of trace elements in soils is most effectively investigated using wet chemical techniques such as selective extraction or incubation. Though it is generally recognized that such techniques may not provide absolute answers, they may provide very useful insights into the chemistry of elements in soils. Specific extraction methods were developed for the investigation of Au soil chemistry in Project P241, as described in Gray *et al.* (1990) and Gray (1990b), and have been developed further as described in this report. These methods have been designed so as to test the solubility of the Au in soils. This solubility can be related to (at least) two factors:

- (i) accessibility of the Au to dissolution by ligands in solution;
- (ii) capacity of the soil to readsorb any dissolved Au.

The accessibility of Au is determined by several factors, including grain size, degree of encapsulation, chemical form, and scavenging properties of the soil. The most soluble Au probably occurs as organic complexes, colloids or even as extremely fine grains, whereas the least soluble Au is likely to be as coarse, encapsulated grains. The capacity of the soil for readsorption will depend on factors that may include the properties of soil surfaces, presence of organisms able to precipitate Au and the soil solution pH. Thus, the results of extraction experiments cannot absolutely determine the form of Au present in the soil, but may provide useful information on the processes involved in dispersion of Au from the primary source. In addition, the chemistry of Au in soils can be compared with that in other regolith materials such as laterite or saprolite.

2 EXPERIMENTAL PHILOSOPHY

Previous experiments (Gray et al., 1990) indicated that various weak Au extractants, and, in particular, a buffered iodide solution could extract significant quantities of Au from carbonate-rich soils. In addition, significantly more Au was extracted from coarse jaw-crushed material than from finely pulverized samples. These results suggest that this readily extractable Au is associated with surfaces or otherwise accessible to solution, rather than being within minerals or occluded, and that in the pulverized samples Au dissolved by iodide can then be readsorbed by soil constituents. Indeed, previous work has indicated that Au iodide is adsorbed by a number of different regolith samples (Gray, 1990b). This can be conceptually viewed as an equilibrium between Au₀ (the Au in its original form), Au₁ (Au dissolved by iodide) and Au₈ (dissolved Au readsorbed during the extraction process):

$$Au_0 \longrightarrow Au_I \longrightarrow Au_s$$
 ...(1)

The measured dissolved Au (Au_I) only gives an indication of the amount of Au in solution at one time, rather than the total extractable Au. In this report, this will be denoted as <u>net iodide</u> (or net water) soluble Au. It may be that by pulverizing the soils, other surfaces (e.g., Fe oxides) are exposed that are more efficient at sorbing Au from solution than the phases forming surfaces in unpulverized samples. As incubation experiments (Gray et al., 1990) indicate that carbonate minerals are the most accessible to solution, this suggests that the carbonate minerals are very poor at sorbing Au.

Such hypotheses can be further tested by a method that measures the <u>total</u> amount of Au that has been dissolved, rather than that in solution at any particular time. This is done by performing standard extractions as described in Section 3.2, except that reagent conditions are changed so that the total Au dissolved over the time period could be determined; this includes any dissolved Au iodide that under normal conditions would react with other soil surfaces:

$$Au_{o} \xrightarrow{} Au_{I} \xrightarrow{} Au_{S} \qquad ...(2)$$
Gross soluble Au

This total dissolved Au is denoted as gross soluble Au, and can be compared with net soluble Au. Differences in the extraction by the two procedures indicate the scavenging capabilities of the soil. The two techniques indicate the potential mobility and dispersion of Au in the soil and are therefore expected to be useful in distinguishing differing Au chemistries in differing regolith material. However, as the gross soluble Au method was developed late in the project, it has only been used for a limited number of samples, and most data are for net soluble Au.

3 MATERIALS AND METHODS

3.1 Site locations and sample treatments

Soil and regolith samples used for the investigations described here were taken from the Mt. Hope, Beasley Creek, Panglo, Mt. Percy, Mulline, Lights of Israel, Zuleika, Mulgarrie and Granny Smith Au deposits. These sites provide a broad geographical range of the southern Yilgarn craton, with two (Granny Smith and Beasley Creek) north of the Menzies Line (Figure 1).

Samples were from a variety of sources, including pits, hand and mechanical auger, RAB and RC cuttings and diamond drill core. Samples were commonly prepared either by jaw crushing to < 10 mm (denoted as coarse) and/or by pulverizing to < 75 μm (denoted as fine). The terms coarse and fine have this meaning throughout the report.

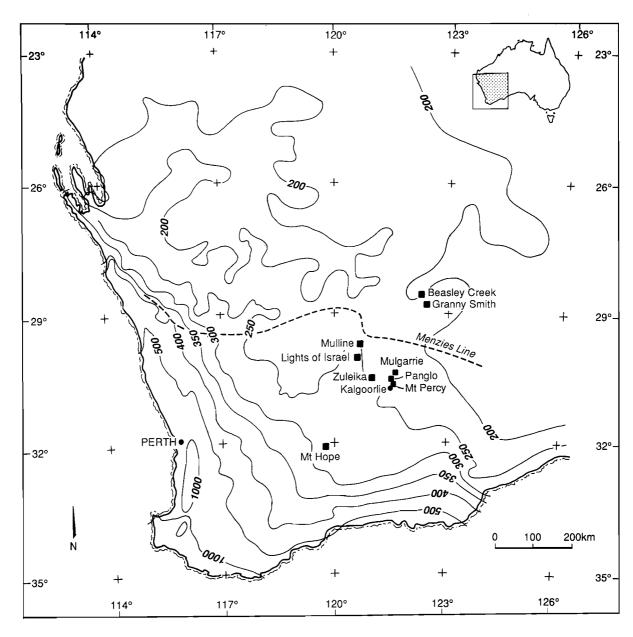


Figure 1: Location of investigation sites, with rainfall (mm) isobars.

3.2 Methods

Specific extraction solutions used were deionized water and an iodide reagent, which consisted of 1 mole/litre ($\underline{\mathbf{M}}$) sodium bicarbonate / 0.1 $\underline{\mathbf{M}}$ potassium iodide, saturated with CO_2 and taken to pH 7.5 with hydrochloric acid. A soil:solution ratio of 1:2 was used with the mixtures extracted in a 125 mL plastic bottle on a bottle roller. Extractions were done for 24 hr, unless otherwise noted in the text. Gross soluble Au was determined using a modification of the extraction procedure. Solutions were centrifuged (4000 rpm, 15 minutes) and analysed by inductively coupled plasma - mass spectroscopy.

4 "SIMPLE" CARBONATE-DOMINATED SOILS

4.1 Introduction

Previous work (Lintern, 1989; Gray et al., 1990) suggested that Au:Ca correlations and high proportions of net iodide-soluble Au are characteristics of carbonate-dominated soils. This has been tested by iodide extractions of soils from Mt. Hope, Panglo and Lights of Israel, which all show clear Au:Ca correlations, in order to obtain a regional understanding of Au chemistry in such soils.

4.2 Mt. Hope

4.2.1 Site description

The Mt. Hope Au deposit (Lintern, 1989) is located 115 km SSE of Southern Cross, in the Forrestania region (Figure 1). Three soil profiles (A, B and C) were selected for intensive study. Profiles A and B are both calcareous, consisting, predominantly, of deep, kaolinite clay infused near the surface with pedogenic carbonate. The close correspondence in molar concentrations of Ca and Mg in Profiles A and B (Figures 2a and 9a) suggests that the major carbonate mineral is dolomite, as confirmed by XRD analysis. Profile A is situated directly over known mineralization, whereas Profile B is on the hanging wall, within 5 m of mineralization. In these carbonate-rich profiles, there was a close association of Au with pedogenic carbonate (Lintern, 1989; also see Figures 2a and 9a). Profile C is a non-calcareous lateritic soil consisting of ferruginous nodules within a sandy matrix, and is within 400 m of the principal zone of mineralization but mineralized quartz stringers may underlie this site. The profile has very low Ca and Mg concentrations (Figure 12a).

4.2.2 Profile A (carbonate-rich)

Profile A lies directly over mineralization and has a high Au content (1000 - 4000 ppb; Figure 2a). The proportion of net iodide-soluble Au is low, particularly for fine material (3 - 4%; Figure 2b), whereas gross iodide-soluble Au is about 50% of total Au in fine material and 30% in coarse material when extracted for 30 days or more (Figures 3 - 5). The higher solubility of Au from fine material may reflect Au that is occluded from solution in natural conditions. The proportion of net iodide-soluble Au is much lower in the upper two samples (Figures 3 and 4), possibly due to readsorption by organic matter (1% and 0.6% organic matter - samples 04-1467 and 04-1468, respectively). This suggestion is consistent with previous work on the net water solubility of Au (Gray et al., 1990), supplemented by recent determinations of gross water-soluble Au (Figures 6 - 8). Thus, both of these "organic" samples have comparable proportions of gross water-soluble Au to the deeper, less organic and more calcareous, sample (04-1470; 0.2% organic carbon) but their net water-soluble Au declines over time, presumably due to sorption, whereas for the calcareous sample net water-soluble Au slowly increases.

Gross water-soluble Au concentrations up to 150 ppb (about 5% of the total Au; Figure 12) are observed, indicating very high potential solubility in this soil. In comparison, the highest groundwater anomaly observed by one of the authors in the Yilgarn block (Gray, 1992, 1993) is 4 ppb, suggesting that Au mobility is potentially higher in soil than in the deeper regolith.

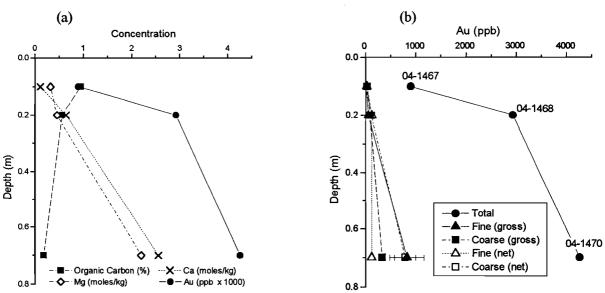


Figure 2: Depth distributions in Profile A, Mt. Hope: (a) Organic carbon, Mg, Ca and Au; (b) Total Au and iodide-soluble Au (where error bars are shown duplicate samples were used).

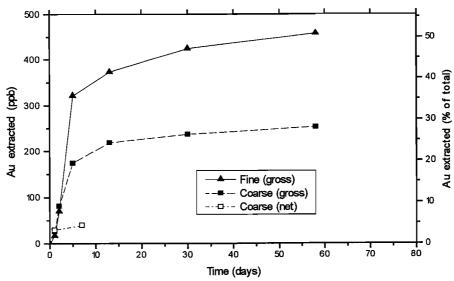


Figure 3: Iodide-soluble Au in organic-rich sample, Mt. Hope Profile A (04-1467).

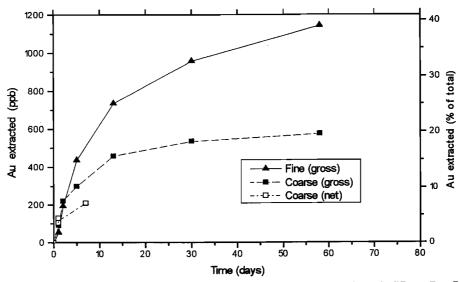


Figure 4: Iodide-soluble Au in moderately calcareous (3.6% CaO) sample, Mt. Hope Profile A (04-1468).

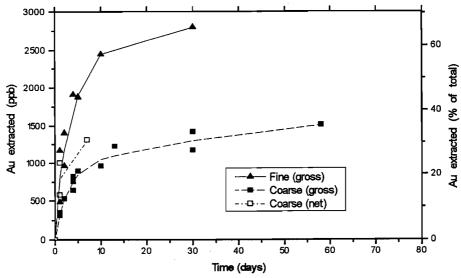


Figure 5: Iodide-soluble Au in carbonate-rich (14.2% CaO) sample, Mt. Hope Profile A (04-1470).

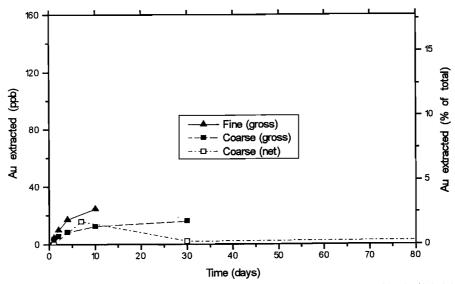


Figure 6: Water-soluble Au in organic-rich sample, Mt. Hope Profile A (04-1467).

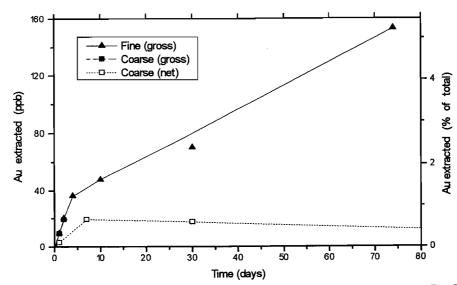


Figure 7: Water-soluble Au in moderately calcareous (3.6% CaO) sample, Mt. Hope Profile A (04-1468).

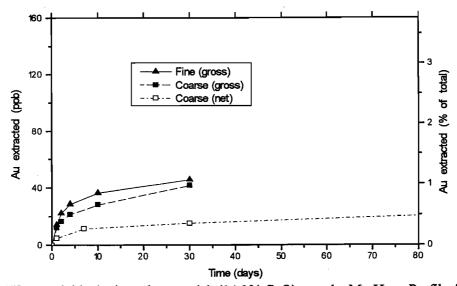


Figure 8: Water-soluble Au in carbonate-rich (14.2% CaO) sample, Mt. Hope Profile A (04-1470).

4.2.3 Profile B (carbonate-rich)

A more extensive sample set was investigated for Profile B and the correlation of total Au with Ca and Mg is clearly demonstrated (Figure 9a). Net iodide-soluble Au comprises about 15% of total Au for fine material and about 30% for coarse material, indicating significant amounts of the Au are present in soluble form and accessible to solution. The solubility of Au is greater in Profile B than in Profile A. Virtually all of the Au in fine material from carbonate-rich sample 04-1206 (Figure 10, with position of sample shown in Figure 9b) is gross iodide-soluble after 10 days, whereas 15% of the Au in the coarse material remains insoluble, suggesting this fraction to be occluded. However, the proportion of net iodide-soluble Au in the fine material is only about 10% that of the coarse material, indicating specific readsorption of the extracted Au. Initially, Au dissolved at a similar rate to the other treatments, but, after one day, net iodide-soluble Au decreased, reaching a constant, low, concentration. When fresh iodide reagent is added, more Au is dissolved, indicating a shift from adsorbed Au to dissolved Au (see Section 2 for further discussion).

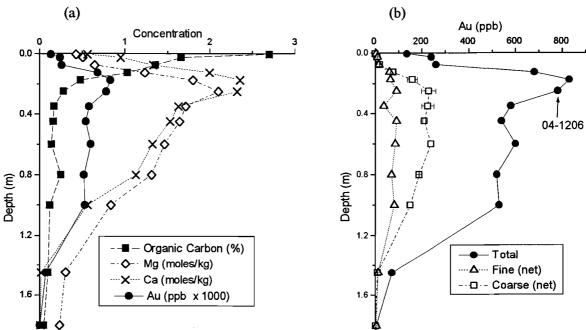


Figure 9: Depth distributions in Profile B, Mt. Hope: (a) Organic carbon, Mg, Ca and Au; (b) Total Au and net iodide-soluble Au (errors determined for extractions of coarse materials only).

The striking difference between coarse and fine material suggests that pulverizing exposes fresh surfaces capable of adsorbing Au, whereas the surfaces exposed to solution in uncrushed carbonate soils are very poor at precipitating Au iodide. The poor ability of carbonates to adsorb Au was noted previously (Gray et al., 1990; Gray, 1990b).

Even deionized water is an effective extractant for Au for carbonate-rich sample 04-1206. The proportion of gross water-soluble Au is greater than 10% for the fine material, and expected to be about 8% for the coarse sample, over 70 days (Figure 11). As with the iodide extractions, this is higher than the proportion of water-soluble Au for the samples from Profile A.

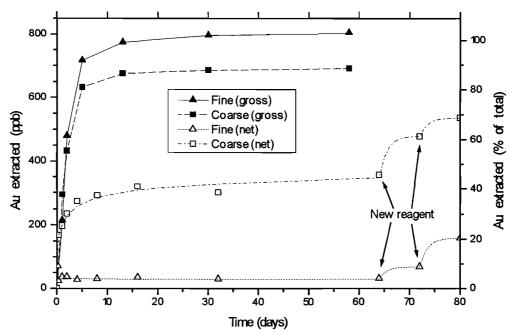


Figure 10: Iodide-soluble Au in carbonate-rich (13% CaO) sample, Mt. Hope Profile B (04-1206).

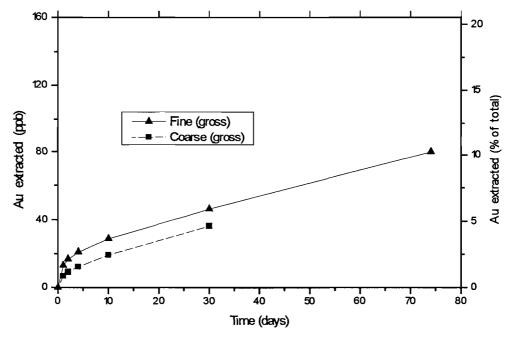


Figure 11: Water-soluble Au in carbonate-rich (13% CaO) sample, Mt. Hope Profile B (04-1206).

4.2.4 Profile C (Fe oxide-rich)

The Au distribution in the ferruginous Profile C differs significantly from that in the carbonate-rich Profile B. Gold contents are approximately constant, at about 200 ppb, down to 0.7 m, and then increase sharply with depth (Figure 12a). There is little correlation between Au and either organic carbon or Fe content. Net iodide-soluble Au is low (< 5% total Au) for both fine and coarse materials (Figure 12b), indicating a significant difference between ferruginous and calcareous soils.

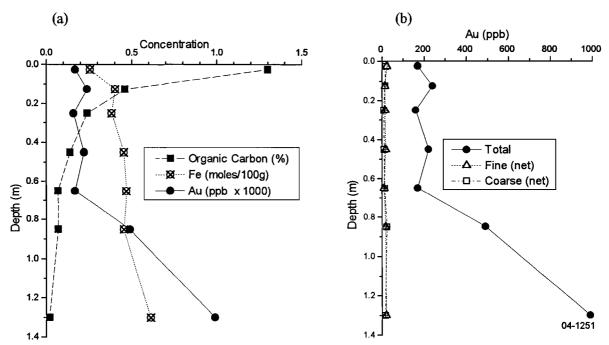


Figure 12: Depth distributions in Profile C, Mt. Hope: (a) Organic carbon, Fe and Au; (b) Total Au and net iodide-soluble Au.

The low net iodide solubility of Au in samples from this profile is due largely to reprecipitation of dissolved Au. Thus, for Fe oxide-rich sample 04-1251 (position shown on Figure 12b), gross iodide-soluble Au (Figure 13), although much lower than in the carbonate-rich sample 04-1206 (Figure 10), is about four times higher than net iodide-soluble Au for the coarse material. The fine material behaves similarly to carbonate-rich samples, with initial dissolution at a similar rate to the other treatments, followed by a fall in dissolved Au after one day. The proportion of net iodide-soluble Au is very low, about 1% of the total Au, indicating strong sorption, particularly when the soil is pulverized to less than $75~\mu m$.

The amount of gross water-soluble Au is considerably less in the Fe oxide-rich sample from Profile C (04-1251; Figure 14) than in the carbonate-rich sample from Profile B (04-1206; Figure 11), suggesting lower mobility of Au in the ferruginous sample.

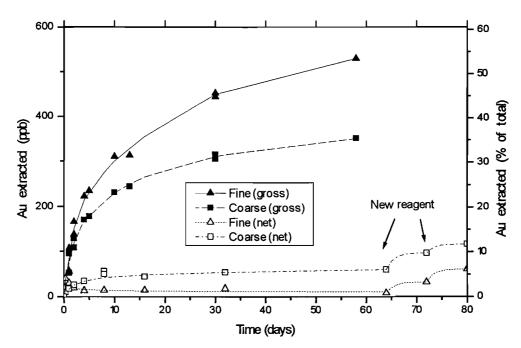


Figure 13: Iodide-soluble Au in Fe oxide-rich sample, Mt. Hope Profile C (04-1251).

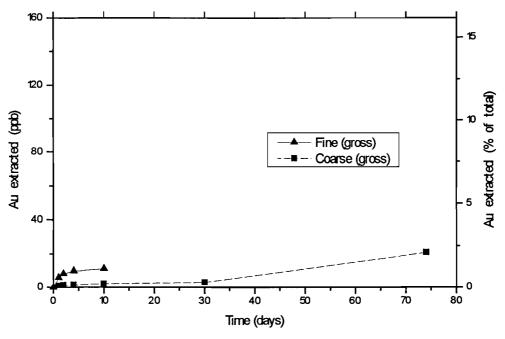


Figure 14: Water-soluble Au in Fe oxide-rich sample, Mt. Hope Profile C (04-1251).

4.2.5 35800N Traverse

Data for a traverse of 0-1 m soil composites on line 35800N (Lintern, 1989) indicate that the Au:Ca association occurs laterally as well as vertically. Thus, Ca, total Au and soluble Au are all correlated, with net iodide-soluble Au in coarse material being greater than in fine material (Figure 15). This is the same as observed in the soil profiles.

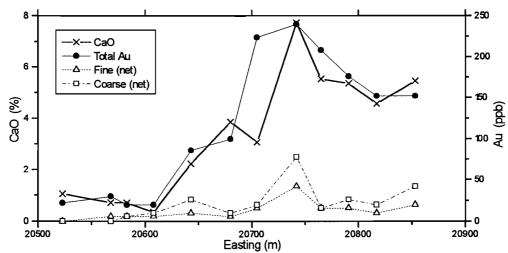


Figure 15: Calcium, total Au and net iodide-soluble Au in 0-1 m soil composites from line 35800N, Mt. Hope.

4.2.6 Summary

Carbonate-rich soils at Mt. Hope show similar behaviours, in particular that net iodide-soluble Au is:

- (i) very low in the organic horizon (0 0.2 m);
- (ii) greatest in the carbonate-rich horizon;
- (iii) greater in coarse samples.

Mobility of Au is considerably lower in ferruginous soil, due, at least partially, to a strong ability of soil surfaces to adsorb Au. These results imply that a significant proportion of the Au in carbonate horizons is soluble and accessible to solution. Net solubility is reduced when other minerals, which are presumably coated or otherwise occluded in "natural" soil, are exposed by pulverizing and therefore able to adsorb dissolved Au.

The proportion of soluble Au in Profile A (directly above mineralization) is lower than in Profile B (adjacent to mineralization). This is consistent with results from other sites (Section 6.2.2), and could indicate a greater proportion of primary or coarse Au in Profile A.

4.3 Panglo

4.3.1 Site description

The Panglo gold deposit is located some 30 km north of Kalgoorlie (Figure 1). Iodide extractions were done on 0-1 m composites and for three profiles of the trench on traverse 3700N (Lintern and Scott, 1990; Figure 16):

Profile A: transported gravels and clays in a Tertiary palaeochannel, consisting principally of ferruginous pisoliths and nodules and some lithic fragments, permeated and cemented by pedogenic carbonate in the top metre;

Profile B: thin, poorly developed soil overlying ferruginous and bleached mafic saprolite, partially cemented by carbonate;

Profile C: sediments in the present drainage channel, dominated by clays and quartz.

Profiles A and B directly overlie the southern limits of the known mineralization.

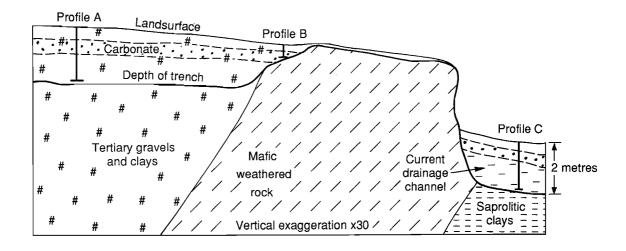


Figure 16: Section through part of the trench at 3700N, Panglo Au deposit, showing position of profiles and depth of trench.

4.3.2 Profile A (carbonate-rich)

The distributions of Ca and Au in Profile A (Figure 17a) resemble those in Profile B at Mt Hope (Section 4.2.3); in addition, net iodide-soluble Au is correlated with Ca (Figure 17b) and Au. However, results differ from Mt. Hope in that both the fine and coarse materials had similar values of net iodide-soluble Au, suggesting that there was not such a major effect of surfaces exposed by grinding.

Detailed kinetic tests on a carbonate-rich sample from this profile (04-2092; Figure 18, with position shown in Figure 17b), indicate very similar Au solubility behaviour to the carbonate-rich sample 04-1206 from Mt. Hope (Figure 10). In particular, gross iodide Au solubility was virtually 100% of the total Au in the fine material after 10 days, with a lesser solubility in the coarse material. The difference in net iodide-soluble Au between fine and coarse material was not as marked as at Mt. Hope, again suggesting lesser sorption by surfaces exposed by grinding.

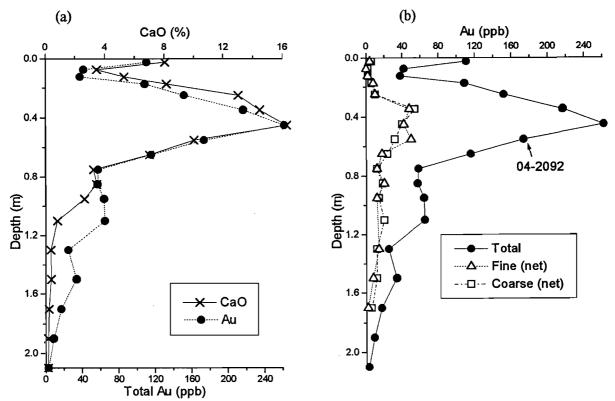


Figure 17: Depth distributions in Profile A, Panglo: (a) Ca and Au; (b) Total Au and net iodide-soluble Au.

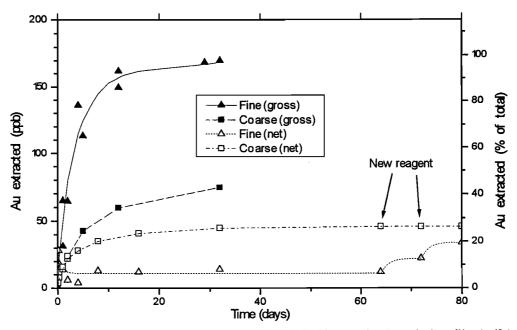


Figure 18: Iodide-soluble Au in carbonate-rich (10% CaO) sample, Panglo Profile A (04-2092).

4.3.3 Profile B (mafic saprolite)

Most of the carbonate in Profile B occurs as carbonate coatings or in cracks (Lintern and Scott, 1990). Neither total nor net iodide-soluble Au appear to be correlated with Ca (Figures 19a and 19b). This may be due to the carbonate being present as hard segregations rather than as friable particles, as in previously described carbonate-rich profiles. Net iodide-soluble Au is considerably less in the fine materials, perhaps due to sorption by surfaces of the ferruginous saprolite that have been exposed by grinding.

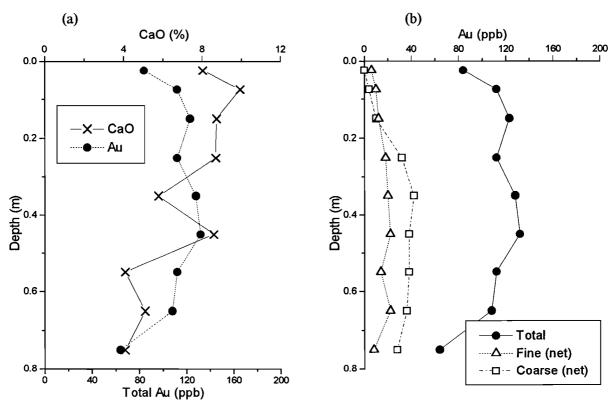


Figure 19: Depth distributions in Profile B, Panglo: (a) Ca and Au; (b) Total Au and net iodide-soluble Au.

4.3.4 Profile C (drainage sediments)

Carbonate is a minor constituent of Profile C (Figure 20a); Ca and Mg are associated with minor calcite, gypsum and fragments of mafic volcanic rocks. There is no correlation between Ca and Au in the profile. Net iodide-soluble Au is about 20 - 30% total Au (Figure 25b). This may reflect specific Au chemistry in drainage channel samples, though further tests on such materials are required to delineate the specific interactions in such soils. One possible explanation is that Au has been precipitated in the soil by a similar mechanism as elsewhere but Ca concentration is retarded by the presence of acid groundwaters (Gray, 1990a); this site is low in the landscape and the water-table is close to the surface (Figure 16). Thus, this may represent a situation where the Au:Ca association does not hold (due to the removal of Ca by acid conditions) even though the mechanism for Au distribution in the profile may be similar to that in other profiles.

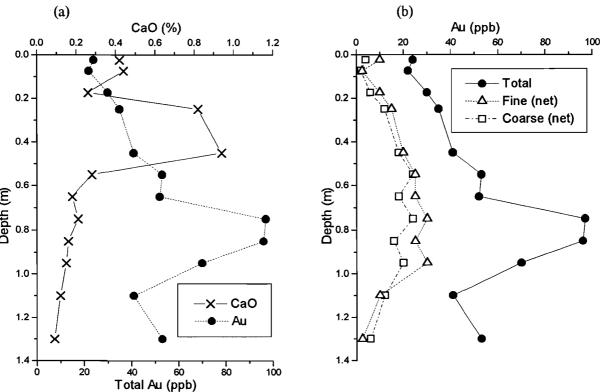


Figure 20: Depth distributions in Ca and Au in Profile C, Panglo: (a) Ca and Au; (b) Total Au and net iodide-soluble Au.

4.3.5 3700N Traverse

Net iodide-soluble Au determinations for 0-1 m composites across the 3700N trench (Figures 21 and 22) show that net iodide-soluble Au is about 20% of the total Au in fine material (Figure 21), both for the Ca-rich soils west of 2500E and for the Ca-poor samples from the drainage channel, suggesting Au to have similar chemistries in both materials. Data for coarse material (Figure 22) suggest that net iodide-soluble Au may even be higher for the drainage channel samples. These results are consistent with the suggestion that Au has been precipitated in the soil by a similar mechanism as elsewhere but Ca concentrations are low because of acid groundwaters.

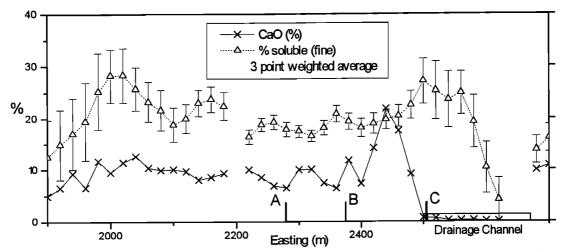


Figure 21: Ca concentration and weighted averages for percentage net iodide-soluble Au from fine samples of 0-1 m composites across the 3700N traverse, Panglo. Positions of Profiles A - C and the drainage channel are also shown.

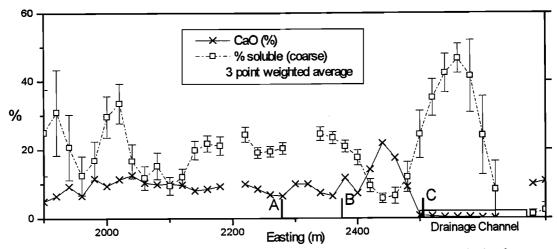


Figure 22: Ca concentration and weighted averages for percentage net iodide-soluble Au from coarse samples of 0-1 m composites across the 3700N traverse, Panglo. Positions of Profiles A - C and the drainage channel are also shown.

4.4 Lights of Israel

This site lies about 2 km northeast of Davyhurst (Figure 1) and has strongly calcareous soils (Robertson and Tenhaeff, 1992). Net iodide-soluble Au was determined in pulverized ditchwitch samples from the top 1 m. As with carbonate-rich soils at Mt. Hope and Panglo (Sections 4.2 and 4.3), there is a very close correlation between total and soluble Au ($r^2 = 0.95$; Figure 23) and a similar trend to Ca (Figure 24).

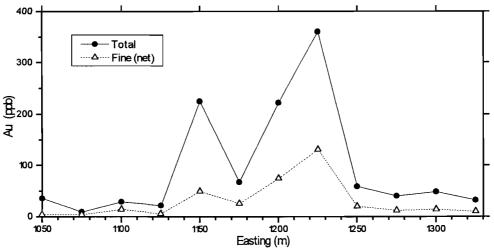


Figure 23: Total Au and net iodide-soluble Au in soil from line 1200N, Lights of Israel.

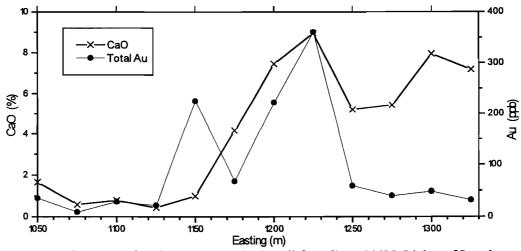


Figure 24: Calcium and total Au in soil from line 1200N, Lights of Israel.

4.5 Summary

The three sites Mt. Hope, Panglo and Lights of Israel all contain profiles dominated by friable, pedogenic, carbonate with clearly observable correlations between Ca and Au. In these soils net iodide-soluble Au is about 30% of total Au, with gross iodide-soluble Au in some cases being virtually all of the Au. This indicates that the Au associated with carbonate in these soils is potentially highly soluble, and that the mechanism for the Au:carbonate association is not primarily chemical. The reduced net iodide solubility of Au in fine materials suggests that surfaces exposed by grinding are more effective at readsorbing Au than the *in situ* soil surfaces.

Ferruginous soils have lower Au solubilities, due to lesser gross solubilities, and to enhanced readsorption of dissolved Au, especially when pulverized. Enhanced sorption of Au is also observed for the upper organic horizon in the top 0.2 m.

5 "COMPLEX" SOIL PROFILES

5.1 Introduction

"Simple" soil profiles have been defined (Section 4) as those profiles whose Au geochemistries are dominated by association with one mineral e.g., pedogenic carbonate or Fe oxides. Where association with more than one mineral is found to affect the distribution of Au, the profile is termed "complex". This situation prevails at Mt. Percy and Mulline, where lateritic gravels have been infused with carbonate. Extraction techniques assist in the understanding of the multiple associations of Au in these profiles.

5.2 Mt. Percy

Mt. Percy is 2 km north of Kalgoorlie (Figure 1). There is an extensive database on Au and other elements across two traverses, related to geology and weathering processes (Butt, 1991). Extractions were carried out on selected samples from a west-east section, down to 80 m depth (Figure 25). At the surface, there is a change from lateritic duricrust in the west (containing up to 75% Fe₂O₃; Figure 26), to calcareous soil with abundant lateritic nodules in the east (up to 20% CaO; Figure 27). Gold concentration is highly variable (Figure 28), but much appears to be associated with the carbonates.

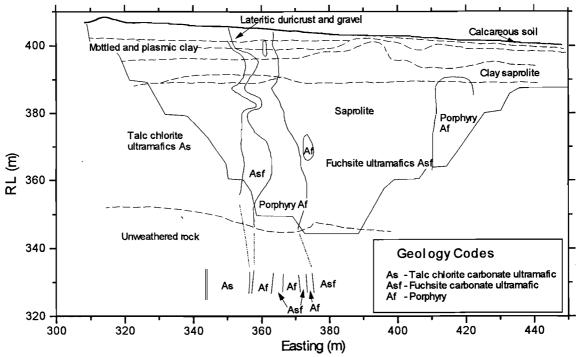


Figure 25: Geology and weathering profile of Mt. Percy section 15850N.

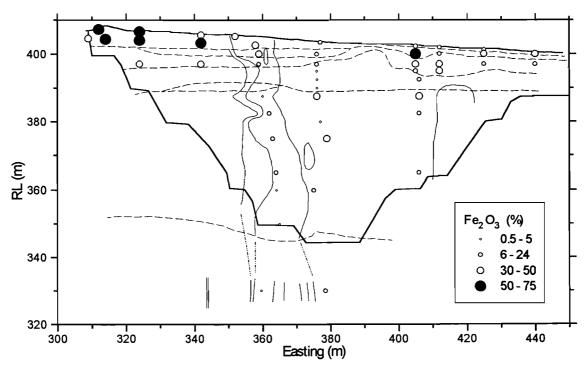


Figure 26: Fe concentration in selected samples from Mt. Percy section 15850N.

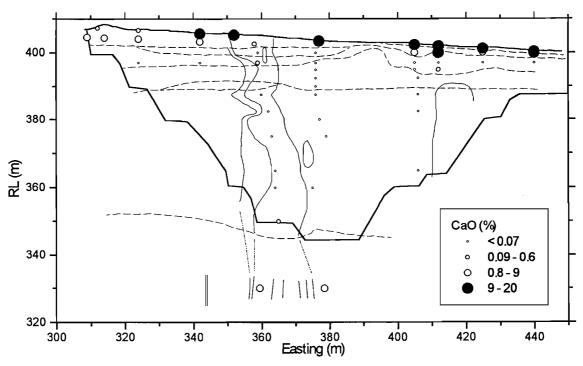


Figure 27: Ca concentrations in selected samples from Mt. Percy section 15850N.

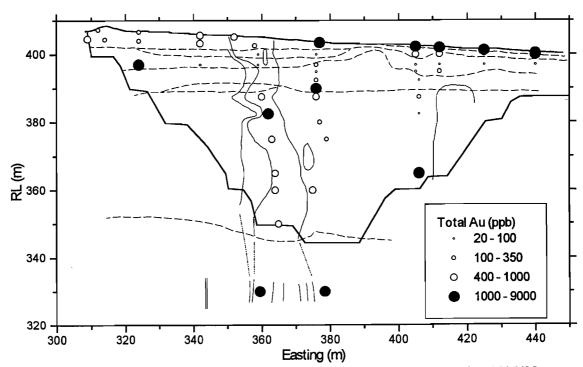


Figure 28: Au concentrations in selected samples from Mt. Percy section 15850N.

Net iodide-soluble Au determinations indicate that, at Mt. Percy, like Panglo but unlike Mt. Hope, the proportions of net iodide-soluble Au is similar in fine and coarse materials (Figure 29). For calcareous soil samples, about 10 - 30% of the total Au was extracted, whereas the Ca-poor samples, even when Au-rich, had very low net iodide-soluble Au (Figure 30); indeed soluble Au and Ca concentrations show a general correlation. The distributions of Ca (Figure 27) and net iodide-soluble Au in fine (Figure 31) and coarse (Figure 32) materials are very similar.

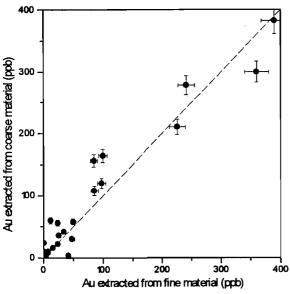


Figure 29: Net iodide-soluble Au from coarse vs. fine regolith from Mt. Percy.

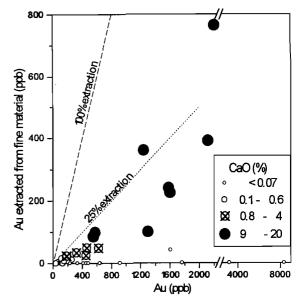


Figure 30: Net iodide-soluble Au for fine material vs. total Au, with respect to Ca concentration, for regolith from Mt. Percy.

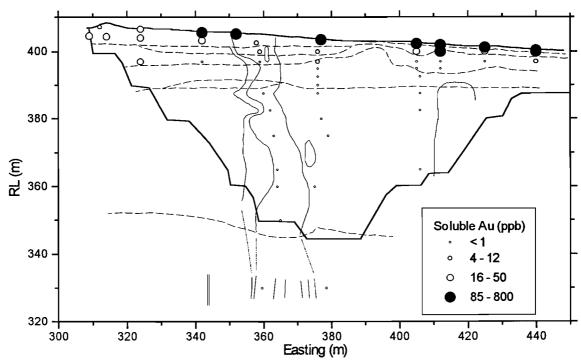


Figure 31: Net iodide-soluble Au in fine materials from Mt. Percy section 15850N

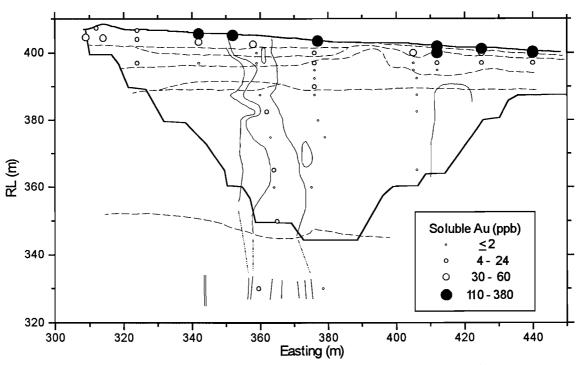


Figure 32: Net iodide-soluble Au in coarse materials from Mt. Percy section 15850N

Net iodide-soluble Au is very low in regolith below the carbonate horizon and in the underlying unweathered rock. This is observed even in carbonate-rich unweathered rocks, suggesting that high proportions of soluble Au associated with carbonate is a specific property of soils.

Although there is no correlation between total Au and Ca when all samples are included, there is a good correlation between soil carbonate and net iodide-soluble Au. This is consistent with results for "simple" calcareous soils (Section 4) indicating that high net iodide-soluble Au concentrations are characteristic of carbonate soils, even where total Au is also related to other factors, such as Fe oxides.

5.3 Mulline

5.3.1 Site description

Mulline is about 50 km west of Menzies and close to the Menzies line (Figure 1). The soil samples tested were from a trench at the Peach Tree Au deposit (Lintern and Butt, 1991; Figure 33), which contained several distinct soil horizons:

- (i) Sandy calcareous loam with Fe-rich nodules;
- (ii) Calcareous loam and carbonate nodules;
- (iii) Pseudo-bedded calcrete and ferruginous pisoliths.

In addition, a "bar" of massive, strongly indurated carbonate cross-cuts the trench. The bar may reflect a Ca-rich rock (i.e., carbonate alteration) and hence represent the source unit for much of the pedogenic carbonate. The trench can also be viewed as 4 soil profiles (Figure 33) which can be examined separately, in a similar manner to other sites (Sections 4.2 and 4.3).

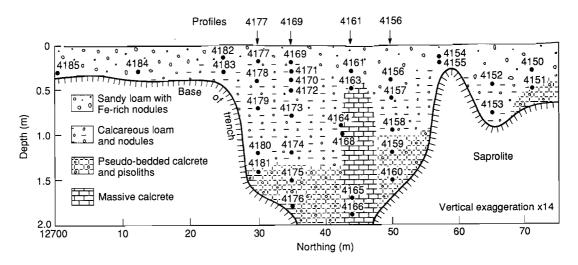


Figure 33: Section of the trench at Mulline showing pedology and locations of samples.

5.3.2 Results for the trench at Mulline

Calcium concentrations (Figure 34) are highest for the calcareous loam and within the massive calcrete. However, as observed at Mt. Percy, total Au concentration (Figure 35) bears no clear relationship with Ca. Lintern and Butt (1991) suggested that Au may be correlated with Ca in the top 0.5 m of the soil and then with Fe at depth. This is supported by the extraction results: for both fine (Figure 36) and coarse (Figure 37) material, the calcareous loam has the highest net iodide-soluble Au. Thus, the poor correlation of total Au with Ca and the good correlation of iodide-soluble Au with Ca for the entire profile matches the conclusions drawn at Mt. Percy.

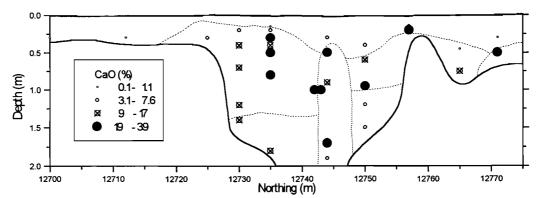


Figure 34: Ca distribution in the trench at Mulline.

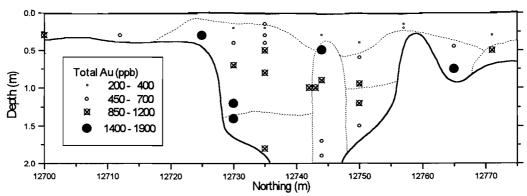


Figure 35: Total Au distribution in the trench at Mulline.

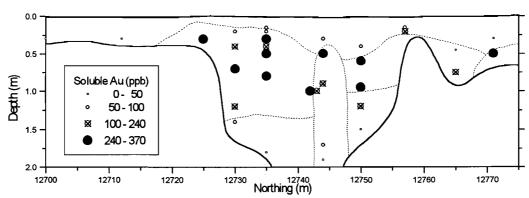


Figure 36: Net iodide-soluble Au distribution of fine material in the trench at Mulline.

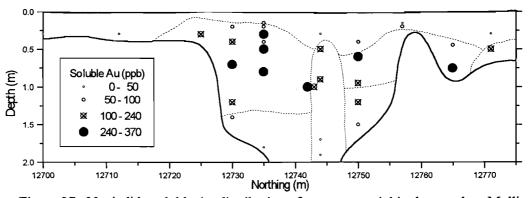


Figure 37: Net iodide-soluble Au distribution of coarse material in the trench at Mulline.

5.3.3 Results for individual profiles

This correlation of net iodide-soluble Au with Ca is also demonstrated by examining the individual profiles (Figures 38 - 41), the locations of which are shown in Figure 33. The correlation between Ca and total Au for each of the profiles is generally poor, although the data are generally consistent with an association between total Au and Ca in the top 1 m. However, there is a better correlation between net iodide-soluble Au and Ca, with the exception of Profile 4161. In this profile, Au solubility is very low below 1 m depth, despite an increased Ca concentration. This is possibly due to Ca in the deeper samples of profile 4161 being present in massive, rather than friable, carbonate (Figure 33). This matches results for Panglo Profile B (Section 4.3.3; Figure 19), which also showed low net iodide-soluble Au concentration in the presence of indurated carbonate. The data thus strongly support the hypothesis that net iodide-soluble Au is a measure of Au associated with friable, pedogenic carbonate, even in complex profiles with Au distribution controlled by two or more minerals.

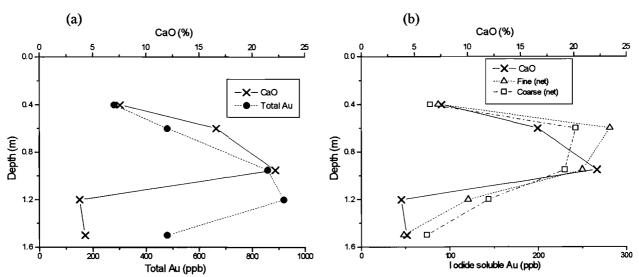


Figure 38: Depth distributions for Profile 4156, Mulline: (a) Ca and total Au; (b) Ca and net iodide-soluble Au.

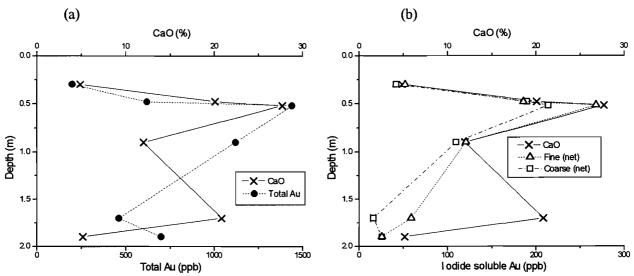


Figure 39: Depth distributions for Profile 4161, Mulline: (a) Ca and total Au; (b) Ca and net iodide-soluble Au.

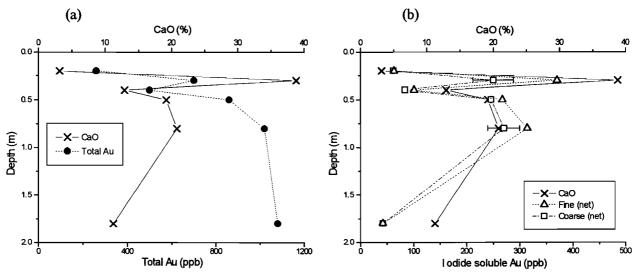


Figure 40: Depth distributions for Profile 4169, Mulline: (a) Ca and total Au; (b) Ca and net iodide-soluble Au.

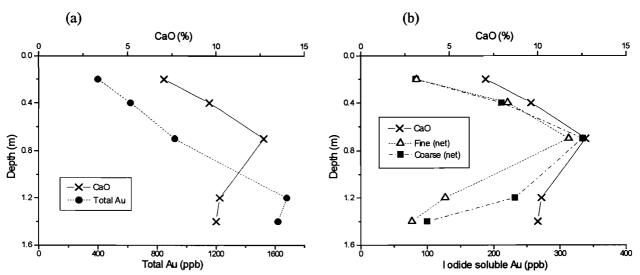


Figure 41: Depth distributions for Profile 4177, Mulline: (a) Ca and total Au; (b) Ca and net iodide-soluble Au.

5.3.4 Kinetic studies

Kinetic studies of iodide Au solubility of calcareous and ferruginous samples (4171 and 4176 in Figure 33) indicate similar features to analogous samples from Mt. Hope (Section 4.2) and Panglo (Section 4.3). Thus, net iodide solubility of Au in the carbonate-dominated sample (4171; Figure 42) reached about 50% of total Au after about 5 days, with gross iodide solubility expected to be higher than this. In comparison, even gross iodide-soluble Au is only 30% of total Au in the Fe oxide-dominated sample after one month (4176; Figure 43), with net iodide-soluble Au only about 5% of total Au after 2 months, demonstrating much lower Au solubility.

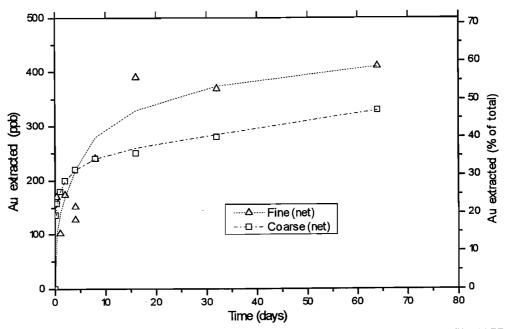


Figure 42: Iodide-soluble Au in carbonate-rich sample (4171), Mulline Profile 4177.

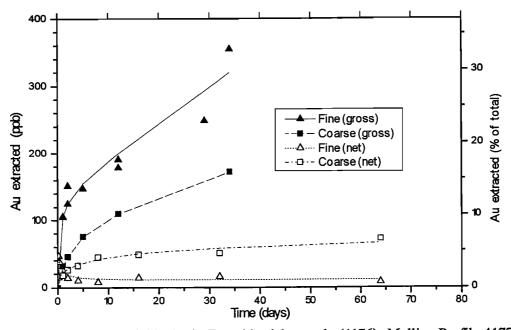


Figure 43: Iodide-soluble Au in Fe oxide-rich sample (4176), Mulline Profile 4177.

5.4 Summary

Results from Mt. Percy and Mulline suggest that the good correlation observed between Ca and net iodide-soluble Au for "simple" carbonate-dominated soils is also observed in environments where total Au and Ca are not correlated. Thus, this extraction technique enables delineation of associations that are not clear from elemental abundances alone. The data also further demonstrate the particularly high solubility of Au in friable carbonate soils, indicating that this carbonate occurs in an environment where Au is being precipitated in a form that is easily redissolved.

6 PALAEOCHANNEL SITES

6.1 Introduction

Palaeochannels are ancient fluvial features that have since become filled with transported sediments. Their presence is not easily detected and the course they follow is often poorly defined, even after drilling. Substantial Au deposits are associated with some palaeochannels but they present a special problem for exploration because they are usually overlain with several metres of barren material, although surficial anomalies have been reported directly above the buried mineralization. Work has been undertaken to seek to understand the chemistry of Au in soils overlying such deposits; such an understanding may lead to improved detection techniques.

6.2 Mulgarrie

6.2.1 Site description

The Mulgarrie Au deposit is located 40 km north of Kalgoorlie (Figure 1), with the area investigated being a traverse from outcropping Au mineralization in mafic and ultramafic rocks through to a palaeochannel infilled with about 35 m of barren sediments (Gray, 1992; Figure 44). Net iodide-soluble Au was determined for samples primarily from three drill holes (MC500, MC505 and MC529) located across the traverse. Common with many sites south of the Menzies Line, total Au in the soil is associated with carbonate (Figure 44). The origin of anomalous Au values in the soil above the palaeochannel mineralization, however, is equivocal because the Au may have originated from adjacent, residual soils up-slope, particularly for Profile MC500, which is close to outcropping mineralization.

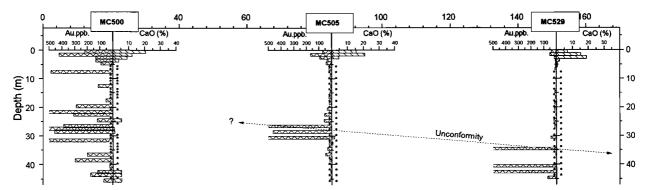


Figure 44: Au and Ca distributions for the Mulgarrie section. The dotted line is the interpolated unconformity between drainage sediments and Archaean material. The stars indicate that the interval was not analysed.

6.2.2 Soil profiles

For the upper carbonate-rich zone of profile MC500, which is close to outcrop (Figure 44), net iodide-soluble Au is less than 15% of the total Au (Figure 45), suggesting that the soil has a large proportion of detrital primary Au. In contrast, 20 to 60% of the Au from the upper zone in MC529, within the palaeochannel, is net iodide-soluble for both coarse and fine samples (Figure 46), indicating that much of the Au in this zone is highly mobile. Indeed, the absolute values of net iodide-soluble Au are similar in both profiles, despite total Au being 5 - 10 times lower in profile MC529.

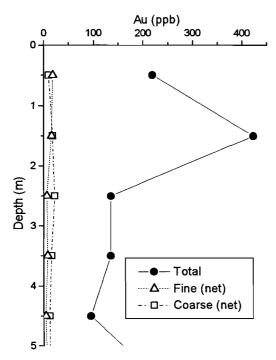


Figure 45: Distribution of total and net iodidesoluble Au in Mulgarrie profile MC500 (close to outcrop of lode mineralization).

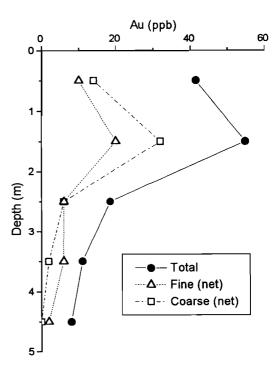


Figure 46: Distribution of total and net iodidesoluble Au in Mulgarrie profile MC529 (above secondary mineralization in palaeochannel)

6.2.3 Saprolite and rock.

Below the carbonate-rich surficial zone, Au generally has a low extractability (Figure 47a), consistent with observations at Mt. Percy. This is also supported by kinetic investigations of a saprolite sample (04-4176, Figure 48) in which net iodide-soluble is very low. However, net iodide-soluble Au does occur at 22 - 24m in the palaeochannel, where up to 37 % of Au in coarse material, and 93% of Au in the fine material was dissolved from a Mn-rich zone (Figure 47b; discussed further in Section 6.2.4).

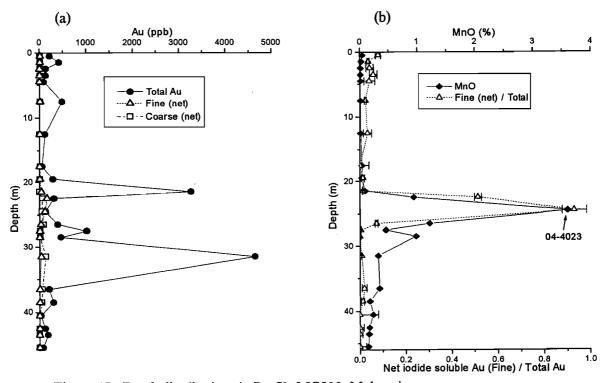


Figure 47: Depth distributions in Profile MC500, Mulgarrie:

- (a) Total Au and net iodide-soluble Au in coarse and fine samples;
- (b) MnO (%) and proportion of net iodide-soluble Au in fine samples.

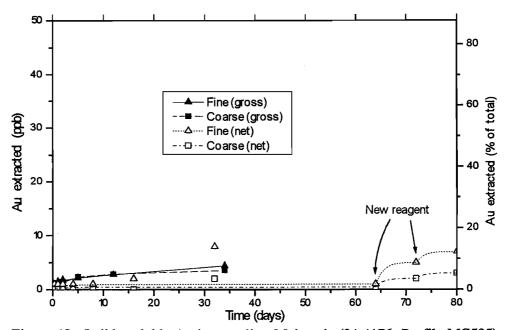


Figure 48: Iodide-soluble Au in saprolite, Mulgarrie (04-4176, Profile MC505).

6.2.4 Mn-rich material

Kinetic studies of a Mn-rich sample (04-4023, location shown in Figure 47b) indicate high net iodide solubility, with 90% of total Au dissolved from fine material within 5 days (Figure 49); in comparison, only about 50% of total Au was dissolved from coarse material. Results from other samples, and from differing degrees of pulverization prior to extraction (Appendix A1.5), indicate that net Au solubility is very high in all Mn-rich samples, with the solubility increasing with the amount of pulverizing. This suggests that the Au is chemically soluble, but occluded. Hydrogeochemical studies have indicated the importance of Mn for the mobility of Au in Cl-rich groundwaters (Gray, 1990a).

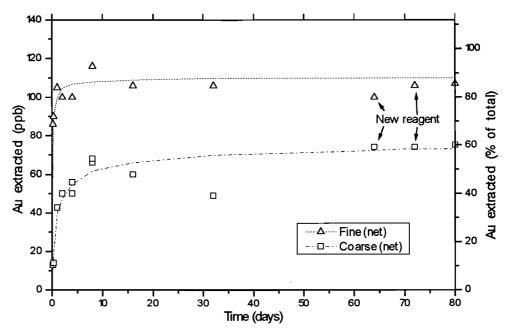


Figure 49: Iodide-soluble Au for Mn-rich sample, Mulgarrie (04-4023).

6.3 Zuleika

6.3.1 Site description

Zuleika is about 50 km north west of Kalgoorlie (Figure 1), with Au anomalies present in both residual and alluvial soils in a floodplain. Gold mineralization occurs in vein systems in residual areas and in sand, gravel and saprolite horizons at the base of, and below, a palaeochannel located in the floodplain. The floodplain contains up to 20m of barren clays (Lintern and Butt, 1992). Three soil profiles were studied (Sections 6.3.2 - 6.3.5) with an additional investigation of the Au extractability of 0-1 m composites from a soil traverse (Section 6.3.6).

6.3.2 Floodplain; Profile C

Profile C is from the floodplain on the margin of the palaeochannel and overlies palaeochannel mineralization. The profile consists of silty red clays, with an indurated horizon rich in Si and Al between 0.25 and 0.45 m. Calcite abundance increases sharply with depth below the indurated horizon. Iron oxides are present in moderate amounts (10 - 20% Fe) throughout the profile. This profile differs from others in the southern Yilgarn (Sections 4.2 - 6.2) in that Au and Ca distributions are unrelated (Figure 50a), possibly because of the indurated horizon. However, as with Ca-rich profiles, the proportion of net iodide-soluble Au is high and strongly related to total Au (Figure 50b) in both coarse and fine materials, giving similar results to the palaeochannel profile at Panglo (Profile A, Section 4.3).

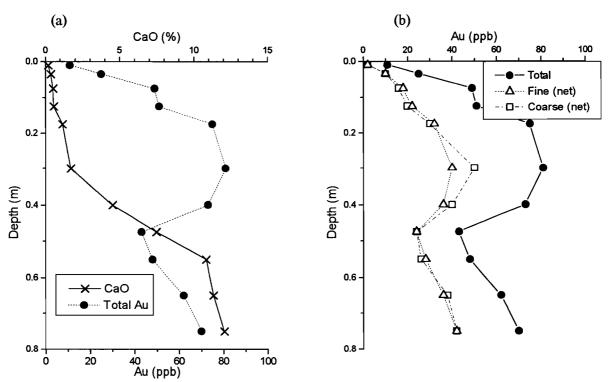


Figure 50: Depth distributions in colluvial soil, Zuleika Profile C: (a) Ca and total Au; (b) total and net iodide-soluble Au.

6.3.3 Residual soil with friable carbonate; Profile F

Profile F is a residual soil with a quartz-rich upper horizon, light textured clays diluted by carbonate in the top metre, becoming progressively more kaolinite- and Fe oxide-rich in the second metre. Small quantities of albite occur in the top 30 cm, presumably in lithorelics. Goethite dominates towards the base of the profile and appears to be associated with variably coloured materials. Some palygorskite occurs at the base of the calcareous horizon. Total Au and Ca are strongly correlated (Figure 51a), with over 50% of the Au being net iodide-soluble Au in coarse material and <10% in the fine material. This suggests that more than 50% of the Au is in surface accessible, soluble form. The low net solubility in fine material is probably due to pulverization exposing surfaces able to sorb the Au dissolved by iodide. These results are similar to those from calcareous residual soils from Mt. Hope (Section 4.2).

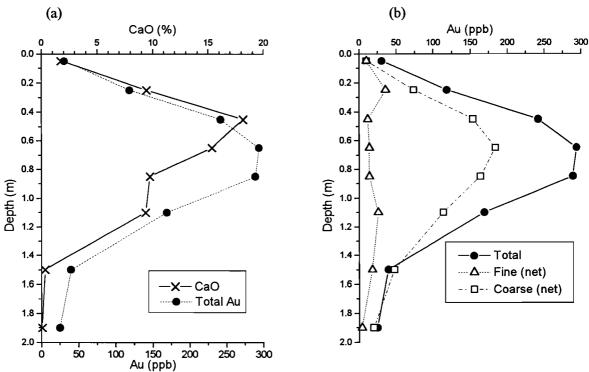


Figure 51: Depth distributions in residual soil, Zuleika Profile F: (a) Ca and Au; (b) total and net iodide-soluble Au.

6.3.4 Residual soil with indurated carbonate; Profile K

Profile K is a residual soil on a low ridge. Carbonate concretions, particularly of calcite, are abundant near the surface (0.2m) and decrease steadily with depth. Quartz abundance also decreases with depth, whereas Fe oxide contents generally increase; hematite is more abundant in the first metre and goethite dominates in the second metre. As with the other residual profile (Profile F), total Au and Ca show a strong relationship (Figure 52a), but the correlations of these elements with net iodide-soluble Au (Figure 52b) is less than in other carbonate-rich soils. This may be related to much of the carbonate being concentrated as massive segregations, rather than as friable forms. Lower Au solubilities in soils containing indurated calcrete were observed at Panglo (Profile B; Section 4.3.3, Figure 19) and Mulline (Profile 4161; Section 5.3.3, Figure 39).

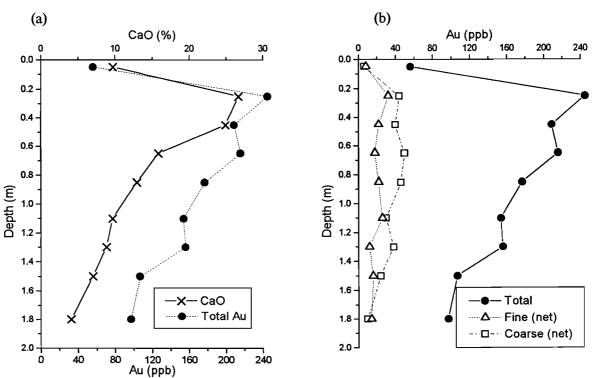


Figure 52: Depth distributions in residual soil, Zuleika Profile K: (a) Ca and Au vs. depth; (b) Total and net iodide-soluble Au.

6.3.5 Summary for profiles

In summary, the results indicate that the residual profiles (Profiles F and K) are typical of soils for the southern Yilgarn, whereas the floodplain soil (Profile C) behaves anomalously, perhaps reflecting induration and different surface hydrology.

6.3.6 Sequential extraction of samples on Traverse 4200N

The principal objective of the research at Zuleika was to determine whether buried mineralization in the palaeochannel has a discrete surface expression. However, although the overlying soils do have anomalous concentrations of Au (mean 28 ppb), these are much lower than in adjacent residual soils (mean of 141 ppb), and may be due to "natural" contamination from the residual soils, rather than from mineralization at the base of the palaeochannel. A procedure of sequential Au extraction was used to determine whether it might be possible to distinguish different forms of Au that may be related to these different sources. Twelve soils (0-1m) were selected, representing a traverse from the floodplain to residual soils on a low rise on section 4200N. In addition, two samples (one calcareous, one Fe-rich) from Mt. Hope were included for comparative purposes.

Three reagents with increasing ability to extract Au were used: deionised water, iodide $(0.1 \, \underline{M} \, \text{KI})$, with no pH control) and 2000 ppm potassium cyanide (CN), with 30 mL reagent added to each 10g sample and the gross solubility determined after each 7 day treatment. After three treatments, the soil samples were analysed for residual Au by neutron activation (NAA).

The results (Figure 53) indicate that, on average, the least water-soluble Au is present in the residual soils, and the most from the floodplain adjacent to the residual soils. The most iodide-soluble Au is found in the floodplain above mineralization in the palaeochannel; moderately iodide-soluble Au is also found in the residual areas. The residual soils are the most variable in the proportion of CN-soluble Au

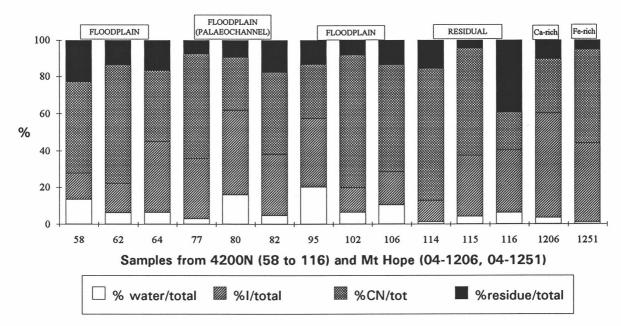


Figure 53: Sequential extraction results for 12 samples from 4200N (Zuleika) and 2 from Mt. Hope. Results expressed as a percentage of total. The "palaeochannel" locates the position of buried mineralization

The results suggest that this extraction procedure is poor at distinguishing different forms of Au in this suite of samples. There is no indication that Au in soils developed above the palaeochannel is any more or less soluble than that from either adjacent floodplain samples or the residual samples. Tests on other surficial samples *e.g.*, carbonate-rich or 0-10 cm, may yield more useful information. Data for the two control samples from Mt. Hope are not significantly different, but the carbonate-rich sample (04-1206) does have the highest proportion of iodide-soluble Au (see also Section 4.2.3, Figure 10).

7 NORTH OF MENZIES LINE

7.1 Introduction

The Menzies Line defines a narrow east-west transitional zone, across which there are marked changes in soil types, vegetation, and groundwater quality. Soils south of the Menzies Line are predominantly neutral to alkaline, orange to red loams, with extensive development of pedogenic carbonate. Non-calcareous gravelly soils occupy some high landscape positions, principally over granitic rocks. North of the Menzies Line, soils are predominantly neutral to acid, red, non-calcareous earths, sands and lithosols, with extensive development of siliceous red-brown hardpan. These soils present special problems for exploration since Au concentrations are generally lower than those south of the Menzies Line, and the hardpan is not particularly easy to sample or penetrate.

7.2 Granny Smith

7.2.1 Site description

Granny Smith is approximately 120 km north of the Menzies Line and has an extensive hardpan cover. Five profiles were studied and the Au chemistry of two of them investigated in detail; the extraction methods, results and conclusions are given in Lintern and Butt (1993), but the more important findings with regards to Au chemistry are summarized below.

7.2.2 Total vs. aqua regia extractable gold

All profile samples were analysed for total Au by NAA and by atomic absorption spectrometry following aqua regia (AR) extraction. Gold is most abundant in the hardpan (up to 190 ppb), moderate in the saprolite (up to 80 ppb) and least abundant in the unconsolidated topsoil (3 to 18 ppb) (Figure 54). Profile 6, closest to mineralization, contains the highest concentrations of Au. Comparing analytical data for AR vs. NAA indicates a considerable proportion (up to 47% in Profile 6) of Au present in hardpan is occluded within AR-resistant matrix (Figure 54). However, this characteristic is not observed in the saprolite. The Au content in the topsoil is too low for meaningful comparisons to be made.

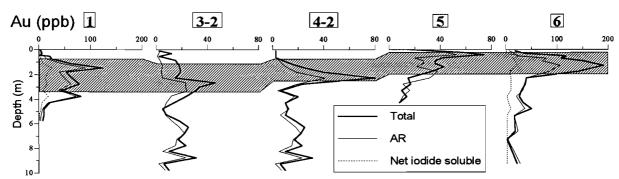


Figure 54: Gold distribution as determined by NAA and by AR for Profiles 1 - 6, Granny Smith. Extractions using 0.1 M KI were performed on fine material from Profile 1 and 6 only. Shading indicates approximate position of hardpan.

7.2.3 Net iodide-soluble gold

Net iodide-soluble Au (10 g sample in 30 mL of 0.1 M KI over 7 days with no pH control - see Section 3.2) was determined for fine (Figure 54) and coarse samples from Profiles 1 and 6. The results suggest that, for fine samples, the distribution of net iodide-soluble Au has a similar trend as for Au determined by AR and NAA, but with an overall lower abundance. A maximum of 25 to 30% of the total Au was net iodide-soluble, which is similar to the proportion from carbonate-rich material from

the southern Yilgarn sites (Sections 4.2 - 4.8). The Au extraction data for coarse and fine fractions are similar in Profile 1, but are different in Profile 6, where (i) more Au was extracted from the fine fractions of hardpan and (ii) more Au was extracted from the coarse samples of saprolite. This suggests that in Profile 6 there may be considerable re-adsorption onto saprolite and that pulverizing exposes more adsorption sites, in a manner similar to carbonate-rich material from Mt. Hope (Section 4.2).

7.2.4 Gross water-soluble gold

Gross water-soluble Au was determined for Profile 6 samples (10g, 30 mL, 7 days). The results indicate that a greater proportion of Au is extracted from the saprolite than hardpan and that, in some saprolite samples, an astonishing near 40% of the Au is gross water-soluble. Interestingly, gross water-soluble Au was greater than net iodide-soluble Au in saprolite samples, even though iodide is a more powerful reagent than deionised water. This indicates that dissolved Au has been re-adsorbed by constituents present in the saprolite. The low extractability of Au from hardpan using water and AR supports the suggestion that a greater proportion of Au is immobile in the hardpan (even when pulverized) than the saprolite.

7.2.5 Additional extractions on hardpan material

Further extraction studies were performed to investigate the nature of soluble Au in the hardpan. Four hardpan samples were selected from Granny Smith, and two samples (one Fe-rich and one Ca-rich) from areas close to Au mineralization at Mt. Hope for comparative purposes (Table 1). Samples were boiled for two hours with four different reagents (water, hydrogen peroxide, sodium carbonate and sodium hydroxide), then bottle rolled for one week with and without iodide $(0.1 \, \underline{M} \, \text{KI})$ present. Unboiled water was used as a control.

Table 1: Location, description, and Mn and organic carbon (org C) concentrations of samples used in selective extractions.

Sample	Location	Description	Mn (ppm)	org C (%)	Au (ppb)
04-5060	Granny S (Profile 5, 0.4 m)	Hardpan, heavy Mn-staining	524	nd	74
04-5073	Granny S (Profile 6, 0.5 m)	Hardpan, cemented	396	0.04	79
04-5076	Granny S (Profile 6, 1.25 m)	Hardpan, some Mn staining	142	0.04	165
04-5008	Granny S (Profile 1, 1.45 m)	Hardpan, some saprolite, Mn.	144	0.04	62
04-1470	Mt. Hope	Red clay, carbonate-rich	295	0.18	4260
04-1251	Mt. Hope	Laterite gravel, Fe oxide rich.	73	0.02	990

nd: not determined.

The results (Figure 55) indicated that:

1. Some Au was easily dissolved by water. Iodide will dissolve more Au than water alone, hence Au remaining undissolved after iodide addition is either even coarser, occluded or present as a weakly soluble complex. The relative proportions of the different types of Au can be interpolated from the differences observed with or without iodide (note that 04- prefixes are removed for clarity):

- (i) the highest proportion of highly soluble (water) Au is: hardpan/laterite> carbonate (5008 > 5073 > 1251 > 5076 > 5060 > 1470).
- (ii) the highest proportion of medium soluble (iodide) Au is: laterite > hardpan > carbonate (1251 > 5008 > 5076 > 5073 > 5060 > 1470).
- (iii) the highest proportion of weakly soluble (not iodide) Au is: carbonate > hardpan > laterite (1470 > 5060 > 5073 > 5076 > 5008 > 1251).

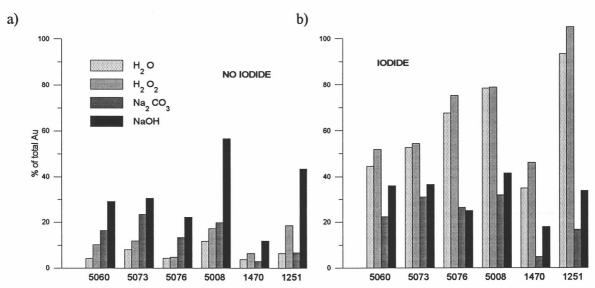


Figure 55: All digestion results (except unboiled water control) either (a) without KI and (b) with KI added. All trials measured gross soluble Au. Locations and brief sample descriptions are given in Table 1.

- 2. Samples selectively dissolved with peroxide consistently released more Au than those without, suggesting that minor amounts (<10%) of Au may be associated with organic matter or Mn oxides in the hardpan. However, the proportion of extracted Au does not appear to be related to the concentration of Mn or organic carbon. Little extra Au was extracted after the addition of iodide to the peroxide digest compared with the water with iodide extraction, which suggests that most of the additional Au made available after peroxide digest is water-soluble.
- 3. For all experiments, the highest proportion of extractable Au (approximately 100%) was for the Ferich sample (04-1251) extracted with iodide, with or without peroxide. This is contrary to previous results for this sample that indicated only about 30% gross solubility (Figure 13) and may be related to the different pH conditions of the digest mixtures.
- 4. There is little extra Au dissolved after Na₂CO₃ and NaOH digestion in the presence of iodide, suggesting, at first, that most Au released by these reagents is water-soluble. However, in all cases, the reagents with iodide added actually extract <u>less</u> Au than with iodide alone (i.e. without the alkaline reagents). This is possibly due to:
 - (i) rapid adsorption of AuI₂⁻ onto soil under alkaline conditions, or
 - (ii) the relatively low dissolution rate of Au in iodide under alkaline conditions, or
 - (iii) chemical transformation of the iodide in alkaline conditions, thereby reducing Au dissolution and/or solubility.

The saprolite-bearing hardpan sample has the highest proportion of Au soluble in hydroxide (50%), although nearly half of this Au can be leached with iodide alone. The Fe-rich sample has a significant

amount of Au released by hydroxide; it contains no hardpan cement but has abundant kaolinite. The Na₂CO₃ extraction results suggest that the most Au associated with soluble silica (9 - 17%) is present in hardpan with little or none in carbonate- or Fe oxide-rich samples.

5. The carbonate-rich sample has the lowest percentage of extractable Au by all reagents. This result is unexpected, but as the sample is taken from close to sub-crop this may be due to the presence of some coarse grained Au (Section 4.2.2).

7.2.6 Summary

The experiments indicate that some Au is associated with specific phases within the hardpan e.g., Mn oxides, organic material and soluble silica but, compared with Au that can be dissolved using iodide alone, they do not represent a highly significant proportion. As with soils south of the Menzies Line, the proportion of gross iodide soluble Au is significant but, at Granny Smith, its actual mobility in the surficial environment may be restricted due to encapsulation within the hardpan material. There is some indication that gross water-soluble Au is related to the Ca concentration, as found south of the Menzies Line. Some re-adsorption of dissolved Au by hardpan does occur, but not as strongly as by Fe oxide-rich material.

7.3 Beasley Creek

Beasley Creek is about 250 km NNW of Kalgoorlie, north of the Menzies Line and 30 km NNW of Granny Smith. Soils were sampled on two traverses; 38820N and 38940N, across a low rise centred at about 33950E. The soil is thin (0.1 m) near the top of the hill and thickens slightly (0.3 - 0.5 m) on either side. The base of the soil is generally marked by a substrate of hardpan or saprolite. Calcium content is low (< 1% CaO). The soil was divided into several size fractions, namely:

- (i) 710 4000 µm;
- (ii) 75 710 μm (largely wind-blown sand);
- (iii) $< 75 \mu m$;
- (iv) $< 4 \mu m$.

Net iodide-soluble Au was determined on pulverized whole soil (*i.e.*, fine materials). There is a very poor correlation between total Au and net iodide-soluble Au for both traverses (Figures 56 and 58). However, net iodide-soluble Au strongly correlates with Au content in both the $< 4 \mu m$ and the $< 75 \mu m$ fractions (Figures 57 and 59, Tables 2 and 3).

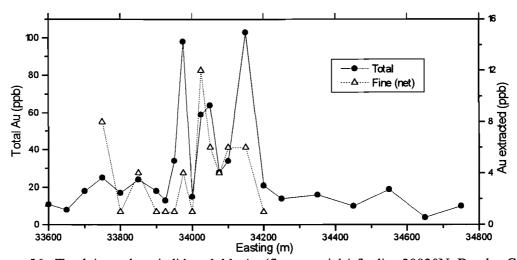


Figure 56. Total Au and net iodide-soluble Au (fine materials) for line 38820N, Beasley Creek.

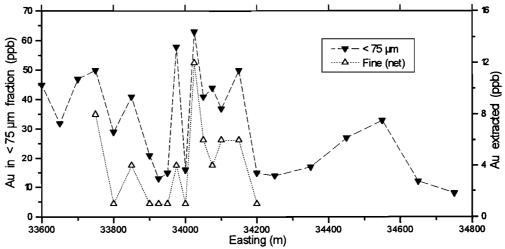


Figure 57. Total Au in the < 75 μ m fraction and net iodide-soluble Au (fine materials) for line 38820N, Beasley Creek.

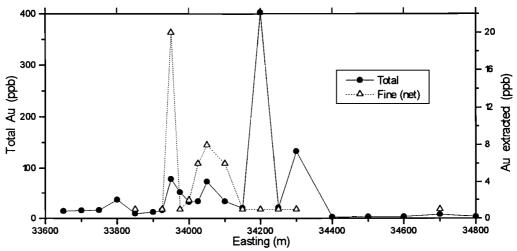


Figure 58. Total Au and net iodide-soluble Au (fine materials) for line 38940N, Beasley Creek.

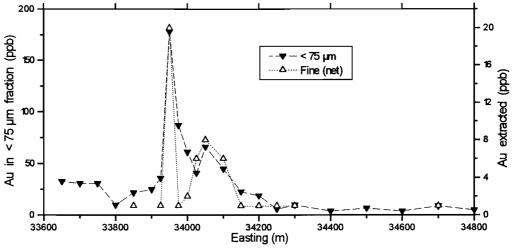


Figure 59. Total Au in the < 75 μ m fraction and net iodide-soluble Au (fine materials) for line 38940N, Beasley Creek.

Table 2: Correlation coefficients for total Au, Au in different size fractions, and net iodide-soluble Au (fine materials) for line 38820N, Beasley Creek. 99% significance for co-efficient greater than 0.61.

	Au	Au	Au	Au	Soluble
	(total)	(710-4000µm)	(<75µm)	(<4µm)	Au
Au (total)	1				
Au (710-4000μm)	0.66	1			
Au (<75μm)	0.63	0.46	1		
Au (<4μm)	0.70	0.52	0.85	1	
Soluble Au	0.47	0.43	0.85	0.78	1

Table 3: Correlation coefficients for total Au, Au in different size fractions, and net iodide-soluble Au (fine materials) for line 38940N, Beasley Creek. 99% significance for co-efficient greater than 0.63.

	Au	Au	Au	Au	Soluble
	(total)	(710-4000µm)	(<75µm)	(<4µm)	Au
Au (total)	1				
Au (710-4000μm)	0.17	1			
Au (<75μm)	0.08	0.62	1		
Au (<4μm)	0.08	0.66	0.97	1	
Soluble Au	-0.03	0.59	0.86	0.79	1

The strong correlation of soluble and total Au with Au in the <75 and <4 μm fractions clearly suggests that the most soluble Au is in the fine fractions. This may reflect original dispersion of Au into finely divided Fe oxides during the earlier humid weathering period.

8 SUMMARY AND DISCUSSION

8.1 Introduction

The extraction results have important implications for understanding the mobility of Au in the regolith, particularly the surficial environment. A number of samples have been studied and consistent patterns across sites have been observed for a variety of regolith materials.

8.2 Unweathered rock and saprolite

At Mt. Percy and Mulgarrie (Sections 5.2 and 6.2.3), without exception, the proportion of net iodide-soluble Au in unweathered rock and saprolite is relatively low (generally <1% of total Au), independent of the degree of sample crushing. This includes samples that contain significant primary carbonates (Figures 27, 31 and 32), indicating that the association of soluble Au with carbonate is specific to soils. These data are supported by kinetic experiments on saprolite from Mulgarrie (Figure 48). The low extractability of Au in rock and saprolite suggests that Au is in relatively insoluble forms such as native Au and Au tellurides, or occluded in sulphides or quartz.

8.3 Laterite and lateritic soils

Soils and regolith dominated by Fe oxide at Mt. Hope, Mt. Percy and Mulline (Sections 4.2.4, 5.2 and 5.3) have low to moderate gross Au solubilities in iodide solution. This indicates that some Au is soluble, perhaps in part due to smaller grain size of native Au. In addition, the net iodide solubility is very low, presumably because of sorption onto Fe oxides or other surfaces.

8.4 Manganese-rich horizons

Manganese-rich materials from Mulgarrie (Section 6.2.4) yield nearly 100% net iodide-soluble Au in fine materials and about 50% in coarse material, *i.e.*, the Au is easily dissolved and the Mn oxides are very poor at readsorbing the Au. This suggests that the Au is chemically soluble, but occluded. This correlates with groundwater studies (Gray, 1990a) indicating the importance of Mn for the mobility of Au in Cl-rich groundwaters. It is likely that any Au that is not occluded could be leached from a Mnrich horizon, given its high extractability.

8.5 Carbonate-rich soils

For carbonate soils across the southern Yilgarn, (Sections 4 - 6), net iodide-soluble Au comprises about 30 - 50% of total Au. At least as much, and in some cases considerably more, Au is soluble in coarse rather than fine material, suggesting much of the Au to be in a form that is highly accessible to solution. In "simple" carbonate soils, both soluble and total Au are proportional to total carbonate, suggesting that Au, Ca and Mg are precipitated by similar mechanisms or in response to similar factors, as discussed in Section 8.8.

The relationship between Au and pedogenic carbonate is also applicable for complex profiles. At Mt. Percy and Mulline (Section 5), total Au appears to be correlated with Ca when only carbonate-rich soils are considered, and with Fe oxides in Ca-poor materials occurring at greater depth or in other parts of the landscape. However, at both sites, soluble Au correlates closely with Ca concentration, even when all samples are included, which is consistent with iodide-soluble Au being an empirical measure of Au associated with pedogenic carbonate.

There is some evidence, from Mt. Hope, Mulgarrie and Zuleika (Sections 4.2, 6.2 and 6.3.6) that the proportion of iodide-soluble Au <u>increases</u> away from outcropping mineralization. This may be due to a greater proportion of Au close to mineralization being coarser grained and therefore of low solubility,

whereas away from mineralization more Au may be chemically mobilized and therefore precipitated in an iodide-soluble form. This hypothesis may have exploration significance, though further work is required to substantiate these observations.

The association between soluble Au and carbonate is observed for <u>pedogenic</u> carbonate only and not for carbonate-rich rocks that also have a low Au solubility. Thus, the association between Au and pedogenic carbonate is presumably more related to soil processes leading to deposition of carbonate and Au in the same position in the profile, rather than a specific bonding between Au and carbonate. This is discussed further in Section 8.8. Results from the southern Yilgarn follow a consistent pattern for Au mobilization in surface soils, especially where dominated by carbonate. This pattern is not followed north of the Menzies line, where soils are commonly carbonate-poor and/or dominated by hardpan.

8.6 Organic matter

The top 0.2 m of Yilgarn soils commonly contain over 1% organic carbon. Organic-rich samples at Mt. Hope and Panglo (Sections 4.2 and 4.3) have low (0 - 14%, mean 6%) net iodide-soluble Au. The proportion of gross iodide-soluble Au, however, is greater (up to 50%), indicating that Au can be dissolved from the organic-rich material, but is readsorbed.

Minor amounts of Au are dissolved by alkaline reagents from the upper organic horizon (Appendix A1.4), in comparison with deeper material for which Au was insoluble in these conditions. This alkaline soluble Au is possibly located within humic material, which is extracted by this reagent.

These observations apply only to most organic-rich surface horizons. Slightly deeper soils that still contain moderate levels of organic matter (< 1% organic carbon) and therefore are still biologically active, do not show this behaviour.

8.7 Hardpan

Laboratory experiments indicate that some Au is associated with specific phases within the hardpan e.g., Mn oxides, organic material and soluble silica but, compared with Au that can be leached using just water and/or iodide, these fractions are not highly significant. Gold in hardpan is generally found to be at least as soluble in water and iodide as in calcareous soils south of the Menzies Line but, its mobility in the surficial environment may be restricted due to encapsulation within the hardpan. The Au may remain encapsulated even after the hardpan has been pulverized to $<75\mu m$. There is some indication that water-soluble Au is related to the Ca concentration immediately beneath the hardpan, as found in calcareous soils. Re-adsorption of dissolved Au by hardpan does occur, but not as strongly as with Fe oxide-rich material.

8.8 Discussion

Soil extraction procedures have been successful at distinguishing differing features of Au chemistry in regolith materials, particularly in the southern Yilgarn. These are:

- (i) unweathered rock and saprolite low Au solubility;
- (ii) laterite and other Fe oxide-dominated regolith moderate Au solubility, with significant readsorption of any dissolved Au;
- (iii) Mn oxide-dominated regolith high Au solubility when pulverized;
- (iv) carbonate high Au solubility even without pulverizing;
- (v) organic-rich low Au solubility, possibly due to readsorption of dissolved Au;
- (vi) hardpan high Au solubility when pulverized.

These observations have significant consequences for understanding of Au mobility during regolith development. The most critical feature is that Au solubility in the regolith increases closer to the surface, particularly for soils with present-day pedogenic activity such as carbonate formation and/or movement of organic colloids. This is possibly due to two factors. <u>Firstly</u>, Au mobility can be enhanced by the presence of biologically-derived molecules (particularly those that contain S) that can readily dissolve Au. This is suggested by incubation experiments that demonstrate the ability of deionized water to dissolve Au from organic surface soils and the retardation of this dissolution by irradiation (Gray *et al.*, 1990). <u>Secondly</u>, closer to the surface, and particularly in carbonate-rich horizons, Au is in highly soluble forms.

It is expected that these two aspects are related. Biologically-derived ligands bond with Au and impart a high solubility. This soluble Au may have a high mobility, depending on mineral charge characteristics, pore size and other soil properties. Based on these data, it appears that Au distribution is at least partially controlled by evaporative processes. Thus, Au, can be highly mobile in soil horizons, as a result of biologically generated ligands. Gold is known to be taken up by plants, both in the southern Yilgarn study areas (Lintern 1989; Lintern and Scott, 1990) and elsewhere (Warren, 1982; Smith and Keele, 1984; Erdman and Olson, 1985). As humus decomposes, Au-organic complexes are formed that then percolate down the soil profile. Once these complexes reach the carbonate horizon, they will be immobilized, not necessarily by chemical means, but because these horizons are an evaporative zone. As the soil solution evaporates, precipitating additional carbonate, the Au may also precipitate in this zone. Thus, the primary controls on Au distribution in soils with pedogenic carbonate may be biological and physical, rather than chemical, as first expected. If this is the case, as all evidence suggests, then Au in soils is in a highly dynamic state. For example, plant roots may take up Au in the carbonate zone, which may then eventually be shed onto the soil surface, thus beginning the cyclic process again. In particular, unusually wet years, such as seen in 1992, could cause major Au redistributions in soils. Given these effects, it is not surprising that Au dispersion may give rise to enrichments, even in geologically recent overburden, that reflect underlying buried mineralization.

Gold may also have a high mobility in deeper regolith, if Mn oxides are present. This may be due to Mn oxidation reactions leading to conditions conducive to Au oxidation as halide complexes. Such Au may have a high mobility, until contacting reduced conditions, where the Au could be reprecipitated. Such a mechanism could contribute to the development of sub-horizontal zones of supergene Au.

Although many of the processes of redistribution of Au in soil are now defined, at least at a conceptual level, the process whereby Au is transported from mineralized rocks at depth to the soil surface is not clearly understood. This mechanism needs further investigation, because it is critical to further development of more effective soil or shallow regolith sampling, particularly in areas dominated by hardpan and/or transported overburden. In particular, further work is required north of the Menzies line, where the conceptual understanding of the soil Au redistribution processes is not as clear as for the southern Yilgarn.

Acknowledgements

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APPENDIX: Development of solution extraction methods

A.1 Sample treatments

The samples used for this set of experiments were those from Mt. Hope Profiles B and C (described in Section 4.2). Extracting solutions used were iodide reagent (Section 3.2) and alkaline reagent $[1 \, \underline{M}]$ sodium carbonate (Na₂CO₃) taken to pH 10]. Various sample procedures were investigated, including:

- (i) soil extractions in glass bottles;
- (ii) soil extractions in plastic bottles;
- (iii) centrifuging (15 min., 4000 rpm), then decanting waters for direct analysis;
- (iv) centrifuging, then filtering (0.45 µm membrane filter) supernatant for direct analysis;

Results are described in detail below.

A.2 Effect of differing bottles

In earlier experiments (Gray, 1990b; Gray et al., 1990), extractions had been done in glass rather than plastic bottles, so as to ensure no adsorption or side-reactions on bottle walls. However, for ongoing experimentation, plastic bottles were considered to be a simpler and cheaper alternative. Accordingly, extractions were done in both bottle types to check whether there was any significant difference. Comparison of soluble Au from plastic vs. glass bottles (Figure A1), indicates a linear trend. On the basis of this information, it was decided that plastic bottles would be used for all ensuing extractions.

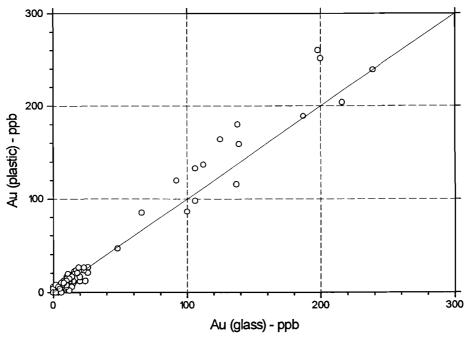


Figure A1: Effect of extractions in plastic vs. glass bottles, with line of equality included (see Section A1.2 for details).

A.3 Effect of filtering

Previous extractions (Gray et al., 1990) involved filtering (0.45 µm) of the solution prior to analysis. Due to the high content of suspended solids, the suspensions were centrifuged prior to filtering.

Centrifugation has the effect of sedimenting particles, at a rate dependant on temperature, particle density and particle size. Calculations indicate that, for example, in the particular laboratory centrifuge being used, centrifuging of 50 mL of solution (with a solution height of less than 5 cm) in the plastic reagent bottles at 4000 rpm for 15 min. would result in the sedimentation of:

(i) all particles greater than 0.45 μm that have densities of 1.16 g/cm³ or greater (i.e. everything except for pure organic colloids);

and/or

(ii) all particles greater than 0.14 μ m that have densities of 2.65 g/cm³ or greater (i.e. normal density of clay material).

Therefore, with the possible exception of organic colloids, centrifugation at 4000 rpm for 15 min. should render filtering unnecessary.

Comparison of the analytical results from samples centrifuged then filtered, with samples that were merely centrifuged (Figure A2), indicates the unfiltered samples contained up to 50% more Au. This could result from a substantial amount of the Au being present in colloids that were close to or greater than $0.45~\mu m$ in size and therefore retained in the filter paper, or that the filter paper in some manner (e.g., sorption) retained dissolved Au. Note that though the nominal pore diameter of the filter membranes used was $0.45~\mu m$, filters can become partially clogged and the effective pore size may become much smaller, so that fine colloidal particles may be filtered out by this technique.

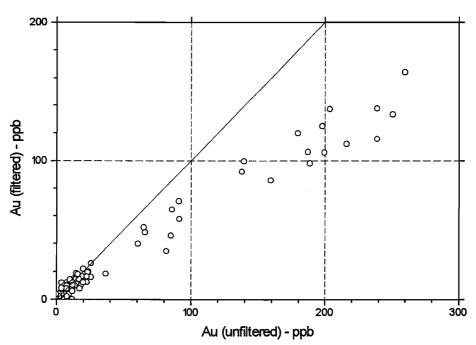


Figure A2: Effect of extractions with filtering vs. without filtering, with line of equality included (see Section A1.3 for details).

Therefore, centrifuging without subsequent filtering was considered to be more representative of potentially soluble Au than using filtering, both in terms of simplicity and in obtaining a better measure of soluble Au. All results and discussion in this report are for extracts that were only centrifuged (4000 rpm, 15 min.) prior to analysis.

A.4 Alkaline extraction results

The alkaline reagent was tested due to some early results (Gray et al., 1990) suggesting enhanced Au solubility in this reagent from carbonate-rich samples. However, further testing indicated that this reagent was very poor at extracting Au from Mt. Hope Profiles B or C (Figures A3 and A4; profiles described in Section 4.2), except at the very top of the profile (i.e., the top 0.2 m), where a minor proportion of the Au, possibly representing Au associated with humic matter, was extracted.

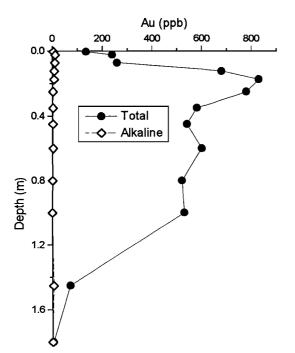


Figure A3: Total Au and alkaline soluble Au in coarse material from carbonate-rich Profile B, Mt. Hope.
(Error is less than symbol size).

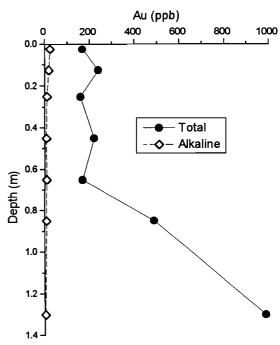


Figure A4: Total Au and alkaline soluble Au in coarse material from Fe oxide-rich Profile B, Mt. Hope.
(Error is less than symbol size).

Based on the colour of the solution extracts, the alkaline extractant was effectively extracting significant proportions of the humic matter from the soil, and considerably more than the iodide extract. This implies that very little Au is directly associated with humic matter, except possibly in the top 0.2 m.

On the basis of this data, alkaline extraction was not considered to be an effective tool for the investigation of these soils.

A.5 Effect of pulverization on net iodide solubility in Mn-rich samples

Manganese-rich samples from Mulgarrie were extracted in a similar manner to other sites (Section 3.2). Net iodide-soluble results for selected samples are given in Table A1. Samples within the Mn-rich horizon (22 - 27 m) at MC500 (also see Figure 47b) had high proportions of net iodide-soluble Au, especially for the fine material.

Table A1: Specific elemental concentrations and net iodide-soluble Au for selected Mulgarrie samples.

Sample	Origin	Depth	Fe_2O_3	MnO	MgO	CaO	Gold	Gold ext	tracted	% Extr	acted
	•	(m)	(%)	(%)	(%)	(%)	(ppb)	Coarse	Fine	Coarse	Fine
04-4021	MC500	21.5	13.7	0.1	0.5	0.0	3260	< 1	40	<0.00	0.01
04-4022	22	22.5	13.7	0.9	0.5	0.0	308	62	158	0.20	0.51
04-4023	11	24.5	12.3	3.6	4.0	5.1	125	46	116	0.37	0.93
04-4024	"	26.5	13.7	1.2	1.5	0.1	386	84	28	0.22	0.07
04-4025	11	27.5	13.8	0.5	1.6	0.6	1010	14	4	0.01	0.00
04-4163	Mn-rich Horizon	28	27.7	8.4	6.55	9.16	117	8	90	0.07	0.77

The high solubility of Au in Mn-rich regolith was further examined by kinetic tests of the net iodide solubility of Au from Mn-rich sample 04-4023 (Table A2; Figure 49). As described in Section 6.2.4, 90% of the total Au is dissolved from the fine material within 5 days, with only 50% dissolved from the coarse material. This indicates significant occlusion of Au in this sample.

Table A2: Net iodide Au solubility in sample 04-4023 (125 ppb Au) vs. time.

Time	Gold ex	tracted	
(days)	Coarse	Fine	
0.17	13	86	
0.33	14	90	
1	43	105	
2	50	100	
4	53	100	
8	67	116	
16	60	106	
32	49	106	
64	74	100	
72	74	106	
80	75	107	

The effect of pulverization to different particle size on Au solubility was tested for Mn-rich sample 04-4163, using the following sub-samples:

- (i) < 10 mm (coarse), using a jaw crusher with Mn steel plates;
- (ii) < 4 mm, using a disk pulverizer with alumina plates;
- (iii) < 1 mm, using a disk pulverizer with alumina plates;
- (iv) < 0.075 mm (fine), using a case hardened steel swing mill.

The three different extraction reagents used were standard iodide reagent (Section 3.2), deionized water and $1 \, \underline{M}$ sodium chloride solution at pH 3 (denoted as acid salt). There is a clear increase in the solubility of Au with decreased particle size, particularly following pulverizing to < 0.075 mm (Table A3). Gold even had a moderate solubility with water and acid salt solution in the fine material, indicating that at least some of the Au is in a very soluble form. Gross solubility was not greater than net solubility for any of the reagents, indicating that sorption of the dissolved Au was not significant.

This differs from other, Mn-poor materials (e.g. Figure 10), for which gross solubility was significantly greater than net solubility.

Table A3: Effect of particle size on net iodide Au solubility of Mn-rich sample 04-4163 (117 ppb Au).

	Time	Nominal Particle Size			
	(days)	< 10 mm	< 4 mm	< 1 mm	<0.075 mm
Iodide (net)	1	9	7	13	79
	4	nd	19	19	76
Iodide (gross)	1	6	5	15	50
	4	4	nd	13	61
Water (net)	1	< 1	< 1	< 1	8
	4	2	< 1	< 1	10
Water (gross)	1	1	1	1	9
	4	1	1	1	10
Acid Salt (net)	1	< 1	< 1	< 1	9
	4	< 1	< 1	< 1	6
Acid Salt (gross)	1	1	1	1	10
	4	1	1	3	11

nd: not determined

It is concluded that Au in Mn-rich material from Mulgarrie is highly soluble. Net solubility appears to be as great as gross solubility, indicating very little readsorption of Au dissolved by any of the extraction reagents used. Solubility increases with increased pulverizing, suggesting that the potentially soluble Au is occluded in *in situ* soil.