Transported cover in northwestern Victoria, Australia – an impediment to geochemical exploration for gold

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Abstract

At the Kewell and Wildwood prospects in northwestern Victoria, where transported cover (20-130 m depth) masks gold mineralization, the use of partial extraction analyses of regolith profiles, soil and pedogenic carbonate were assessed. Such techniques gave inconsistent results. Arsenic, Au and Li were the only elements that had greater abundance in the mineralized bedrock and saprolite than the background samples and dispersed vertically through the saprolite, but not extensively into the cover. The interface between sedimentary units, corresponding also to the water table depth prevents further vertical hydromorphic dispersion, but identifies a zone of pathfinder element enrichment. No vertical dispersion of these elements reached the surface, discounting the use of the surface partial extractions even though the proprietary Bacterial Leach extraction of soil predicted mineralization in the shallow cover regions (<20 m) based on hypergeometric statistical evaluation and a multi-element index of Ni, Cu, Ga, Ge, Se, W and Bi. Near-surface sampling and any combination of partial extractions are not a viable approach for exploration through cover in northwestern Victoria. The cover is too thick and the provenance of the sediments has more influence on variation in geochemical abundance than dispersion from any underlying mineralization.

Key words: vertical dispersion, selective extraction, partial digestion, bacterial leach, pedogenic carbonate, Murray Basin, soil, regolith, mineralization

1. Introduction

Geochemical exploration is difficult in the northwestern landscapes of Victoria, Australia. Sediments up to 130 m thick effectively mask northern extensions of known Au mineralized systems, such as those of the Golden Triangle area: Bendigo, Ballarat and Stawell (Fig. 1). These three sites have produced 697, 408 and 82 t of gold, respectively (Phillips and Hughes, 1996). Most discoveries were made by panning stream sediments, initially leading to alluvial Au deposits and subsequently to the discovery of auriferous quartz veins in nearby outcropping bedrock. More recently, Au-bearing sulfides have become the targets for deep underground mining. Now, exploration focus has shifted to the northern regions of Victoria, with an emphasis on geophysical methods, whereas geochemical methods have not been tested extensively.

Stawell is on the western-most extent of the Golden Triangle and the Stawell gold mine, operated by Northgate Minerals Corporation, is one of only two currently operating mines. Since the late 1990s, exploration geologists have used a simplified geological model for exploring the basalt domes, typified by that at the Stawell mine that occurs along the
concealed Stawell Corridor NW of the town (Fig. 1). Magnetic targets, possibly reflecting mafic volcanic host rocks, have been explored with some success by drilling through up to 150 m of Murray Basin sediments. The deposits of Kewell, Wildwood, and other deposits and prospects in the Stawell Corridor (Fig. 1) were discovered using this method. Localized targeting of mineralization has been improved by fluid flow and 3D deformation modeling of the basalt domes (Schaubs et al., 2006) and by use of alteration mineralogy mapping (Dugdale et al., 2006, 2010). Exploration geochemistry (excluding bedrock alteration) has not been a major part of these models, but understanding the geochemical dispersion into the cover and testing geochemical techniques may enhance current exploration strategies in the region.

Vertical migration of elements from a primary source at depth to the surface is necessary to create anomalies. Potential metal migration mechanisms have been investigated (Aspandiar et al., 2004, 2006; Cameron et al., 2004; Hamilton et al., 2004; Mann et al., 2005), but studies of a complete regolith profile such as those by Sergeev and Gray (2001), Tonui et al. (2003) and Lintern (2007) are not always possible. Partial extraction analyses of soils are commonly used in an attempt to detect subtle geochemical dispersion signatures (Bajc, 1998; Cameron et al., 2004; Cohen et al., 1998; Kelley et al., 2003; Mann et al., 1998; Noble and Stanley, 2009; Williams and Gunn, 2002; Xueqiu, 1998).

Geochemical exploration for Au through transported cover has been locally successful in other parts of the world including the western part of Australia (Butt et al., 2005), central and eastern Canada (McClenaghan et al., 2000), northern China (Wang et al., 2007) and western Brazil (Cornelius et al., 2007) using a variety of sample media. However, in eastern Australia, more specifically Victoria, there are few examples. Commonly, the depth of cover is <10 m in areas where successful results have been obtained.

Using surface soils, Scott and Turner (2007) and Scott and van Riel (1999) investigated three gold prospects over different depths of cover (0, 5 and >40 m) in northern Victoria with some success. Proximal to the Stawell Gold Mine, Noble et al. (2010) determined strong surface soil anomalies for As and Cr to delineate the Au mineralization, but in a dominantly residual setting.

Apart from soil, other near surface geochemical sample media are available. Pedogenic carbonate has been used for Au exploration with great success in southern Australia over the past few decades (Anand and Williamson, 2000; Chen et al., 2002; Hill et al., 1999; Lintern, 2001; McQueen et al., 1999), but not tested in the Stawell Corridor. Likewise, groundwater investigations have taken place in northwestern Victoria (Giblin et al., 1992; Giblin, 1997; 2002), but not in the Stawell Corridor. Giblin (1997, 2002) did show Au and As anomalies in groundwater associated with major gold deposits to the south and east of Stawell, but this region does not have the complexity of a thick, transported cover. Biogeochemistry has been tested in the Ballarat East Goldfield approximately 80 km SE of Stawell (Arne et al., 1999; Fig. 1). They determined numerous plant species such as *Pinus radiata*, *Cassina aculeata* and *Eucalyptus* sp. were able to accumulate anomalous metals, including Au, near mineralized sites, but again there was little to no transported cover in this region.

Indentifying methods and sample media in new environments is difficult to establish. Surface signatures and anomalies may not always be linked to the buried mineralization, but determining this relationship is critical for successful geochemical exploration. This paper presents an assessment of the effectiveness of numerous partial extractions with the near surface sample media of pedogenic carbonate and soils, coupled with profile geochemistry to evaluate element dispersion from the mineralized source.
2. Geological and regolith setting

2.1 Location and climate

The Wildwood and Kewell Au deposits are 30 and 100 km NE of Stawell, Victoria, respectively. Wildwood is located at 36°52'S, 142°40'E, and Kewell is located at 36°25'S, 142°19'E (Fig. 1). The climate is temperate with warm summers and cool winters. Mean minimum and maximum temperatures at Stawell are 13 and 28°C in February, and 4 and 12°C in July. The mean annual rainfall is 576 mm (Bureau of Meteorology, 2006). Vegetation is dominated by crops interspersed with mixed woodlands of *Eucalyptus* with minor *Acacia* species.

2.2 Geology

The Stawell Goldfield, encompassing the Kewell and Wildwood deposits, occurs within the Stawell Zone of the Lachlan Fold Belt in the strongly deformed early Palaeozoic Saint Arnaud Group turbidites, which contain fault-bounded Cambrian volcanic and volcaniclastic rocks (Miller et al., 2006; Schaus et al., 2006). These rocks are intruded and contact-metamorphosed by the large Devonian I-type Stawell Granite (Miller et al., 2001). A number of basalt domes, important for mineralization, occur within a 15 km wide belt, bounded by the east dipping Moyston Fault on the west and the west dipping Coongee Fault to the east (Schaus et al., 2006).

Mineralization at Wildwood and Kewell is hosted by the Stawell Facies (Dugdale et al., 2006), which are deformed and chlorite-sericite-altered mudstones. The sulfide-enriched Stawell Facies which occurs adjacent to barren basalt domes, is referred to as Magdala-style mineralization. The Wildwood basalt dome is approximately 3 km long, with the mineralized Stawell Facies along the eastern flank. At Kewell, there is a similar-sized 3 km long basalt dome with Au mineralization along both flanks, and ore-grade mineralization (>3.46 g/t Au) on the southwest flank of the dome (Dugdale, 2004). Gold is hosted within sulfide minerals including pyrite, pyrrhotite and arsenopyrite. Palaeozoic bedrock is overlain by Tertiary and Quaternary sediments discussed in the following section. A review of the regional and local geology is provided by Dugdale et al. (2010).

2.3 Regolith

The Palaeozoic bedrock is commonly weathered, with variable thicknesses (1-30 m) of saprolite and saprock, occur beneath the Murray Basin sediments at Kewell and Wildwood (Noble, 2007; Fig. 2). The transported Murray Basin sediments comprise the Geera Clay and Loxton Parilla Sands of variable thickness (30-100 m; Fig. 2). The Geera Clay is late-Oligocene to middle-Miocene, and consists of black, olive grey, dark grey or dark green silt and clay, deposited in a shallow to marginal marine environment (Brown and Stephenson, 1991). The dominant minerals in the Geera Clay are smectite, kaolinite and illite, with pyrite, hematite, siderite, natrojarosite and dolomite. At Kewell, there are distinctive bands (1-5 m thick) of highly calcareous material, dominantly shells (Fig. 2). The Geera Clay is approximately 20–40 m thick at Wildwood, 70 m thick at Kewell and does not outcrop (Noble, 2007).

The late Pliocene-Miocene Loxton-Parilla Sands are coarse to fine grained, well-sorted quartz sands deposited in marginal to shallow marine, estuarine and fluvial environments
Poorly-sorted quartz sand and micaceous gravels occur locally, with some marine fossils. The unit is generally friable to unconsolidated with <15% clay; the clay content typically increases with depth. The upper sections of the unit are pale yellow to reddish-brown, whereas the lowest sections are grey and pyritic. The Loxton-Parilla Sands are approximately 10 and 30 m thick at the Wildwood and Kewell prospects, respectively (Noble, 2007). The unit rarely outcrops, being overlain by a thin cover of more recent Quaternary (Pleistocene) fluvial and aeolian sediments, and soil.

The soils in the Stawell Corridor are moderately weathered, with smectitic and kaolinitic clays, moderate to high cation exchange capacity, exhibit high base saturation and are classified as vertosols and sodosols using the Australian soil classification system (Isbell, 1996), and as vertisols and alfisols using the U.S. Soil Taxonomy (Soil Survey Staff, 1999).

The soils immediately above the Wildwood mineralization are dominated by smectite, kaolinite and some illite, the pH ranges from 5.7-9.0 with most samples showing a pH of 6.5 - 7.5 (Noble, 2007). Dry soil colors in the argillic horizons (35-85 cm) are brown, pale brown and yellowish brown with 7.5YR to 10YR hues (Munsell® colors). The lighter soil colors in these horizons are associated with pedogenic carbonate. Gleyed features are also evident in these soil profiles.

The commonly flat terrain of the Wimmera Plains have some minor ephemeral drainages and local depressions of a few metres in depth. Slight topographical rises have a discontinuous ferruginous and/or siliceous duricrust at the surface (Williams and Radojkovic, 2004). The water table occurs at approximately 30 m depth, often associated with the transition from Loxton Parilla Sand to Geera Clays. Other seasonal perched water zones may be present between the water table and the surface.

3. Sampling and analysis

3.1 Sampling

3.1.1 Regolith profile. At Kewell, eleven regolith profiles were sampled using air core drill cuttings. Approximately 1 kg of sample was collected every 5 m from profiles 80 to 130 m deep. Prior to shipping, bags were left open allowing the bulk of the moisture to evaporate from the samples. All samples were sealed and prepared at the Environmental Inorganic Geochemistry Group (EIGG) laboratory, at Curtin University of Technology, Perth.

3.1.2 Soil. Initially, 21 soil samples were collected by Stawell Gold Mine personnel along a 500 m traverse at Kewell to test a Bacterial Leach extraction (described below). Samples were collected at 1.5 m depth by hydraulic auger with approximately 2 kg of sample placed in a sealed plastic bag. At Wildwood, soils were collected along five traverses perpendicular to the strike of the underlying mineralization. The length of the traverses varied from 300 to 400 m, with sample spacing of 28 m. Samples were collected by hand auger from depths of 30 - 85 cm, targeting a recognizable illuvial clay or strongly argillic horizon (B-horizon). Approximately 750 g of soil was collected at each site. Eight field duplicates were also taken 1 m away from the original sample points.

3.1.3 Pedogenic carbonate. Approximately 1600 samples of pedogenic carbonate were collected by Stawell Gold Mine personnel over an area of 525 km² to the NW of Stawell. Samples were collected from pits excavated with a small backhoe along approximately 60 traverses. Hydrochloric acid (~1M) was used to identify the strongest carbonate development for sampling. Two kg from the strongest carbonate horizon was sampled and placed in calico
bags. The depths sampled varied from 50-180 cm, however, depths were uniform across a single traverse (S. Harrison, pers. comm. 2004, Stawell Gold Mine Geochemical Consultant).

3.2 Analysis

3.2.1 Sample preparation. Samples were air dried, split and sieved. The <2 mm fraction was used for bulk soil properties. Most geochemical analyses were conducted on the <250 µm fraction (Soil Survey Staff, 1996), the Bacterial Leach was conducted on the <63 µm fraction.

3.2.2 Bulk property analysis. All samples were tested for soil pH and EC using a 1:1 soil to water ratio (McClean, 1982). Munsell moist soil color, pH and EC were determined on the bulk or <2 mm size fraction (Soil Survey Staff, 1993). Clays and other dominant minerals were identified by near infrared spectral analysis using an ASD field spectrometer with The Spectral Geologist®, and dry powder (<63 µm) X-Ray Diffraction analysis (Philips® X’Pert MPD, Almelo, Netherlands) to provide a qualitative estimate of the minerals present (CSIRO laboratories, Kensington, WA).

3.2.3 Geochemical extractions. Three main extractions were used in this study: total dissolution for a complete composition, a weak hydroxylamine hydrochloride (HA) extraction to digest elements bound in the amorphous Mn oxide fraction (Chao, 1984) and a Bacterial Leach (BL) partial, unselective extraction (Table 1). The BL extraction was believed to be a partial digestion, with no consistent phase preference, although recent work suggests that it has a preference for amorphous Mn oxides similar to the HA extraction (Noble, 2007).

An aqua regia digestion of the regolith carbonate samples was conducted by an unidentified commercial laboratory contracted by the Stawell Gold Mine.

Total dissolution. Soil (0.5 ±0.01 g) was placed in a 60 mL Teflon® beaker, to which 16 mL of HNO₃ (15.1M) and 4 mL of perchloric (9.2M) acid (4:1) were added, followed by approximately 40 mL of hydrofluoric acid (22.6M). The closed beakers were placed on hotplates at 160°C for 12 hrs. The lids were then removed, the temperature increased to approximately 200°C and the sample reduced to incipient dryness. Nitric (0.75 mL; 15.1) and hydrochloric acids (0.25 mL; 11.65M) were added to the beaker to dissolve the residue and the solution was made up to 50 mL with milliQ water (Noble, 2007).

Weak hydroxylamine hydrochloride (HA). Soil samples (0.5 ± 0.01 g) were combined with 12 mL of a 0.1M HA and 0.01M HNO₃ mixture in a 15 mL polypropylene centrifuge tube. The sample was then shaken for 30 minutes, centrifuged for 10 minutes (4500 rpm), and the supernatant decanted into test tubes for analysis.

Bacterial Leach (BL). Soil (1 ± 0.01 g) was placed in 120 mL plastic screw-top containers. One millilitre of bacterial carbohydrate food source diluted with 6 mL milliQ water was added to the soil, followed by 0.5 mL of bacteria solution diluted with 7.5 mL of milliQ water. The method used a bacterial strain that was proprietary technology of the Department of Applied Chemistry at Curtin University of Technology at the time of analysis (now registered as LocatOre®, by Sologic Pty Ltd). Samples were rolled for 1.5 h at approximately 20 rpm. During this time, the bacteria replicate about 4 times, using up the food source before dying. The samples were then placed on the bench and allowed to settle for approximately 10 minutes. Approximately 10-12 mL of the relatively clear solution was poured into a 15 mL plastic tube and centrifuged for 5 minutes at 3000 rpm. The supernatant of each sample (7-12 mL) was then poured from the centrifuge tube into a plastic disposable tube and 100 µL of HNO₃ (70%) was added using a micropipette to kill any remnant bacteria prior to analysis.
3.2.6 Analytical instruments. All extractions were analyzed by ICP-MS (VG-PlasmaQuad3, United Kingdom) and ICP-OES (Perkin Elmer-PE3300DV, U.S.A) for Al, As, Au, Ba, Be, Bi, Ca, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mo, Mn, Na, Ni, Pb, Sb, Sn, Te, Th, Ti, U, V, W and Zn. Commercially available standards and previously analyzed internal standards, as well as reagent blanks were included to check accuracy and precision. Field duplicates, method duplicates and analytical duplicates (split solutions) were randomly incorporated into all analytical batches (Noble, 2007). The pedogenic carbonate samples had been previously analyzed by ICP-MS/OES and AAS for Ag, As, Au, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Te, Th, Ti, U, W and Zn (following an aqua regia digest) at a commercial laboratory with no details available.

3.3 Data treatment

3.3.1 Element indices. Various pathfinder and target element concentrations have been used to improve definition of anomalies related to ore systems. The BL used the following element indices (EIs) provided by the proprietor to enhance the identification of anomalies:

Element Index 1 = \(\frac{(Ni \times Cu \times Ga \times Ge \times Se \times W \times Bi)}{1 \times 10^7}\)

Element Index 2 = \(\frac{Element \ Index \ 1}{(Ti \times V)}\) \(\times 1 \times 10^6\)

Element Index 3 = \(\frac{(Ni \times Cu \times Se \times W \times As \times Sb \times Te)}{1 \times 10^8}\)

Element Index 4 = \(\frac{(Element \ Index \ 1 \times V \times Cr)}{1 \times 10^6}\)

Whilst some of the elements (Ni, Cu) are pathfinders for sulfide ore systems, others are used as lithological discriminators, and were tailored by the proprietor to the Kewell orientation survey over Au mineralization. Some of these elements are considered an oxidation suite by Clark (1996), suggesting the following elements can migrate as halide volatiles or halogen gases: Cl, Br, I, As, Sb, Mo, W, Se and Te. Others were used to differentiate weathering environments and rock types (Cr, V and Ti).

For comparison to other methods of interpretation using multiple components, the following index was also used: Arsenic (or other pathfinder elements) / Mn

This was used for the HA extraction, which targets the amorphous Mn oxide fraction.

The CHI*6 index (As + 3.56*Sb + 10*Bi + 3*Mo + 30*Ag + 30*Sn + 10*W + 3.5*Se) was developed by Smith and Perdrix (1983). It has been effectively used to detect anomalous corridors of chalcophile elements in Western Australia (Anand et al., 1989; Cornelius et al., 2008; Smith et al., 1989) using laterite residuum. This index is the weighted sum of important pathfinder elements and removes some of the bias associated with a simple summation. The CHI*6 index is, however, influenced by extreme single element concentrations (Cornelius, et al., 2008), as is the case with many other multi-component index, and was empirically customized for use with lateritic residuum.

3.3.2 Hypergeometric probability. Hypergeometric probability statistics based on the work of Stanley (2003) and Stanley and Noble (2007, 2008), were used to give a quantitative comparison between the geochemical extractions and to assess the predictive accuracy. The initial evaluation at Wildwood used a threshold = 3\textsuperscript{rd} Quartile + 2.5 * interquartile range (IQR), which by definition falls between the defined mild outlier (3\textsuperscript{rd} Q + 1*IQR) and extreme outlier (3\textsuperscript{rd} Q + 3*IQR; Tukey, 1977).
4. Results

4.1 Profiles

Element distribution in the regolith at Kewell shows that little dispersion has occurred vertically above the mineralization. The mineralized profiles are above sulfides and basalt that contain significant Au and As, whereas the other profiles are considered barren and are situated above sulfides and basalt with low Au and As concentrations.

Arsenic, has been dispersed across the interface of the unconformity between saprolite and the Geera Clay, and presents a broader vertical (and probably horizontal) target (5 m) at low concentrations (>50 ppm) compared to the primary Au-As mineralized source (Table 3). Both four-acid (Total) and hydroxylamine hydrochloride (HA) extractable As showed similar vertical dispersion patterns, although the concentrations of As extracted from the HA were much lower. The Geera Clay has greater total As concentrations on one sample over mineralization, immediately above saprolite, suggesting little dispersion of As into the transported cover and certainly not extending to the surface (Fig. 5A and B). The total As concentration in the background profiles was not interpreted as few data points exist.

The HA extracted As was greatest in the saprolite and decreased towards the surface (Fig. 5B), indicating that some As is weathered and released into the transported cover, but at a depth of tens of meters below the surface. The regolith profiles over barren bedrock show a similar As abundance throughout much of the profile to those over mineralization, with the exception of some lower concentrations in the Geera Clay (60-90 m). This dominant As signature is attributed to sediment provenance.

The HA extracted Mn concentrations were different in profile between those above mineralization and those above barren basalt. The vertical distribution trend or shape is similar, but less Mn is present in the mineralized profiles at 15-30 m depth and more at 30-50 m depth (Fig. 5C). These depths correspond to the regions above and below the water table. Since the weak HA extraction commonly liberates metals bound to Mn oxides (Chao, 1984) abundances of other elements were normalized against Mn concentration. Arsenic:Mn abundance in the mineralized profiles increases just below the surface in the seasonally saturated zone and in the capillary fringe above the water-table at 20-30 m (Fig. 5D). The As:Mn data were also marginally greater in the Geera Clay between 55 and 100 m for regolith above mineralization compared to that above barren sulfides, although this is not obvious and or consistent as the results near the water-table (Fig. 5D). The significant contrast is not only due to the greater As concentrations, but also to the apparent depletion of Mn in the profiles above the water table and enrichment of Mn below the water table for the samples associated with mineralization (Fig. 5D).

Iron oxides also host As, and can be weakly extracted by HA, but Fe concentrations were not determined. Concentrations of other elements, such as Pb, Te, Zn and Co, were also higher in the seasonally saturated/capillary fringe zone at 10-30 m in some of the profiles over mineralization than the profiles over the barren rocks, particularly when normalized for Mn abundance (Noble, 2007). Lithium consistently increased towards the surface, using the HA extraction, and is greater above the mineralization in one of the three profiles. However, Li concentrations show no discrimination between barren and mineralized profiles at the surface (Fig. 6).

The BL extraction was not tested on the vertical profiles. However, the BL targets Mn oxides in a similar mechanism to the HA extraction (Noble, 2007), so results from the HA were used as a proxy for the BL extraction and the Element Indices used for BL were applied
to the HA data. Element Index 1 shows no indication of vertical migration from mineralization. The Element Index 1 and CHI*6 Index (Fig. 6) for the mineralized samples are slightly greater in the deepest sections of the profile, again attributed to some minor dispersion from the saprolite into the transported materials. The EI 1 results for the mineralized profiles are lower than the barren profiles near the water table and the in the Loxton Parilla sands, and not distinctive from the barren samples in the near-surface environment.

The EC varies from approximately 2 to 20 mS/cm, with a decreasing trend moving up the profile and increasing again slightly at the surface (Fig. 6). This pattern is similar for some of the major elements (Ca, Fe, K, Mg, Na) due to the direct relationship between conductivity and salt content. Some of the mineralized profiles have slightly lower pH values in the middle of the Geera Clay (Fig. 6). The near surface pH is not different between mineralized and barren profiles, with pH ranging between 6.8 and 8.2, as is common for soils in this area (Noble, 2007).

4.2 Soils

The single orientation survey at Kewell showed the BL gives a greater response over mineralization using the Element Index 1 (Fig. 3). Applying EI 1 from Kewell to five traverses at Wildwood produced 2 of 5 successful predictions of mineralization based on a vertical migration model and hypergeometric statistical evaluation (Fig. 4; Table 2). Both traverses with successful predictions are in the southern section of the prospect where the depth of cover is shallow (20 - 30 m). A surface signature may be masked where the cover is deeper (~ 50 - 70 m) to the north.

These results indicate the method is 40% successful in predicting mineralization, but there is no evidence to link the combination of elements in EI 1 to the mineralization style, i.e. no As or Au. A large multipoint anomaly in traverse 4 exists 50 m east of the mineralization. This may indicate either that the dispersion from mineralization is not vertical or that the anomaly is due to other pedogenic or older sedimentary processes. The other tested extractions (total and HA) did not show anomalous results linked to mineralization, either for single elements or using element combinations. Surface soil geochemical results thus appear too inconsistent to provide a viable exploration guide.

4.3 Pedogenic carbonates

Pedogenic carbonate has few anomalous Au concentrations (>99th percentile or 4-20 ppb) in the study area. The mean and median Au concentrations are 1.42 ppb and 1.25 ppb, respectively (Table 4). Of particular interest is the region 2 km west of the Ashens prospect, where the Au anomaly has a trend consistent with the NNW-SSE strike of mineralization in the Stawell Corridor (Fig. 7). This area also has a localized As anomaly, although not evident in the regional data set (Fig. 8). Few single point anomalies (>99th percentile or 4 ppb Au) are also present, but are not clear targets. Consequently, these areas have not been explored further.

Other geochemical patterns are observed in the pedogenic carbonate. Arsenic (Fig. 8) and Bi abundances increases to the north. Greater As concentrations occur in carbonate north of Kewell, but do not overlie mineralization (Fig. 8). The trend observed in As concentrations near Kewell has some relationship to the elevated U (compared to K and Th) observed in the
radiometric geophysical data and is linked to present drainage systems and Holocene alluvium (compare Fig. 8A with 8C background). Other geochemical patterns are also observed: Cr, Co, U and Ni (not shown) are found in greater concentrations in the southern parts of the study area (Fig. 8).

5. Discussion

Understanding dispersion, both in extent and probable mechanisms of metal migration, is critical to successful geochemical exploration, particularly in linking surface expression to buried mineralization through transported cover. At Kewell, dispersion does not extend significantly above the water table, suggesting it to be predominantly hydromorphic. Capillarity may also provide the mechanism for metal migration just above the water table, and be responsible for the greater concentrations in the Loxton Parilla Sands (Fig. 5), but significant migration of metals further above this zone is too subtle to detect. The likely hydromorphic dispersion mechanism agrees with the model suggested by Scott and van Riel (1999) where mechanical dispersion was important in shallow (<5 m) cover and hydromorphic dispersion would dominate the dispersion in deeper covered environments (as occurs at Kewell).

The only comparable study of vertical dispersion in regolith profiles in the region is that at Broken Hill, New South Wales, by Tonui et al. (2003) approximately 500 km to the north and in a different basin setting. There, significant hydromorphic dispersion of base metals occurred in the residual regolith, and to a lesser extent the overlying sediments, and the distribution was associated with the amorphous mineral phases. These results are similar to those of this study, which has shown some minor dispersion of As into the overlying transported cover.

Arsenic is the best pathfinder in this study and this is confirmed in other studies (Noble et al., 2010; Scott and van Riel, 1999; Scott and Turner, 2007). Antimony was also valuable pathfinder in other areas (Scott and Turner, 2007), but was not the case at Kewell or Wildwood. Arsenic concentration above mineralization is greater where the interface between the Geera Clay and Loxton Parilla Sands corresponds to the water table. This zone may be important for exploration. Drilling to 20-30 m for regolith sampling is not recommended, as it is expensive and the additional costs and time for drilling to saprock are not much greater and will provide better results. However, regional groundwater sampling from existing wells and bores or biogeochemical sampling of deep rooted trees could be cost-effective methods for regional targeting that has not been tested in the Stawell Corridor. Hydrogeochemistry has been useful in other regions of Victoria (Giblin et al., 1992; Giblin, 1997; 2002) and biogeochemistry has shown potential in limited study (Arne et al., 1999). Any future investigation in the Wildwood and Kewell regions of Victoria should evaluate groundwater sampling as a method of regional exploration through cover. Other studies in Australia have successfully delineated sulfide ore bodies using groundwater (Gray and Noble, 2006) and this may also be effective in NW Victoria. Vegetation sampling may be useful, but the rooting depths and saline groundwater may limit the viability of biogeochemical exploration for Au in this area.

Overall, the thicker cover (40 -100 m) produced less successful predictions in the study by Scott and Turner (2007), which is common with the findings of this study. Based on the limited dispersion in the profiles it remains unlikely that the surface anomalies are clearly linked to the mineralization even through 20 m of cover and the results of the surface geochemistry of this study is a statistical coincidence. The application of partial extraction
techniques was provided as a possible improvement to geochemical exploration in northern Victoria (Scott and van Riel, 1999), but this study at Wildwood and Kewell, and the additional work by Noble (2007) on partial extractions indicates there is limited value in using these techniques.

Gold is commonly associated with pedogenic carbonate (calcrete), and sampling these carbonate facies is a common exploration strategy. However, at Stawell the soil samples with the highest Au concentrations are not high in Ca or Mg, and indeed were not as strongly developed pedogenic carbonates as other samples. This observation in NW Victoria is similar to work conducted at the Goornong South Au deposit in northern Victoria, where Au was preferentially concentrated in the fine (<63 µm) size fraction and not associated with the carbonate fraction (Scott and van Riel, 1999). Although greater Ca concentrations may result in greater Au concentrations as observed in vertical profiles in other studies with shallow cover <10 m (Lintern and Butt 1997; Lintern 2001; Hill et al. 1999), the morphology and composition of the carbonate facies is also shown to be important (McQueen et al. 1999). Nodules have higher Au concentrations than weakly developed powdery carbonates, although consistency of sampling carbonate morphology is most important (McQueen et al. 1999). Similar carbonates with a higher Ca:Mg ratio have higher concentrations of Au than low Ca:Mg carbonates, and give greater contrast. The anomalous Au-in-carbonate samples from NW Victoria have low to average Ca (4-6%) and Mg (0.5-1%) concentrations (Table 4), and show poorly developed carbonate facies. As a result of this low concentration of carbonate, this may make the anomalism of the samples in this study even greater. It would be expected that these samples should have low Au concentrations. Even with this finding the lack, the lack of Au anomalous responses over known targets indicates this surface geochemical technique is ineffective in this environment.

The numerous elements analyzed from the pedogenic carbonates are not valuable for exploration, but are important for baseline characterization and for environmental management (Table 4). Pedogenic carbonate is not pure and reflects the composition of the substrate. Changes in the environment may be reflected in pedogenic carbonates, and having a large background data set will invariably aid any future comparison to present conditions. Whereas Au concentrations are sporadic in pedogenic carbonate, elements such as Ni, Cr, Co and U have more congruent patterns, with greater concentrations in the southern area of the study. These variations may be related to a change in underlying parent materials, as the southern section of this region is less influenced by the Tertiary Parilla sands of marine origin, and has a thicker cover of Quaternary non marine sediments (Fig. 8A; Brown and Stephenson 1991; Department of Primary Industries, 2008). This geochemical transition is also evident in the radiometric geophysics (Fig. 8C; Department of Primary Industries, 2008).

The use of pedogenic carbonate as an exploration sampling medium could be valuable in areas of cover, especially where the cover is <10 m. Carbonates form in areas that receive less than 500 mm rain, but only a small area in Victoria exists that fits both the criteria for formation (rainfall) and depth of cover (Fig. 9).

6. Conclusions

This study demonstrated the difficulty of Au exploration in the covered region of NW Victoria where no consistent surface expression of underlying mineralization exists. In the deeper profiles (>100 m) the surface geochemistry did not reflect the bedrock because no elements were dispersed from the mineralization to the surface. Hydromorphic dispersion occurs for As and Li, but only over a small distance. The interface between the Loxton Parilla
Sand and the Geera Clay that is associated with the depth of the water table limits further dispersion, but identifies a zone that may be targeted for future geochemical exploration in this region, with interface/vadose zone regolith sampling via a proxy such as deep-rooted species for biogeochemistry or groundwater sampling of pre-existing wells the most likely strategies to succeed. Hydrogeochemistry and biogeochemistry may be viable exploration strategies that should be evaluated further.

The surface geochemical exploration techniques tested in this study (soil and pedogenic carbonate) did not consistently detect mineralization through cover in Victoria. Future studies for geochemical exploration through cover in the area should examine the geochemical gradient of shallower profiles (<30 m) e.g., the southern extent of the Wildwood prospect.

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References


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TABLES

Table Captions:

Table 1. – Analytical procedures applied to the different samples used in this study.

Table 2. – Hypergeometric evaluation of five traverses using the Bacterial Leach Element Index1 at the Wildwood prospect.

Table 3. – Sample media summary table with dispersion distances

Table 4. – Descriptive statistics of the measureable elemental composition of the regolith carbonate materials in the studied region. Not all of the 1624 samples analysed were
reported for all the elements and many were below detection limits, hence the n values associated with each element varies.* *All values in mg kg\(^{-1}\), except Au in µg kg\(^{-1}\).

FIGURES

Figure Captions:

Fig. 1. Location of the study area and the historic “golden triangle” region. The Stawell Zone; geology with targets under Murray Basin cover (modified from Leviathan Resources, 2004).

Fig. 2. Generalized cross section through Kewell prospect, 60 km NW of Stawell. Depth to basalt is approximately 100m.

Fig. 3. Near surface (B-horizon) soil traverses at Kewell using bacterial leach (BL), hydroxylamine hydrochloride (HA) and a four-acid near-total (Total) extraction with Element Index 1 \([(Ni \times Cu \times Ga \times Ge \times Se \times W \times Bi) / 1 \times 10^7]\). Underlying mineralization is indicated by the solid bar.

Fig. 4. Near surface (B-horizon) soil traverses at Wildwood using bacterial leach (BL), hydroxylamine hydrochloride (HA) and a four-acid near-total (Total) extraction with Element Index 1 \([(Ni \times Cu \times Ga \times Ge \times Se \times W \times Bi) / 1 \times 10^7]\). General geology profile is shown with the underlying mineralization indicated by the solid bar on each traverse. The x axis indicates the distance (m).

Fig. 5. Regolith profile geochemistry. Total As (A), hydroxylamine hydrochloride-partially extracted As (B), hydroxylamine hydrochloride-partially extracted Mn (C), and the ratio of partially extracted As to Mn (D), based on the partial digest targeting amorphous Mn oxide bound elements. The profiles above mineralization (top) are compared with the profiles above barren sulfides (bottom). The different line colors are individual profiles. * Indicates the data has been smoothed as an average of the nearest neighboring concentrations to improve pattern recognition.

Fig. 6. Regolith profile geochemistry. A) pH, B) EC, C) Element Index 1, D) CHI*6 Index and E) Li concentration. C, D and E are from the hydroxylamine hydrochloride extraction results. The profiles above mineralization (top) are compared with the profiles above barren sulfides (bottom). The different line colors are individual profiles. * Indicates the data has been smoothed as an average of the nearest neighboring concentrations to improve pattern recognition.

Fig. 7. Regolith carbonate Au distribution from 60 traverses in NW Victoria. Confirmed or conceptual targets are shown as well as the most prominent anomaly (inset). Concentration breaks are based on 95\(^{th}\), 99\(^{th}\) and 99.8\(^{th}\) percentiles.
Fig. 8. Regolith carbonate As, Co, Cr and U distribution from 60 traverses in NW Victoria: A, B, C and D, respectively. Background image data is geology (A), digital elevation (B), U, Th, K ternary radiometric (C) and Total Magnetic Intensity geophysical data for reference (Department of Primary Industries, 2008). Element concentration breaks are based on 25th, 75th, 90th and 95th percentiles.

Fig. 9. Map of Victoria indicating the 500 mm isohyete, the boundary of the Murray Basin, as well as the areas of highly calcareous soils (Northcote, 1978) and an estimated region that could potentially be used for regolith carbonate sampling for exploration targets.
Table 1

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<th>Chemical Extractions**</th>
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** T = Total acid dissolution, BL = Bacterial Leach, AR = Aqua Regia, HA = Weak hydroxylamine hydrochloride.
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<th>False Negative</th>
<th>Hypergeometric Probability P(x)</th>
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*Successful prediction is ≤5% Type II Error
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*Results provided from Stawell Gold Mine from initial drilling and assay of mineralized zones (April 2004)
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