

ASSESSMENT OF SOIL PARAMETERS AND PATHFINDER ELEMENTS FOR GOLD EXPLORATION IN A MINING- DISTURBED GRANITIC TERRAIN, SOUTHEAST NEW SOUTH WALES, AUSTRALIA

K.G. McQueen¹ and C. J. Nichols¹

¹IAE, University of Canberra, ACT, 2601, Australia

Introduction

Geochemical exploration for gold in historic or mature goldfields can be complicated by mining-related surface disturbance, including alluvial workings, reef mining and ore processing, as well as from other related anthropogenic activities such as land clearing and farming. The Braidwood region in southeast New South Wales is such an area, having been extensively worked for alluvial gold from the first gold rush of 1851 to the period of large scale mechanical dredging, which ended in 1914. Total gold production was 1.25 million ozs, making this the 6th largest alluvial goldfield in Australia (Middleton 1970). Major disturbance was along the rivers, creeks and alluvial flats, but also extended to adjacent slopes, which were commonly worked by ground sluicing or 'surfacing' and to areas of reef mining.

Modern gold exploration in the area is focussed on locating primary bedrock gold deposits within the Braidwood Granodiorite, the major host unit to the known deposits, such as Dargues Reef, near Majors Creek. These intrusion-related gold deposits appear to be the source for the extensive alluvial gold concentrations and have a primary geochemical association of Au-Cu-Pb-Bi-Te-Sb with As and Fe in pyrite (McQueen & Perkins 1995). Geochemical exploration using shallow 10-15 cm A horizon) soil sampling has had limited success, even in areas away from major disturbance from historic alluvial mining (e.g. Duncan 1984).

The aim of this study was to make a detailed assessment of the soils in the area, particularly around Majors Creek, and to determine the most appropriate soil fraction, horizon and components to sample and the most useful suite of elements, for improved geochemical exploration.

Methodology

Soils were sampled at eight sites in the area north of the Dargues Reef gold deposit and at two regional background sites in the Eurodux area 5 km NNE of Braidwood (Figure 1; Table 1). These sites were indicated to be of potential interest and suitable variability by Unity Mining Ltd, who are currently exploring in the region. The sites covered a range of landscape settings, with some close to previously known soil anomalies and some from background areas. All sites were in soils on

granitic bedrock (mostly Braidwood Granodiorite, western phase). Soil profiles were extracted with a hand auger and 0.5 kg samples collected from the different horizons and bagged in plastic sample bags. At the time of sampling each soil profile was logged according to depth (cm) and described in terms of soil horizon, soil texture, colour, major constituents and soil pH. Soil pH was measured using a field pH indicator kit and also with a pH meter on a 1:5 soil:water mixture in the laboratory.

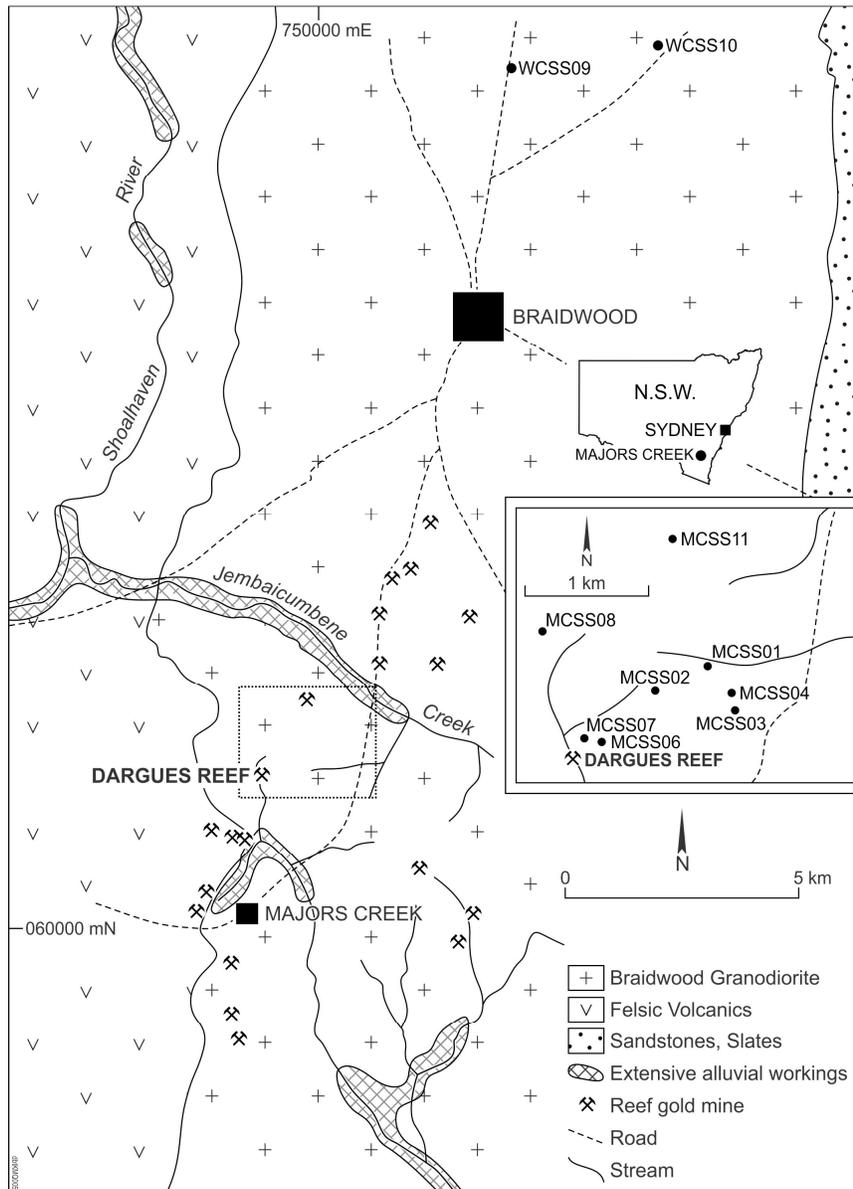


Figure 1. Location of study area and sample sites. Also shown are major rock units and historic gold workings. Inset is an enlargement of the area north of Majors Creek. Geological information and mining sites from the Canberra 1:250 000 Metallogenic Map, 1985, Geological Survey of New South Wales.

Table 1. Location coordinates (Zone 55H) for sample sites (Datum WGS84)

Profile Site	General Location	Easting	Northing
MCSS 1	Honeysuckle Creek	0750127	6063582
MCSS 2	Near drill hole MCR10	0749696	6063401
MCSS 3	Arsenic anomaly	0750339	6063187
MCSS 4	Arsenic anomaly	0750336	6063321
MCSS 6	Just N of Dargues Reef	0749241	6063021
MCSS 7	Just NE of Dargues Reef	0749085	6063005
MCSS 8	Near Copper Ridge	0748816	6063947
MCSS 9	Eurodux Road	0754894	6079384
MCSS 10	Neriga Road - N St Owens Ck	0758409	6079841
MCSS 11	Tory Boy Prospect	0749950	6064662

Samples were dried at 60° C, any peds carefully disaggregated and half the sample dry sieved into three size fractions (<250µm; 250µm-2mm and >2mm) using 2mm stainless steel and 250µm nylon sieves. The coarse and medium fractions were pulverised by ALS-Chemex laboratories before geochemical analysis. A subsample of the non-dried portion of the samples was separately sieved to produce a <2mm fraction for particle size analysis using a Mastersizer with a Hydro 2000Mu manual wet dispersion accessory. Ultrasonic dispersion was undertaken for 30 seconds to improve dispersion before particle size analysis.

Four different analytical methods were used to evaluate the soil geochemistry in the various size fractions and soil horizons (depths). All digestions and chemical analyses were performed by ALS-Chemex at their commercial laboratories in Brisbane, Australia. Replicates and standards were submitted with the sample suite.

1. 1 g of each size fraction from each horizon was digested with *aqua regia* then analysed by ALS-Chemex method ME-MS41 by ICP-MS/OES for Ag, Au, As, Bi, Ca, Cs, Cu, Fe, Hg, Mn, Mo, Pb, S, Sb, Te and Zn.
2. 1 g of each sample, consisting of the fine fraction from all horizons was analysed by ALS-Chemex method ME-MS41L (an *aqua regia* super trace using ICP-MS) for Ag, Au, As, Bi, Ca, Cs, Cu, Fe, Hg, Mn, Mo, Pb, S, Sb, Te and Zn.
3. 1 g portion of a selection of 13 samples was subjected to a four acid digest and analysis following ALS-Chemex method ME-MS61, with ICP-MS/OES. This was done to compare the results from the *aqua-regia* partial leach with results for 'total' analysis for key elements of interest. Elements analysed were Ag, As, Ba, Bi, Ca, Cs, Cu, Fe, Mn, Mo, Pb, Sb, Te and Zn.

4. Selected samples were analysed by fire assay using ALS-Chemex method AU-ICP21 on 30 g sample portions. This was done to cross check with the two *aqua-regia* digest methods.

The mineral components of the samples were identified using optical microscopy combined with analysis of selected sample fractions by quantitative X-ray diffraction (using Siroquant).

Results

Soil Characteristics

The observed soils are duplex, podsollic soils with a light grey to dark brown, sandy to silty-loam A horizon (20-45 cm thick), a yellowish brown to darker brown, sandy-clay B horizon (24-50 cm thick) and a light brown to yellow brown gravel-sandy clay C horizon (30-60 cm thick) . Profiles in the Majors Creek area typically have a lighter coloured A horizon, with very little clay, compared to the A horizon samples from the Eurodux area, where there has been no mining disturbance (Figure 2).

Particle Size Analysis

Particle size analyses for each profile show that most soil samples have a distinctly bimodal particle size distribution. Dominant particle sizes are in the 250-1000 μm and the less than 90-100 μm ranges. The soil at MCSS7 and the A horizon of MCSS9 are exceptions, having very weak bimodal patterns. There is some variation in the particle size distribution down the soil profiles, with a trend towards greater abundance of the fine fraction relative to the coarse fraction with depth. The finer component also shows a decrease in maximum particle with depth from the A to the C horizon. It is important to note that the particle size analysis does not include large nodules and aggregates above 2 mm in diameter. Ferruginous nodules larger than 2 mm were observed at some sites.

The sieved fractions used for the geochemical analysis include the dominant <100 μm range in the <250 μm fraction, the dominant 250-1000 μm range in the 250 μm to 2 mm fraction and larger aggregates in the >2 mm fraction (the latter are not included in the particle size analysis, which is for sample material <2 mm).

Soil Mineralogy

The medium and coarse size fractions of the soil samples are dominated by quartz and variably weathered granitic rock fragments. The quartz includes both granite-derived grains (clear to light grey) and vein quartz (typically milky to greyish). Much of the quartz shows iron oxide staining. The fine fraction, particularly in the B horizon samples, has a higher abundance of clay, predominantly kaolinite with minor illite. Goethite and trace hematite comprise up to 10% of the coarse fraction in the A

horizon, generally as irregular ferruginous aggregates and distinct pedogenic nodules. These are well developed at sites MCSS3 and MCSS11. Minor manganese-bearing nodules were observed at site MCSS3. The coarse fraction of the C horizon samples commonly contains partly altered biotite and hornblende and at several sites these persist into the B and A horizons (e.g. MCSS9). At site MCSS11 (Tory Boy Prospect) greenish, granitic fragments and preserved muscovite/illite were noted, consistent with hydrothermal (sericitic) alteration. Also at this site a single gold particle (150 um in size) was observed, attached to a quartz grain in the coarse fraction of the B horizon sample.

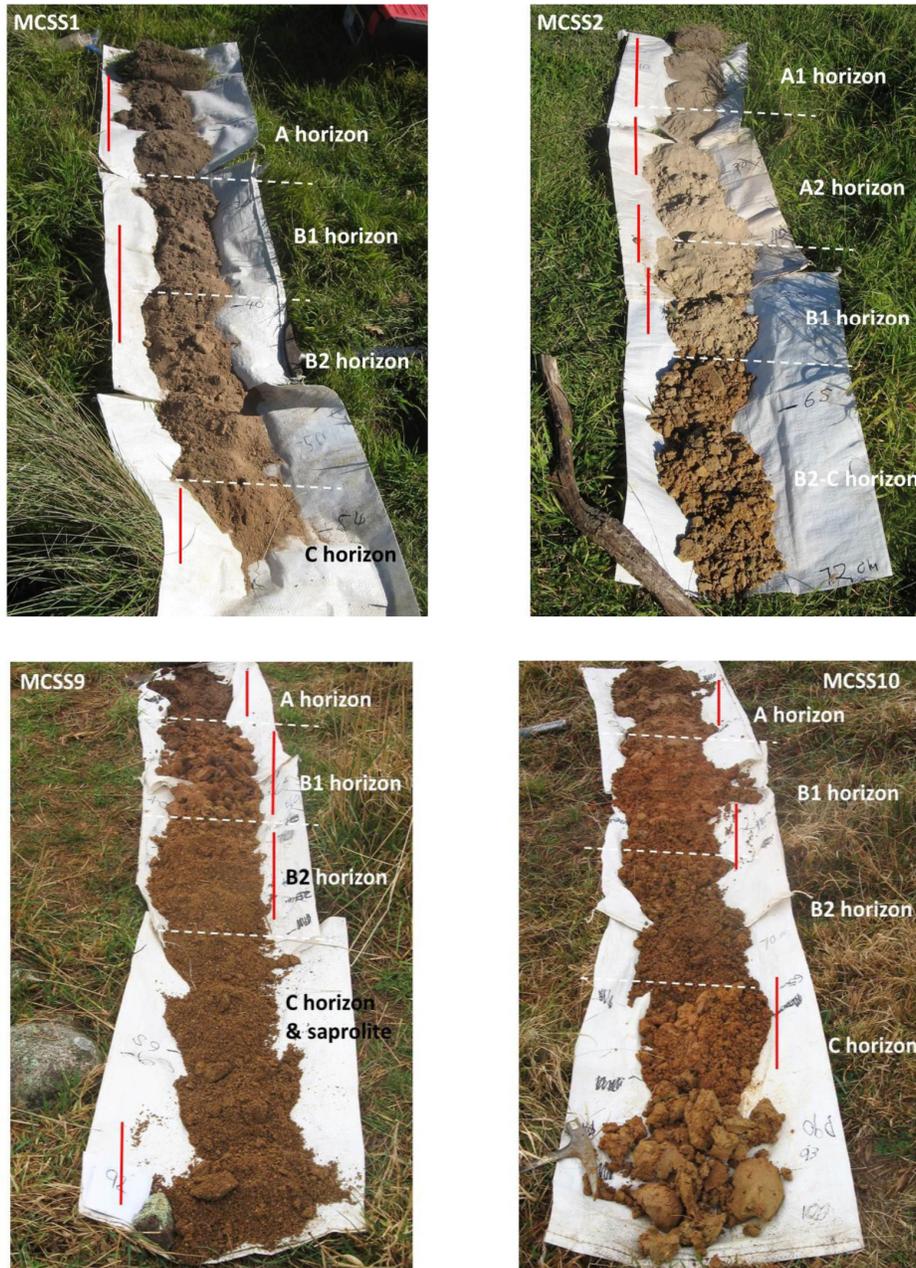


Figure 2. Examples of soil profiles from the Dargues Reef (MCSS1, MCSS2) and Eurodux (MCSS9, MCSS10) sites (auger cuts are approximately 10 cm).

Soil pH

The soils show slightly acid to neutral pH (total range 5.5-7.5). There is typically limited pH variation down individual profiles, generally to slightly higher pH. However, some A horizons are slightly more alkaline than the underlying B and C horizons (e.g. MCSS1, pH 7.5-7).

Geochemistry

Element abundances and distributions

Results from the standard *aqua regia* digest analysis show that the B and C horizons in most profiles generally have the highest concentration (response) of key pathfinder elements (Ag, As, Bi, Cu, Pb, Sb, Te, Zn). There are major exceptions where the A horizon has a high Fe content in the coarse fraction, in which case a number of elements, particularly As, Cu, Mn, Mo and Pb, also have higher abundance. Many of the profiles have the highest Fe and Mn abundances in the coarse fraction of the A horizon consistent with concentration of both elements in observed pedogenic nodules and irregular ferruginous fragments. The B horizon shows the most consistency in element abundance between the different size fractions and there appears to be no systematic relationship between fraction size and element abundance. The C horizon commonly, but not invariably, shows greater pathfinder element abundance in the fine size fraction, but this is also complicated by high-Fe in some of the coarse fraction samples in this horizon. If allowance is made for the complication of the Fe-rich coarse fraction from the A horizon, the B horizon shows the highest abundance of pathfinder elements consistently across all fraction sizes.

Gold has low abundance (<0.02 ppm) in most of the profiles sampled and a 'nuggety' distribution. Two high values were found in the A horizon at site MCSS7 and site MCSS3 (2.4 ppm in fine fraction and 0.6 ppm in coarse fraction respectively) using the standard *aqua regia* leach analyses (ME-MS41). The highest values detected using the Super Trace' method (ME-MS41L) were at site MCSS3 (0.107, 0.074, 0.060 ppm for the fine fraction in the A, B, C horizons respectively) and at site MCSS11 (Tory Boy prospect, 0.032 ppm for the fine fraction of both the B and C horizons). The check analyses by fire assay (method Au-ICP21) confirmed detectable gold in the fine fraction of the A horizon at site MCSS7 (0.06 ppm). Anomalous gold values were thus restricted to sites MCSS3, MCSS7 and MCSS11.

Frequency distribution analysis indicates possible anomalous populations in the total data set for As (>30 ppm), Cu (>75 ppm), Bi (>2.5 ppm), Mo (>5 ppm in the coarse fraction), Ag (>0.2 ppm) and Sb (>4 ppm).

Illustrative examples of key element distributions down some of the sampled profiles analysed using the standard *aqua regia* leach method are shown in Figures 3-6.

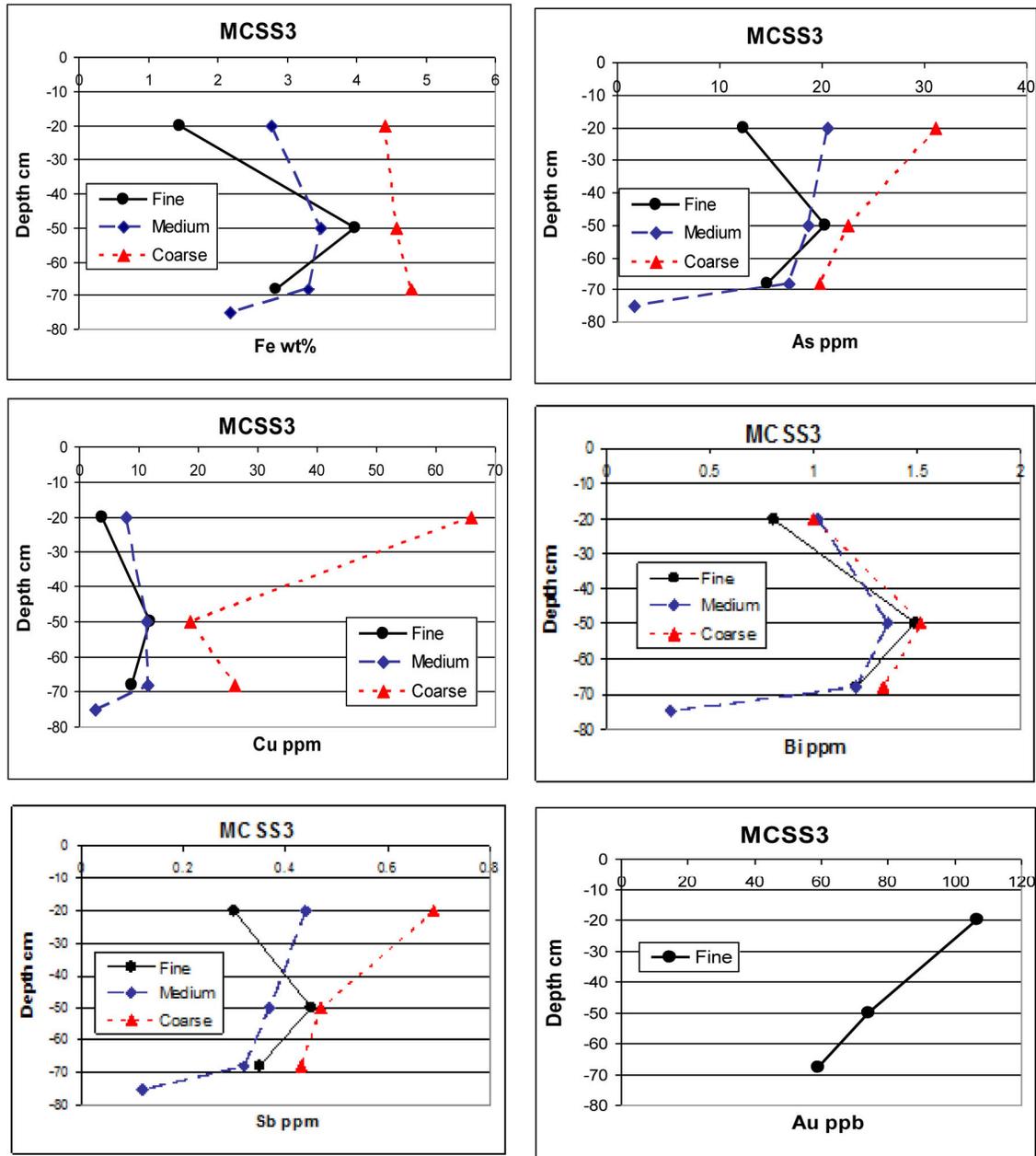


Figure 3. Soil profile plots showing some element distributions at different depths and for different size fractions (fine <250 μ m, medium 250 μ m-2mm, coarse >2mm) for site MCSS3 (arsenic anomaly). Note that for most elements the B horizon at 50 cm depth has the least variability across the three different size fractions.

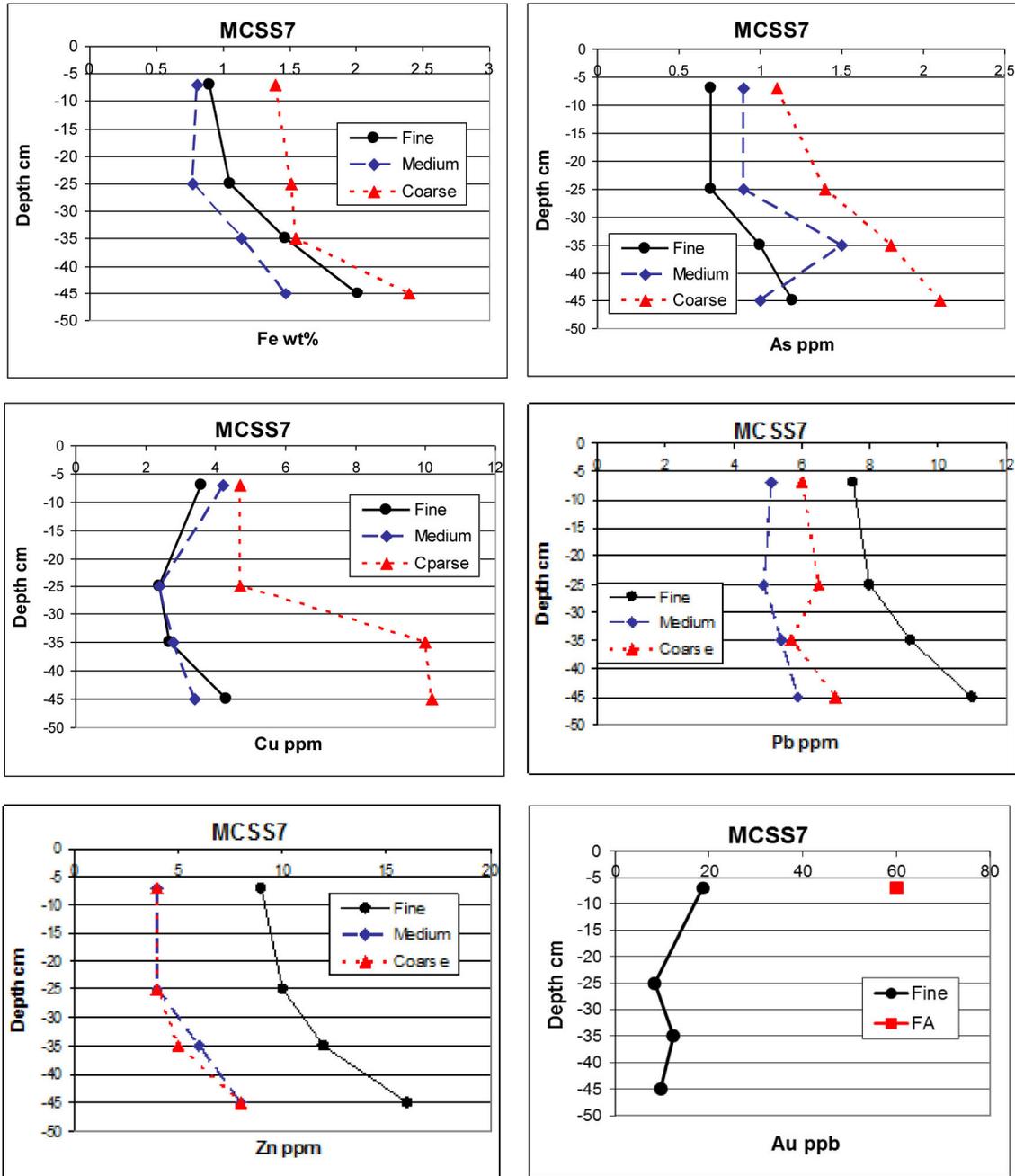


Figure 4. Soil profile plots showing some element distributions at different depths and for different size fractions (fine <250 μ m, medium 250 μ m-2mm, coarse >2mm)for site MCSS7 (40 m north of the Dargues Reef gold deposit). The B1 and B2 soil horizons correspond to the 25 and 35 cm depths respectively. FA for gold is a separate fire assay analysis of the bulk fraction of the A horizon.

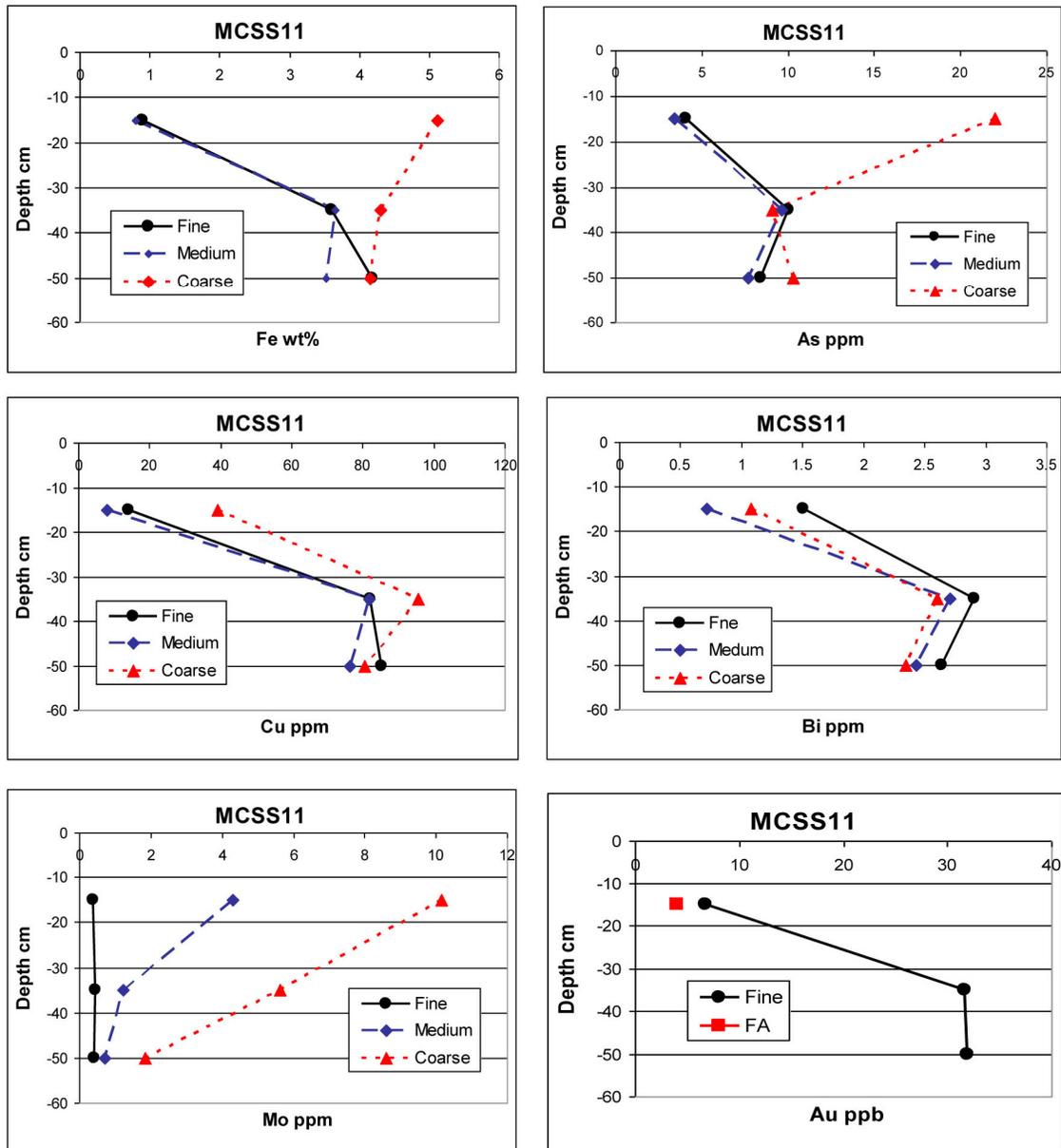


Figure 5. Soil profile plots showing some element distributions at different depths and for different size fractions (fine <math><250\mu\text{m}</math>, medium $250\mu\text{m}-2\text{mm}$, coarse >$2\text{mm}$) anomalous site MCSS11 (Tory Boy Prospect). FA for gold is a separate fire assay analysis of the bulk fraction of the A horizon.

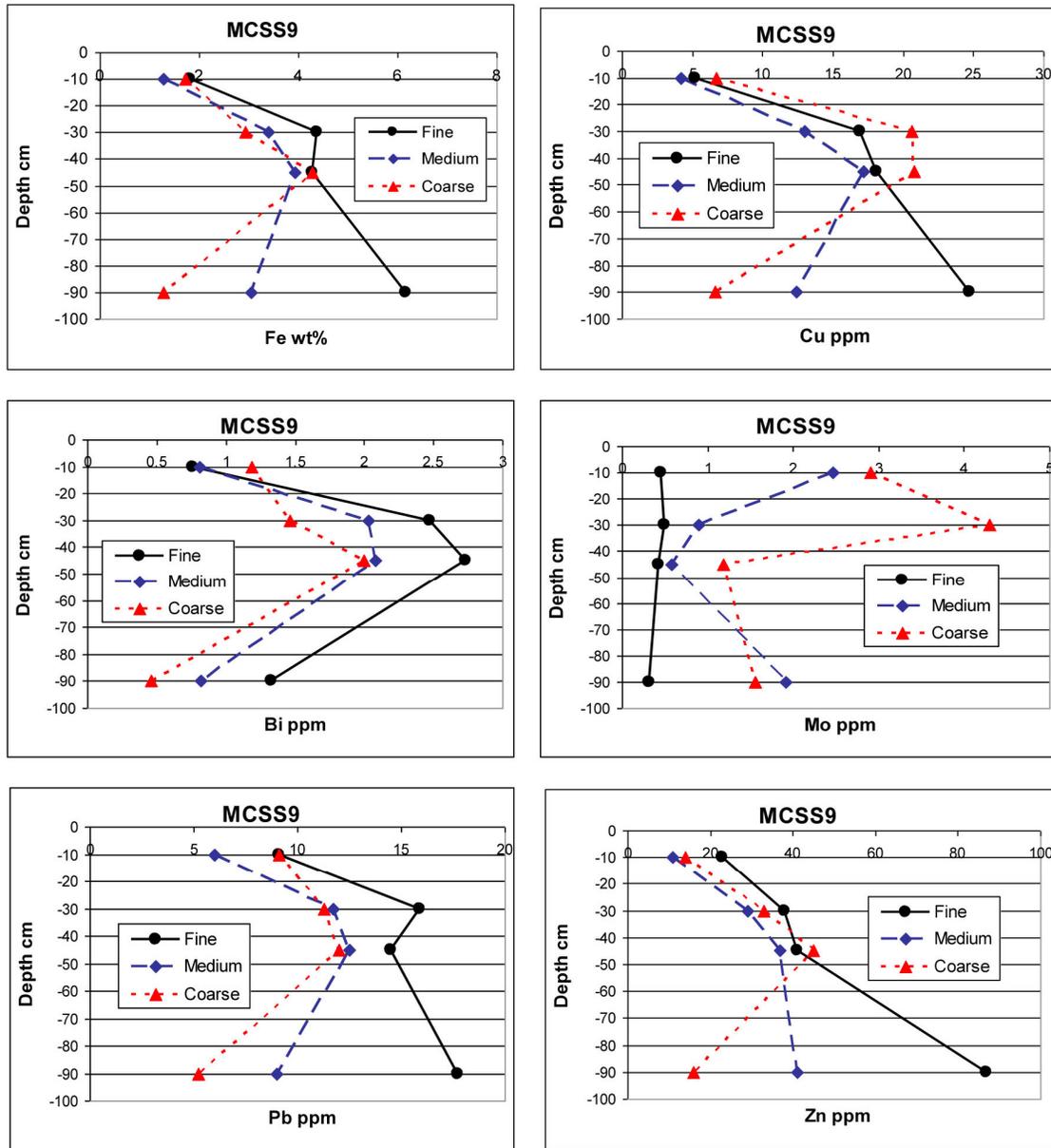


Figure 6. Soil profile plots showing some element distributions at different depths and for different size fractions (fine <250 μ m, medium 250 μ m-2mm, coarse >2mm) for regional background site MCSS9 (Eurodux Road). The B1 and B2 soil horizons correspond to the 30 and 45 cm depths respectively.

Splitting the different size fractions (Figure 7) for the full data set highlights the higher concentration of Fe in the coarse fraction. Also apparent are distinctly different background populations between the size fractions for Cu (in the coarse fraction) and Mo in all fractions. The fine fraction shows anomalous outliers for As, Cu, Bi, Ag, Sb and Pb and Zn.

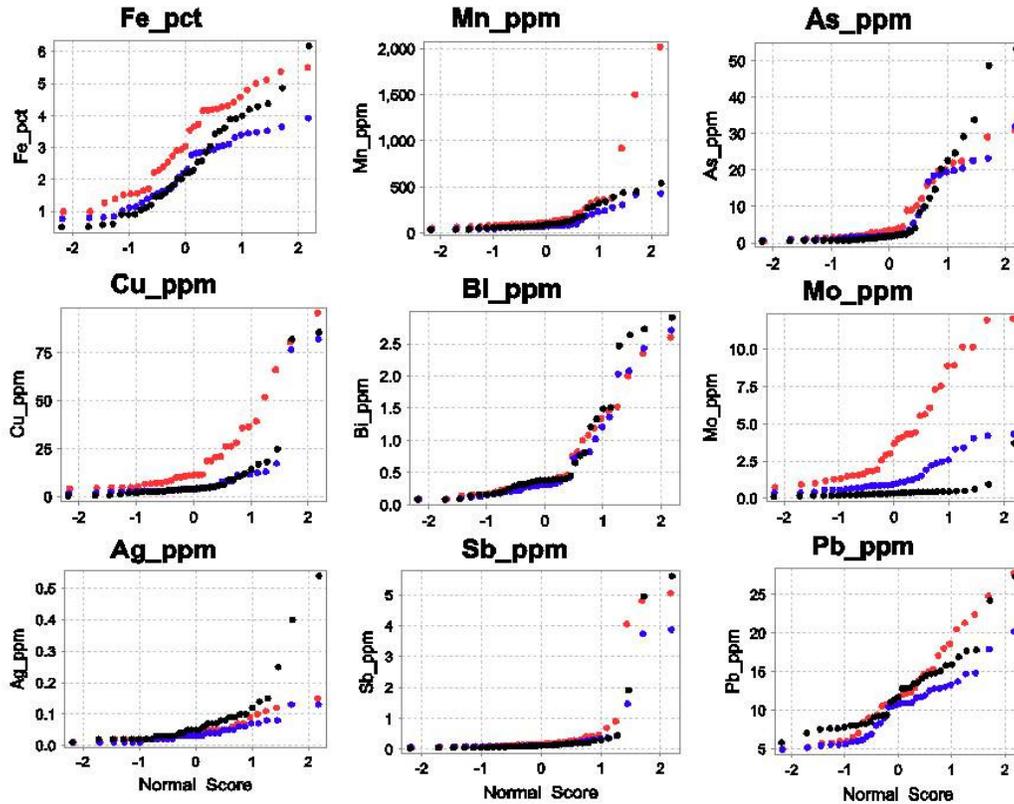


Figure 7. Normal probability plots for some element abundances in the coarse (red) medium (blue) and fine (black) fractions of the total soil data set from all horizons (Method ME-MS41).

Element correlations

There is moderate to strong positive correlation of the key pathfinder elements, Pb, Zn, Bi, Cu and Te, with Fe. This is apparent in the total data set for both the *aqua regia* leach (ME-MS41) and ‘Super Trace’ (ME-MS41L) methods (Table 2). There are also moderate positive correlations between Cu, Bi, Sb and Hg in the total data set. Gold does not show strong correlation with any other elements, in part due to its low abundance in most of the samples and observed particulate occurrence. In the A horizon, Cu and Mo show strong positive correlation, particularly related to the coarse fraction, and Pb is strongly correlated with Fe in the coarse and medium fractions. In the B horizon the strongest positive correlation is between Cu and Sb and there are moderate positive correlations between Zn and Bi and Zn and Fe. The strong positive correlation between Cu and Mo seen in the A

horizon is not present in the B horizon. In the C horizon the strongest positive correlations are between Cu and Sb and Cu and Bi. There is moderate positive correlation between Zn and Fe. Arsenic has a weak to moderate positive correlation with Fe in the standard *aqua regia* digest data (ME-MS41), being more marked where the As content is less than 5 ppm. However, As is not correlated with Fe in the fine fraction samples analysed by the ‘Super Trace’ method (ME-MS41L). The difference may be due to greater sensitivity of the latter method at low concentrations of As.

Table 2. Significant correlations between elements in the total data set for analytical method ME-MS41 and fine fraction for ME-MS41L

Elements Correlated	Correlation Coefficient ME-MS41 n=112	Correlation Coefficient ME-MS41L n= 40
As-Fe	0.45	0.09
Bi-Fe	0.50	0.57
Cs-Fe	n.a.	0.71
Cu-Fe	0.51	0.44
Pb-Fe	0.77	0.78
Te-Fe	0.53	0.63
Zn-Fe	0.73	0.89
Bi-Cu	0.72	0.78
Sb-Cu	0.84	0.93
Hg-Cu	0.82.	0.94
Bi-Sb	0.65	0.66
Hg-Sb	0.85	0.94
Bi-Te	0.59	0.68
Bi-Zn	0.65	0.60

Pearson PM correlation; n.a. = not analysed.

Cluster analysis

Cluster analysis using Ward’s Method to cluster data standardised through the use of Z scores (squared Euclidean distance) indicates important differences for the different soil horizons and size fractions (Table 3). The B horizon for all fractions and the fine fraction of all horizons give similar clusters with the closest grouping of Ag, As, Hg, Sb, followed by Au, Cu, Fe, Mn, Mo, Pb, S and then Bi, Te, Zn for the total B horizon fractions and closest grouping of Ag, As, Hg, Sb, followed by Au, Cu, Mo and then Bi, Fe, Mn, Pb, S, Te, Zn for the fine fraction of all horizons. These groupings appear to reflect associations related to both primary and secondary mineralogical controls on the elements (note that Au is calculated on a very limited number of significant analyses). The primary gold ores in the area are pyritic, with accompanying gold, chalcopyrite, minor sphalerite, galena, bismuth- and copper-sulfosalts and a range of telluride minerals (McQueen & Perkins 1995).

Table 3. Summary of hierarchical cluster analysis showing different element clusters for analytical method ME-MS41 (1st to 3rd clusters)

Soil Horizon	Size Fraction	Cluster	Elements in Cluster
All	All	1	Ag, As, Au, Mn, S
All	All	2	Bi, Ca, Cs, Fe, Pb, Te, Zn
All	All	3	Ca, Hg, Sb
All	Coarse	1	Ag, Cu, Hg, Sb
All	Coarse	2	As, Au, Bi, Ca, Cs, Fe, Pb, Te, Zn
All	Coarse	3	Mn, Mo, S
All	Medium	1	Ag, As, Au, Mo
All	Medium	2	Bi, Ca, Cs, Fe, Pb, Te, Zn
All	Medium	3	Cu, Hg, Mn, S, Sb
All	Fine	1	Ag, As, Hg, Sb
All	Fine	2	Au, Cu, Mo
All	Fine	3	Bi, Ca, Cs, Fe, Mn, Pb, S, Te, Zn
A	All	1	Ag, Au, Mn, Mo, S
A	All	2	As, Cs, Fe, Pb, Zn
A	All	3	Bi, Ca, Cu, Hg, Sb, Te
B ₁	All	1	Ag, As, Hg, Sb
B ₁	All	2	Au, Cu, Fe, Mn, Mo, Pb, S
B ₁	All	3	Bi, Ca, Cs, Te, Zn
B ₂	All	1	Ag, Cu, Hg, Sb
B ₂	All	2	As, Mn, Mo
B ₂	All	3	Au, Bi, Ca, Cs, Fe, Pb, S, Te, Zn
C	All	1	Ag, Au, Hg, Mo
C	All	2	As, Pb, S, Sb
C	All	3	Bi, Ca, Cs, Cu, Fe, Mn, Te, Zn

Assessment of standard *aqua regia* digest and *aqua regia* 'Super Trace' digest

There is close agreement between analyses from the standard *aqua regia* digest (method ME-MS41) and the 'Super Trace' *aqua regia* leach (method ME-MS41L). Copper, Mo, Bi and Pb show slightly lower values for the 'Super Trace' method, possibly related to some analytical interference or 'rounding up' in the standard (ME-MS41) method. In most cases the differences are within the limit of error for the two methods. The 'Super Trace' method appears to provide finer resolution for those elements present in very low concentrations (e.g. Ag, Au, Bi, Hg, Sb and Te) due to the lower detection limit of the method.

Assessment of *aqua regia* digest and multi-acid digest

A horizon samples from five sites were cross analysed using a multi-acid digest (method ME-MS61). Comparison of the two methods indicates that Fe and Mn have higher values in the multi-acid digest (by 1.14-1.80 times and 1.23-4.78 times respectively), consistent with a component of these elements present in silicates (e.g. mafic minerals) or other phases (including ilmenite) not soluble in the *aqua regia* digest. Calcium and Cs have significantly higher values in the multi-acid digest (between 2.83-8.35 times and 2.7-5.23 times respectively), consistent with a major component of these elements in silicates (including un-weathered plagioclase feldspar, possibly hornblende and micas). Of the pathfinder trace elements, Pb and Zn show relatively higher abundances in the multi-acid digest analyses (by 1.16-2.63 times). Small amounts of Pb and Zn may be hosted by un-weathered silicate minerals. Antimony has significantly higher values (generally 1.63-13.5 times, but in one case up to 49 times) possibly reflecting a problem with the multi acid analytical technique for Sb. Bismuth, Cu and Mo show slightly higher values (by 1.05-2.13 times), whereas Ag and As have comparable values except for one sample with a much higher Ag value in the *aqua regia* digest, probably reflecting the presence of Ag with particulate Au and the 'nugget effect' of the host gold. The comparison of the two analytical methods indicates that the standard *aqua regia* method is able to effectively leach the key pathfinder elements from the non-silicate component of the soil samples (almost to their 'total' amounts).

Discussion

Soil Parameters

The distinct bimodal particle size distribution in soils down all the examined profiles reflects the persistence of quartz particles (in the range 250-1000 μm) and fine clay, derived from feldspars and mafic minerals (in the 2-90 μm fraction), after weathering of the granodiorite bedrock. The high abundance of quartz in the medium and coarse fractions is confirmed by mineralogical analysis. The key pathfinder elements will most likely be associated with the non-quartz component (e.g. clays, iron oxide/oxyhydroxide, specific secondary minerals) except for any primary minerals occluded in quartz and un-weathered rock fragments. Occluded phases will not be available to *aqua regia* digest, unless the sample is sufficiently pulverised.

Differences between the A horizon soil samples from the Majors Creek and Eurodux sites are consistent with relative depletion of the clay fraction and organic component in the former, possibly related to greater surface disturbance. There may also be a component of wind-blown silt in some of the soils in the Majors Creek area, as this material was observed in other soils, particularly on westward facing slopes.

Geochemical Data

Assessment of the geochemical data indicates that Fe as iron oxide/oxyhydroxide has an important influence on pathfinder element geochemistry in the Majors Creek soil profiles. This is indicated by moderate to strong positive correlation between Fe and these elements in the total data set and the individual profile distribution patterns. This influence is particularly marked in the medium and coarse size fractions, consistent with the observed presence of iron oxide/oxyhydroxides in larger aggregates and ferruginous pedogenic nodules, especially in the A horizon. In some profiles there is also a strong relationship between Fe and Mn in the coarse fraction, suggesting that some of the pedogenic nodules are also enriched in Mn. This association with iron oxide/oxyhydroxide highlights the importance of observing and noting the presence of ferruginous concentrations, aggregates and nodules in the soil profiles.

Although the A horizon shows the highest abundances for some elements, this is complicated by the apparent concentration of these elements (particularly Mn and variably Cu, Mo and Pb) with iron oxides in the pedogenic nodules and coarse iron oxide aggregates. The A horizon appears to be variably depleted in some elements and is also more likely affected by anthropogenic disturbance and addition of transported material (such as wind-blown dust and silt). It is thus a less consistent sampling medium.

For most target and pathfinder elements, the clay-rich B horizon (particularly B₂) provides the most consistent soil sampling medium for all size fractions. This is indicated by the consistent association of the key pathfinder elements and lesser variability in their abundance across the three size fractions in this horizon. In this study the B horizon samples detected anomalies for Au, As, Bi, Cu, Hg, Mo, Sb and elevated Ag, at the Tory Boy gold prospect (MCSS11). Depth to the B horizon varies across the region, depending on landscape setting, but is typically at 30-50 cm.

Frequency distributions for pathfinder elements from the total data set, suggest minimum threshold values for anomalies in the soil B horizon (Table 4). These values are similar to those detected in the B horizon at the Tory Boy prospect where there is known gold mineralisation (except for As and Pb which are lower at Tory Boy). Gold values detected in the fine fraction at Tory Boy are around 30 ppb.

Table 4. Potential threshold values for gold and pathfinder elements in B horizon soils Majors Creek area

Element	Ag	As	Au	Bi	Cu	Hg	Mo	Pb	Sb	Te	Zn
Unit	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Value	0,2	10	30	1.5	70	0.05	2.5	20	3	0,1	40

Particular element aspects

Particular aspects related to individual elements have useful implications for designing and interpreting soil geochemical surveys in the area.

Arsenic

Arsenic does not generally show a selective concentration with any particular soil fraction or horizon. The most anomalous levels are in fine fraction samples. It is possible that where abundant, arsenic shows an affinity for the fine fraction due to the larger surface area of finer particles assisting sorption processes (Ljung et al. 2006). Unusually, Arsenic does not show a strong positive correlation with Fe except for samples with low As levels. Cluster analysis of the fine fraction and B horizon samples indicates a clustering of As with Ag, Hg, Sb, but for other fractions it commonly clusters with Fe, Mn, Bi, Pb, Te and Zn which is more typical of an association with iron oxides/oxyhydroxides.

Arsenic in the soils is most likely derived from the weathering of pyrite (Figure 8). Arsenic anomalies thus provide some indication of pyritic mineralisation, but this may not invariably carry gold or associated base metals. A suitable geochemical exploration approach would be to use As as an initial pathfinder or locator of pyritic mineralised areas and then Cu, Pb, Zn, Ag and Au to locate potential gold mineralisation. Detailed follow up should also examine the distribution of the secondary associates: Bi, Mo, Sb and Te.

Antimony

Antimony does not appear to be concentrated in any particular size fraction or horizon and shows its strongest association with Cu and Hg. In the data set collected there is a distinct anomalous population of Sb values (>1.5 ppm) associated with known mineralisation at the Tory Boy prospect (site MCSS11). The source of Sb in the primary mineralisation would be mainly from sulfosalt minerals associated with the pyrite. It is clearly a useful pathfinder element in the area, but because of its relatively low abundance may require careful and low detection level analysis.

Bismuth

Bismuth shows low abundance in most samples (<0.5 ppm), but has anomalous concentrations in samples from sites MCSS3, MCSS9 and MCSS11, in the B horizon. It shows its strongest positive correlation with Cu, particularly in the C horizon, but also shows moderate positive correlation with Sb, Te and Fe in the B horizon. Its association in primary sulfide mineralisation is probably with Sb, Pb, Cu and Te in sulfosalts and tellurides (Figure 8) and it is an element that should be included in the suite of pathfinders for exploration.

Copper

After arsenic, copper is probably the most useful of the major pathfinder elements. In the samples studied Cu has highest abundance in the B and C horizons. It commonly shows higher concentration in the coarse fraction, particularly in the A horizon, probably due to adsorption on iron oxide fragments and soil nodules. Cluster analysis shows that in the B horizon and in the fine size fraction samples Cu groups with Au. The main source of Cu in the primary gold mineralisation is chalcopyrite, which commonly occurs as inclusions and veinlets in the host pyrite, and as less common inclusions of Cu-bearing sulfosalts (Figure 8). There is a very distinct anomalous population of Cu values at site MCSS11 in samples that are also anomalous in Sb.

Gold

For most samples in this study Au was below the detection limit (0.02 ppm) of the standard *aqua leach* method, apart from three samples: A horizon, coarse fraction from site MCSS3 (0.6 ppm); A horizon fine fraction from site MCSS71 (2.4 ppm); and C horizon fine fraction from site MCSS7 (1.7 ppm). Differences between replicates and analyses of 1 g samples by the two *aqua regia* methods and larger sample fire assay analysis suggest that the gold in these samples is in particulate form with a 'nuggety' distribution. This is consistent with the observation of particulate gold attached to quartz in one sample from site MCSS11 (Tory Boy prospect). For these sites there is a strong possibility of gold contamination related to previous mining activity.

Gold analyses from the 'Super Trace' *aqua regia* method (detection limit 0.0002 ppm) include values above 30 ppb at sites MCSS2, MCSS3, MCSS4 and MCSS11. These analyses were all of fine fraction material and Au did not show concentration in a particular horizon. Gold does not show strong correlation with any of the other elements analysed, but cluster analysis shows that it groups with Cu in the fine fraction and B horizon samples.

Lead

Lead is most abundant in the coarse fraction of the A horizon and fine fraction of the B horizon. It shows strongest correlation with Fe, possibly due to uptake on iron oxides (cf. Kaasalainen & Yli-Halla 2003). The highest abundance of Pb is at sites MCSS2, 4, 8, 10 and 11. Within the primary gold mineralisation Pb is hosted in small galena inclusions and rare telluride minerals (Figure 8). A component of background Pb is probably derived from the weathering of K-feldspar. Lead does not appear to be a good discriminating pathfinder element in the suite of samples studied, but should be included as a pathfinder for possible Ag-Pb-Zn mineralisation in the Braidwood system.

Mercury

Mercury generally has low abundance in the samples (<0.03 ppm by 'Super Trace' *aqua regia* method). Some values above this occur at sites MCSS1, 10 and 11), all in the fine fraction (not pulverised). While this is a positive result for site MCSS11, the potential for Hg contamination of soils in areas of historic gold mining and difficulties of Hg analysis at low levels, probably render this an equivocal pathfinder element. It may have a role in follow up surveys of initial anomalies.

Molybdenum

Molybdenum has an unusual distribution pattern relative to the other elements. It shows some association with Cu and Au and clusters with these two elements in the B horizon and fine fraction samples. However, it has its highest abundance levels in the coarse fraction, particularly in the A horizon, in some cases associated with high Fe, suggesting it may be taken up by ferruginous soil nodules. Trace amounts of molybdenite have been observed in miarolitic cavities at Dargues Reef, representing a potential primary source. However, it is also possible that Mo-fortified superphosphate has been applied to the soils in this area.

Silver

Silver shows its highest abundance in the fine fraction of the soils and clusters with As, Hg, Sb. In some samples (including in the coarse fraction) it correlates and clusters with Cu. In the primary sulfide mineralisation, Ag is likely present in its most mobile form in sulfosalts (hence association with As, Hg and Sb), as well as in less mobile form in gold (Figure 8). One high gold sample (at MCSS7) has high Ag probably alloyed with the gold.

Zinc

Zinc is most abundant in the B and C horizons, and appears to have been relatively leached from the A horizon. It does not appear to be preferentially concentrated in any particular size fraction, although it is commonly considered to be associated with the fine fraction in soils (e.g. Kaasalainen & Yli-Halla 2003; Ljung et al. 2006). In the soils studied here it is likely absorbed on clays and iron oxides. Zinc shows its strongest positive correlation with Fe followed by Bi. It also shows moderate positive correlation with Ca. It is not strongly correlated with Pb probably due to its greater mobility. It is difficult to define a particular anomalous population in the data set from the sites in this study except for one value from the fine fraction of the C horizon at site MCSS9 (at 87 ppm). It is nonetheless a useful pathfinder element, for highlighting gold-related Pb-Zn-Ag mineralisation in the area.

Calcium

Comparison of the Ca analyses for the *aqua regia* digest versus multi acid digest confirms that the soils have a low calcium carbonate and gypsum content

(generally corresponding to < 0.3 wt% Ca) and that higher Ca contents reflect Ca in the 'silicate' component (up to ca. 1 wt%). The Ca leached by the *aqua regia* digest shows a moderate positive correlation with Zn. Calcium was included in the study to test for carbonate in the soils (calcrete nodules), which can have an influence on Au mobility/concentration, and the absence of carbonate suggests that this element is not particularly useful.

Caesium

Caesium was included in the study as it was thought it may indicate areas of wall-rock alteration accompanying gold mineralisation. In the *aqua regia* digest methods Cs ranges in abundance from 0.04 to 3.53 ppm and is more abundant in the B and C horizon samples, reflecting association with more abundant clays in these samples. Analyses from the multi-acid digest method have higher Cs content indicating its presence in silicates (e.g. mica and feldspars) not digested by *aqua regia*. Sites of known gold mineralisation (e.g. Tory Boy prospect, Site MCSS11) do not appear to have significantly higher levels of Cs

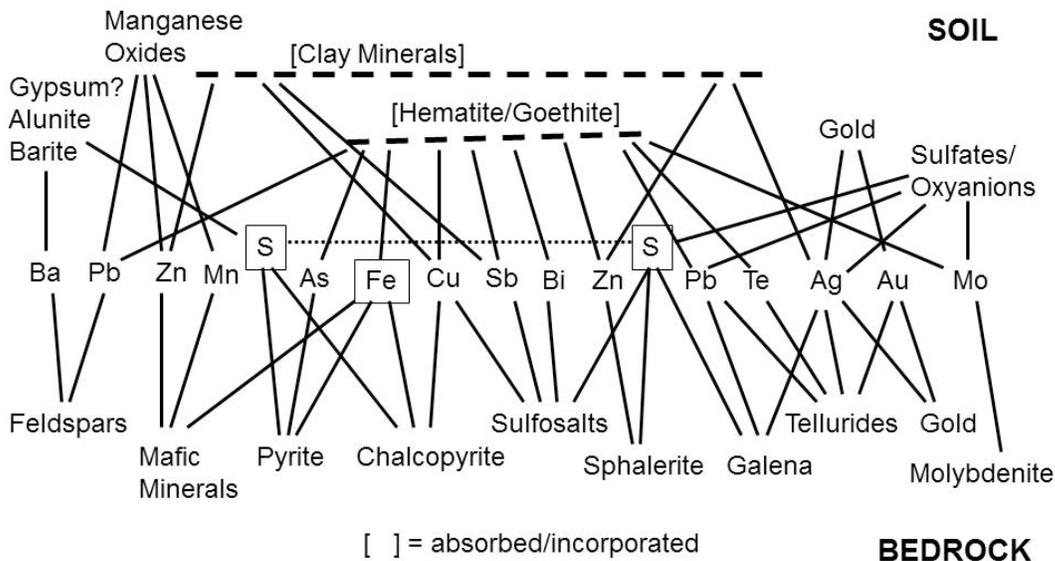


Figure 8. Connectogram showing key target and pathfinder elements and their likely bedrock sources and soil destination host phases in the Majors Creek area.

Conclusions

The typical granitic soils of the Braidwood region show a distinct bimodal particle size distribution related to the granodiorite weathering products of medium-grained quartz and fine-grained clays. The upper A horizon in the soils near Majors Creek is a light coloured sandy-silty loam with a very low clay content and appears to

have been variably disturbed by anthropogenic activity. In some areas it contains a wind-blown silt component.

The recommended strategy for geochemical exploration using soils in the area is to sample the bulk B horizon. Although the bulk fraction is diluted to some extent by quartz in the medium size component (relative to the fine fraction) it includes any coarser Fe-rich fraction (an important host for a number of trace elements) and any mineralised quartz in the medium and coarse fractions with occluded phases, including elemental gold. Samples should be pulverised to thoroughly homogenise and to expose any occluded phases.

In completely undisturbed sites there may be some benefit in sampling the A horizon, but targeting the coarse fraction. This could give a consistent medium, enriched in iron oxides/oxyhydroxides that have absorbed and preserved the key pathfinder elements (i.e. a little like an intra-soil lag component).

Soil sampling is not recommended in the highly disturbed areas of historic alluvial mining. Auger or air core drilling and sampling of the undisturbed saprolite/saprock would be the best alternative.

A standard *aqua regia* digest is a suitable partial leach for the target and pathfinder elements in the granitic soils of the Majors Creek – Braidwood area. A larger sample size would benefit gold detection by this method, due to the ‘nuggety’ distribution of high gold values. The ‘Super Trace’ method may have some advantage for the low abundance pathfinder elements (e.g. Ag, Bi, Hg, Sb and Te) and for low level Au. This method would be suitable for more detailed follow up of anomalies initially indicated by As, Cu, Pb, Zn and Mo.

Due to the influence of iron oxide/oxyhydroxides (goethite and hematite) and possibly also manganese oxides on pathfinder element concentrations, Fe and Mn should be analysed in the soil samples to assist in assessing element associations and anomalies.

Acknowledgments

The authors acknowledge Unity Mining Ltd. and particularly Greg Cozens for supporting this project and providing funding for the geochemical analyses. We also thank the landowners who allowed access to their properties. Andrew Higgins and Richard Greene at the Australian National University assisted with the particle size analysis.

References

DUNCAN, G.L. 1984. Exploration Licence 2063 – exploration summary and drilling report. Canyon Resources Pty Ltd April 1984. Geological Survey of New South Wales Open File Report , GS 1984/28.

KAASALAINEN, M., and YLI-HALLA, M., 2003. Use of sequential extraction to assess metal partitioning in soils. *Environmental Pollution*, **126**, 225-233.

LJUNG, K., SELINUS, O., OTABBONG, E. and BERGLUND, M., 2006. Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry*, **21**, 1613-1624.

McQUEEN, K.G. and PERKINS, C. 1995. The nature and origin of a granitoid-related gold deposit at Dargue's Reef, Major's Creek, New South Wales. *Economic Geology*, **90**, 1646-1662.

MIDDLETON, T.W. 1970. A summary report of the available information on the gold fields of the Upper Shoalhaven-Araluen area, NSW. New South Wales Geological Survey, Report 1970/195.