The role of mineralogy and geochemistry in forming anomalies in areas of deep basin cover: implications for exploration

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ABSTRACT: This paper examines how geochemical dispersion may be used in areas of deep transported cover to locate buried mineralization. Two regions with contrasting weathering history and transported cover were investigated. These were the Mt Isa region of northern Queensland and the Yilgarn Craton of Western Australia. At both locations, transported cover is from 20 to 70 m thick. A range of techniques and instruments, including bulk geochemistry, SEM, electron microprobe and selective extraction analyses were used to understand the vertical distribution and nature of ore-related elements.

At the Eloise Cu-Au Deposit in the Mt Isa region, Mesozoic cover lies over prospective Proterozoic basement which is largely unweathered. At Eloise, the degree of weathering, below the unconformity and transported cover, is minimal so weathering-related dispersion in basement and cover is also minimal. There is no dispersion of indicator elements into the upper parts of the fresh Mesozoic sediments. Mechanical dispersion dominates as is indicated by the SEM and petrographic study and is restricted to basal sediments. Fresh sulphides occur in the basement and in the fragments of clastic basement material and fossil organic matter in the silty matrix of the Mesozoic sediments. The palaeotopography governs the direction of dispersion and needs to be thoroughly understood before meaningful interpretation.

The Lancefield South Au Deposit has a cover of highly weathered Permian to Quaternary sediments on Archaean basement of the Yilgarn Craton. Stacked weathering profiles in each sedimentary unit allowed transfer of Au, As, Cu and Zn across the weathering profiles (paleosols) by hydrogeochemical and vegetation interactions as they evolved. High paleo-watertables within the Permian sediments have allowed upward migration of metals reaching close to the surface. Bioturbation and transpiration pumped the anomalous metals into the overlying Tertiary and Quaternary sediments from the Permian. Although regolith anomalies are weakened, especially in the Tertiary and Quaternary cover by post-depositional weathering processes over a long time, they still clearly remain. Thus, a highly weathered sedimentary cover is likely to trap indicator elements more effectively than a fresh, unweathered sedimentary cover, such as at Eloise. In addition to basal sediments or interfaces, ferruginous metal-rich horizons in weathered sediments high in the sequence, can also be anomalous.

KEYWORDS: exploration, deep transported cover, geochemistry, buried deposits, Eloise, Yilgarn Craton, Lancefield
INTRODUCTION

Transported cover provides significant challenges to geochemical exploration as dispersion of indicator elements to the surface is restricted (Anand et al. 1993; Butt et al. 1997; Butt et al. 2000; Anand, 2005) or geochemical patterns related to any dispersion are masked by geochemical and mechanical processes (past or present) unrelated to mineralization (Anand et al. 1997). These challenges are prevalent in most regolith settings in Australia where considerable regolith transport has occurred and post-Miocene aridity has substantially modified the geochemistry of both in situ and transported cover (Butt & Smith, 1980; Anand & Paine, 2002).

Apart from the expensive option of pattern drilling through transported cover, the most common approach to geochemical exploration in these areas in recent years has been the use of partial extraction geochemistry to assist detection of weak geochemical dispersion haloes by chemically targeting the regolith components that are thought to host these haloes. A comparison of studies from a range of regolith terrains indicates that partial extraction techniques have met with less success in deeply weathered and arid terrains than in terrains with recent glacial or volcanic cover (Cohen et al. 1998; Smee, 1998; Gray et al. 1999; Shen et al. 1999; Wang et al. 1999; Wildman & Longman., 2000; Lintern 2001; Kelley et al. 2003; Cameron et al. 2004; Mokhtari et al. 2009). Many geoscientists are sceptical, as there is no single, accepted, coherent theory for upward migration of ions to surface, yet this is a factor which is fundamental to the formation and continuance of any geochemical anomaly, irrespective of whether it was formed by a conventional or ‘strong’ or ‘more esoteric’ mechanism (Mann, 2010). Despite a number of mechanisms being suggested, including electrochemical, diffusion, groundwater pumping, convection, capillary rise and vegetation (e.g, Hamilton et al. 2001; Kelley et al. 2003; Cameron et al. 2004; Aspandiar et al. 2004; Mann et al. 2005; Anand et al. 2007; Lintern, 2007; Cohen et al. 2010), no single mechanism has yet been shown to be capable of adequately explaining all situations (Mann, 2010). There is an added complexity in Australian environments where preservation of an anomaly in recently transported cover or active alluvial or aeolian terrain is difficult. Here, an anomalous geochemical signal accumulating in soil from sources beneath is being removed by surface mechanical dispersion and dilution. In cases of extreme transport, anomalies are removed or replaced faster than they are formed (Cohen et al. 1998; Anand et al. 2007; Ma & Rate, 2009; Mann, 2010).

An alternative approach to the direct detection of element dispersion from mineralization through transported regolith is the identification of the more general effects of oxidising sulphide mineralization on regolith mineralogy and pH (Smee, 2003). Substantial changes to the mineralogy and mineral distribution within transported regolith, as a result of H⁺ released from oxidizing sulphide mineralization and other reactions, has been recognised in a number of regolith settings. Various approaches to detect these features have been developed, but their application has met with limited success in arid environments typical of Australia (Mokhtari et al. 2009).

In Australia, exploration is progressively moving to areas of deep transported cover (>30 m) as more easy areas become exhausted. Given the cost of deep drilling, high density sampling of weathered basement beneath the unconformity is no longer cost effective. Conventional approaches (e.g. soil and lag sampling) may not be applicable in areas of transported cover and various selective extraction methods and gases have had only limited success, so there is a need for new approaches. A variety of
transported cover sediments, ranging from Quaternary to Permian, are common in Australian landscapes. These have been subjected to weathering under a variety of climates. Sampling these sediments presents challenges because of their exotic origin and variably weathered character, but they also present opportunities, as they may contain mechanical and/or hydromorphic characteristics from concealed mineralization. Furthermore, the effects of processes related to water-saturated regolith during the Tertiary may be preserved in older transported cover following a transition from wet to arid conditions in the post-Miocene (Radford & Burton, 1999; Mokhtari et al. 2009). A first step towards grasping the complexities of the Australian transported cover is to understand the effects that erosional history, past climates and weathering have had on its development and geochemistry.

The Quaternary climate differed from Tertiary and Cretaceous climates, resulting in distinct styles of weathering. Overprinting of weathering styles is common in landscapes today. In contrast, the landscapes and regolith of northern Europe, northern Asia and Canada have experienced periods of extensive glaciation, as recently as 15 000 years ago, that have stripped most of the earlier regolith. This has revealed areas of exposed fresh rock and areas masked by weathered glacial sediments. Consequently, many geochemical exploration methods, and some geophysical methods, imported directly from the Northern Hemisphere, are either unsuitable in Australian environments or perform poorly.

Two study regions with contrasting transported cover were chosen. These are the Mt Isa region in northern Queensland and the Yilgarn Craton in Western Australia. In the Mt Isa region, widespread cover sequences of various types mask potentially mineralized basement (Anand et al. 1997). Mesozoic marine sediments deposited on a land surface of broad river valleys with low hills and interfluves are particularly challenging. The sediments were either weathered after deposition or remain fresh, depending on the environment (Anand et al. 1997). To date, exploration in the basins has been by investigating geophysical targets by drilling.

A variety of sediments, ranging from Permian to Recent, occupy the landscapes on the Yilgarn Craton (Anand & Paine, 2002). Valleys filled with glacial till, dating from the Early Carboniferous and Early Permian are preserved on the eastern margin of the Yilgarn Craton (for example, at Lancefield) (Eyles & de Broekert, 2001). Here, the weathered sediments have profiles similar in appearance and mineralogy to those developed on Archaean rocks. Distinction of weathered sediments from basement may be difficult.

The Eloise Cu-Au deposit is masked by largely unweathered transported cover on basement in the Mt Isa region, whereas the Lancefield South Au deposit in the Yilgarn Craton is partly masked by highly weathered cover on weathered basement. At both locations, transported cover varies from 20 to 70 m thick. A range of techniques and instruments, including bulk geochemistry, SEM, electron microprobe and selective extraction analyses were used to understand the vertical distribution and nature of ore-related elements. At Lancefield South, the mineralogical and chemical data were placed in a geochronological framework determined by paleomagnetic dating of hematite (Pillans, 1998). Process-based models are proposed that explain the distribution of ore-related metals and when the anomaly may have formed.
ELOISE (Cu-Au) SETTINGS

Introduction

The Eloise Cu-Au Deposit is approximately 60 km SE of Cloncurry in the Mt Isa region (Figure 1). Eloise was discovered by regional and local aeromagnetic, ground magnetic and electromagnetic surveys and subsequent drilling by BHP Minerals Exploration (Brescianini et al. 1992; Skrzeczynski, 1993). The surrounding region also hosts a number of major base and precious metal deposits, including Ernest Henry (Cu-Au) to the N, and Cannington (Pb-Zn-Ag) and Osborne (Cu) to the S.

Physical features and environment

The deposit is situated on rolling plains underlain by sediments of the Eromanga Basin. The plains consist of alluvial river terraces and fluvial ridges with a relief of generally less than 10 m. To the SW in the foothills of the Selwyn Range, the rugged Proterozoic Mt Isa Inlier outcrops 150 m above the plain. The exposed Proterozoic is sporadically capped with remnant, flat-lying, late Jurassic to early Cretaceous fluvial sediments (Gilbert River Formation), mainly in the headwaters of the Fullarton, Cloncurry and Bustard rivers. Major streams that flow intermittently after significant rains (Williams and Fullarton streams) are sourced from the eastern flank of the Selwyn Range and drain NE, ultimately into the Gulf of Carpentaria.

The climate is tropical, monsoonal and semi-arid, with a variable annual summer rainfall of about 380 mm. Mean minimum and maximum temperature ranges are 25-37ºC (January) and 10-25ºC (July). A spinifex-eucalypt grass-woodland predominates on deep soils. Grasses with scattered shrubs are common in flat, open, alluvium-filled drainages. Spiky hummocks of spinifex and sparse bushes of eucalypt surround much of the Proterozoic outcrops.

Geological setting

Eloise lies on the western margin of the Eromanga Basin, close to the exposed part of the Eastern Fold Belt of the Mt Isa Inlier (Figure 2). The Inlier runs predominantly N-S and consists mainly of folded and eroded Proterozoic metasediments and metabasalts of the Soldiers Cap Group. Mineralization in these rocks occurs along major faults and shears (Baker, 1994).

The Eloise deposit is buried under 50-70 m of Cretaceous sediments (Figure 3), which incorporate early Jurassic, continental, fluvial, swamp and lake facies sediments (Senior et al. 1978). A marine transgression from the N and NW in the Early Cretaceous deposited thick mudstones, siltstones and sandstones of the Willumbilla Formation, capped by thin beds of Toolebuc Formation limestone. Much of the upper limestone has been eroded (Senior et al. 1978).

Mineralization

Eloise has an indicated reserve of 3.2 Mt at 5.8% Cu, 1.5 g/t Au and 19 g/t Ag. It is hosted by greenschist-metamorphosed metasediments and mafic rocks with major retrograde shears in which early hornblende-biotite-quartz assemblages occur. They were overprinted by chlorite-muscovite-pyrrhotite-chalcopyrite+calcite+magnetite and, later, by calcite-chlorite-quartz+pyrite assemblages during subsequent brittle deformation (Baker, 1994).

Locally, the host rocks consist of N-striking metapelites, amphibolites, psammitic quartz-biotite schists, quartz-muscovite schists and a meta-arkose. The two main
orebodies (western 'Elrose Lode' and eastern 'Levuka Lode') lie within meta-arkoses and biotite schists parallel to and between the major shears. These rocks have been cut by the reverse Median fault with a 40-60° westerly dip. This fault, which thickens with depth from 15 to 30 m, consists of a breccia of silicified host rocks in a matrix of calcite, chlorite and quartz, with minor pyrite and chalcopyrite. The later Middle Fault displaces the Median Fault. As a result of the faulting, the southern part of the deposit is cut off and concealed beneath a wedge of barren Proterozoic metamorphic rocks (Baker, 1994).

**Regolith**

Around Eloise, little pre-Cretaceous weathering is preserved, so that Proterozoic rocks, intersected by diamond drilling, are fresh, except at and near the unconformity, where there is very weak weathering to saprock (Li Shu & Robertson, 1997). Any pre-Cretaceous weathering rind was probably eroded almost as quickly as it formed and the unconformity quickly sealed by thick (50-150 m), impermeable Cretaceous sediments (Figure 3) which were deposited during the marine transgression. This environment was characterized by oxygen-depleted waters and abundant macerated organic material.

Around Eloise, the Mesozoic sediments are in turn buried beneath Tertiary and Quaternary fluvial sediments (Figure 3). The fluvial sediments (2-8 m thick) consist of well-rounded gravel and coarse sand derived from recognisable Proterozoic rocks. Their top part is generally slightly ferruginous and the surface is covered by brown and black soil, strewn with a lag of pebbles and ferruginous pisoliths. These materials were deposited by the ancestral Fullerton River that later changed its course to the E. The Tertiary sediments form fluvial ridges and high river terraces. Quaternary alluvium, in the lower part of the landscape, has built plains and low river terraces directly on Mesozoic sediments. Deposition and redistribution of these post-Mesozoic sediments has formed the rolling plains at Eloise. Where the material is fine and poorly drained, black smectitic soils have developed.

**LANCEFIELD SOUTH (Au) DEPOSIT SETTINGS**

**Introduction**

The Lancefield South Gold Deposit is located 8 km N of Laverton in the Yilgarn Craton (Figure 4). The surrounding region hosts a number of Au deposits, including Beasley Creek and Telegraph. This study has assessed the geochemical dispersion into Permian, Tertiary and Quaternary sediments. The sediments have been affected by post-depositional weathering.

**Physical features and environment**

The mine is situated on a low rise. Archaean inliers are surrounded by Permian glacial channels, wash plains and modern alluvium. Non-marine sediments of the Lower Permian Paterson Formation occur as widely scattered outcrops or buried in paleochannels (Gower, 1976). Some of the deeper glacial deposits are unweathered and carbonaceous material within them has been dated palynologically as Permian (J. Hronsky, Western Mining Services (Australia) Pty Ltd., cited in Butt et al. 1997). At Lancefield South, the Archaean rocks and Permian sediments have been deeply weathered. Only saprolite of the Archaean rocks crop out in a few places. The
climate is semi-arid, with hot dry summers and cool to mild winters. The rainfall is variable (average 225 mm/yr; range 65-453 mm/yr) which is greatly exceeded by evaporation (2700-2900 mm/yr). The vegetation consists of Acacia (mulga), Cassia, Brachychiton (kurrajong) and Casuarina (she-oak). Acacia and Eremophila mark the wash plains.

Geology and mineralization

The bedrock consists of komatiites, Mg basalts, massive to pillowed mafic volcanics, carbonaceous shale and chert (Hronsky et al. 1990). The intrusion of granitoids has deformed the ultramafic stratigraphy in the Lancefield area. These are overlain by Permian sediments. The orebody consists of a mineralized zone some 140 m long and 7-12 m wide, enveloping a 5 m wide chert. The chert has a sulphide (pyrrhotite-pyrite-sphalerite-chalcopyrite-arsenopyrite) content of around 15% near the ore zone. Near the chert, the regolith developed on ultramafic rocks also contains significant supergene gold mineralization (Hronsky et al. 1990).

Regolith

Regolith characteristics and mineralogy

The mine at Lancefield South is situated on a depositional plain, with extremely thin soil, that has been largely disturbed by mining. The mine pit intersects weathered Permian sediments that fill channels eroded into saprolite of the basement. The in situ regolith profile on the Archaean bedrock is overlain by up to 25 m of sediments (Figure 5). The depth of weathering exceeds 50 m on basalt and is represented by well-developed kaolinitic and ferruginous saprolite. In contrast, talc-chlorite ultramafic is weathered to some 10 m. Saprolite becomes ferruginous towards the upper part.

The mineralogy of transported and in situ regolith are summarized in Figure 6. Saprock and saprolite on ultramafic bedrock largely consist of ferromagnesian chlorite and talc, with varying amounts of kaolinite, chloride-vermiculite, quartz, goethite, hematite, ilmenite, chromite, xenotime and magnetite. Goethite is important in ferruginous saprolite. Some of the quartz occurs as coarse sand (probably remnants of quartz veins) within the saprolite. A few grains of chalcopyrite and pyrite are preserved in the quartz grains (Figure 7) and have been protected from weathering.

There are three principal types of sediments (Figure 6): -

(i) The basal Permian fluvioglacial deposits are 10-20 m thick. There is a strong tendency for the Permian channels to follow ultramafic lithologies. A thick, deeply weathered Permian fluvial sequence is exposed abutting and unconformably overlying Archaean ultramafic rocks on the SW and W walls of the pit. The wall of the channel is steep to overhanging, in places. The base of the Permian consists of a matrix supported, coarse, boulder conglomerate. The boulders are rounded to angular and include metavolcanic and granitic lithologies with lesser BIF, set in a gritty matrix. The clast shapes indicate that the sediments were fresh at sedimentation but have been weathered in situ since. The base of the channel sediments is weathered to kaolinite and smectite with abundant quartz and some muscovite. Higher in the profile, the sediments are horizontally mottled; the mottles accentuating bedding in the Permian sediments which is less obvious in the surrounding matrix (Figure 8A). Here smectite is weathered to kaolinite. The mottles consist of goethite, hematite, kaolinite, quartz, muscovite and ilmenite. Goethite bands are common within mottles. The white,
bleached matrix is dominated by kaolinite and quartz with small amounts of muscovite.

(ii) A Tertiary paleochannel clay unit, 3-8 m thick, overlies the mottled Permian sediments. Kaolinitic clays, derived from erosion of saprolite, were deposited in a shallow, swampy wetland, probably during the Oligocene-Early Miocene (Anand & Paine, 2002). Post-depositional weathering, in particular hematitic megamottling (>200 mm) has obliterated much of the primary sedimentary fabric (Figure 8B). Many of the megamottles (>20 cm; Anand & Paine, 2002) have a kaolinite-rich zone around their margins (Figure 8C). In the upper part of the unit, hematite mottles are surrounded by yellow 1-2 mm thick goethite-kaolinite cutans. Vegetation appears to have played an important role in hematitization of these Tertiary sediments compared to the underlying Permian sediments. The elongate shape of the mottles, their dominantly vertical orientation, their decrease in abundance with depth and the fairly uniform depth to which they occur, suggest that mottles formed by the removal and reprecipitation of iron around tree roots (Anand & Paine, 2002). The removal of Fe around tree roots was probably due to microbial decay of organic matter, which generated reducing conditions which dissolved and redistributed Fe oxides and oxyhydroxides.

(iii) Colluvium-alluvium, 0.5-3 m thick, that overlies the Tertiary paleochannel clays (Figure 8B). The lower part of the colluvium-alluvium is largely unchanged whereas the upper part has been silicified by pedogenesis to a red-brown hardpan (Bettenay & Churchward, 1974). Many quartz grains and voids have cutans of poorly crystalline goethite and kaolinite, whereas the matrix is largely kaolinite, opaline silica and quartz with small amounts of hematite (Figure 8D). Detrital minerals are hematite clasts, quartz and lithic fragments. Red-brown hardpan was formed in an arid climate when there was sufficient water during the wet season to dissolve alumina, silica and Fe, but insufficient to leach them (Anand & Paine, 2002; Mahizhnan, 2005).

The Ti/Zr ratios clearly discriminate transported from in situ regolith (see Figure 13). The ratios vary from 19-40 in transported cover and 80-120 in saprock and saprolite. This implies that the transported cover is unrelated to the underlying mafic-ultramafic basement and was mainly derived from distal felsic rocks.

**Dating of regolith**

Dating of weathering profiles and sediments provides useful information on paleoclimates and rates of landscape evolution. In mineralized areas, it may also provide insight into the timing and rates of dissolution of indicator elements, and their transport and reprecipitation. Paleomagnetic dating of Fe oxides has proved successful in dating the regolith materials (Pillans, 1998) and at Lancefield was used to estimate the age of hematite formation in basement saprolite, Permian sediments and Tertiary sediments (Pillans, 2005). These results suggest multi-stage weathering at Lancefield South under wet and warm and later under dry climates. Mottles in saprolite and Permian sediments yield Mid Eocene to Paleocene ages (50-65 Ma) with some evidence of earlier weathering (>250 Ma), whereas mottles in Tertiary sediments are much younger (10 Ma; Late Miocene). No dating of silicified colluvium was done at Lancefield South but paleomagnetic dating elsewhere in the region suggests hardpan formed during the Pleistocene to Recent (Mahizhnan, 2005).
**SAMPLING AND METHODS**

**Eloise**

Geomorphological and sedimentary histories of the Eloise district were established and, using this framework, opportunities for using geochemistry in this difficult environment were investigated with emphasis on Mesozoic cover (Anand et al. 1997; Li Shu & Robertson, 1997). Regolith mapping was by remote sensing, checked by extensive field traverses. Core logging of the Mesozoic sediments at Eloise focused on grain size (mudstone, siltstone, sandstone and conglomerate) to determine the energy of sedimentation and, by analogy, the energy of erosion in the source. The weathered state of the core was also recorded (fresh rock, saprock and saprolite) following terminology of Anand & Butt (1988). This was estimated from the coherence of the core. Even small amounts of readily oxidized sulphides in such sediments can lead to very rapid deterioration of drill core over a few months; these cores were a few years old.

Mesozoic sediments below the casing of the mine decline and core from two nearby geotechnical diamond drillholes (ENG1 and ENG2) were sampled (Figure 9A), concentrating on coarse sediments (gritty mudstone and basal conglomerate) close to the unconformity. These sites comprised a proximal data set and were compared to distal hydrological diamond drilling (boreholes 1TT, 2TT, 3TT and 4BTT; Figure 9B), about 3 km from the mine, where sampling was also concentrated on high-energy sediments near the unconformity.

Each sample for geochemical analysis was split on a PVC riffle. Aliquots of 100 g were pulped to a nominal <75 µm. Mineralogy of pulped samples was determined by Philips PW1050 diffractometer, using monochromated Cu Kα radiation generated at 50 kV and 20 mA. Optical microscopy was followed by scanning electron microscopy (SEM). Scanning electron microscope (SEM) imaging and analyses were performed using a back-scattered electron (BSE) detector on a Philips XL40 controlled pressure SEM fitted with an EDAX energy dispersive spectrometer (EDS).

All samples were analysed by XRF (CSIRO) and by INAA (Becquerel Laboratories), as follows:

**INAA**

Aliquots of 10 or 30 g (depending upon availability) were encapsulated at CSIRO and sent to Becquerel Laboratories for INAA analysis. Elements analysed were K, Fe, Zn, Ba, Na, Rb, Ag, Se, Cr, Mo, W, Ce, Br, U, As, Co, Cs, Ta, La, Eu, Yb, Hf, Th, Sb, Sm, Lu, Sc, Ir and Au.

**XRF**

X-ray fluorescence analysis was performed at CSIRO on fused discs (0.7 g sample and 6.4 g Li borate) using a Philips PW 1080 instrument. Elements analysed were Si, Al, Mg, Na, Fe, Ti, Mn, P, Ca, K, Ba, Ce, Cl, Cr, Co, Cu, La, Ni, S, Pb, Rb, Sr, V, Y, Zn, Zr, Nb and Ga.

**Lancefield South**

Thirty five samples of transported cover (Permian, Tertiary and Quaternary sediments) and *in situ* regolith (saprolite, saprock) from the mine pit wall were collected to investigate regolith mineral paragenesis and to illustrate the vertical
distribution of elements and association of elements with particular mineral phases over Au mineralization (see location of profile sampled in Figures 5). In any near-mine situation, it is difficult but essential to establish background geochemical abundances. Thirteen samples of sediments of natural exposures, distant from known mineralization, were analysed to establish the local background.

Samples were characterized for pH and electrical conductivity using a sample to water ratio of 1:5. Mineral identification was performed using a combination X-ray Diffraction (XRD), optical microscopy and Scanning Electron Microscopy (SEM). Optical microscopy was followed by SEM study in backscattered electron mode (Robinson, 1975) in which image brightness corresponds to relative mean atomic number of a mineral or mineral aggregate. In situ geochemical analyses were performed on polished thin sections by electron microprobe to determine mineral element associations in transported and in situ regolith. In particular, areas of interest such as goethite-kaolinite cutans and bands, hematite-goethite mottles, kaolinite, silicified matrix and pseudomorphs after sulphides were analysed. Elements analysed include Si, Fe, Al, Mg, Ca, Na, K, Mn, As, Cu, Zn and Pb.

Bulk samples of various regolith units were stored in plastic bags, air dried and analysed by total and selective extractions. ‘Total’ analyses were conducted on all samples using a combination of mixed acid digest (HNO₃, HClO₄, HF and HCl) followed by ICP-MS determination for Cu, Zn, Ni, Cr, Mn, P, Sc, V, Fe, Al, Ca, Mg, Ti, Na, K, S, Co, As, Ag, Ba, Bi, Cd, Ga, Li, Mo, Pb, Sb, Sn, Sr, W, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu, Th, U, Se, Rb, In, Te, Cs, Tl and Dy. XRF analysis was on fused discs for major elements (Si, Al, Fe, Ti, Mg, Ca, Na). Analysis for Au, Pt, Pd, Hg, Ir, Rh and Ru was by ICP after an aqua regia digest.

Sequential extractions were by 0.1M hydroxylamine, 0.25M hydroxylamine and sodium dithionite. The three extraction methods are highly selective for specific mineral phases in soils (Chao, 1984).

**0.1M hydroxylamine (0.1MHH):** The sample was mixed with 90 ml of 0.1M hydroxylamine hydrochloride in 0.01M HNO₃ for at least 30 minutes. The mixture was centrifuged and the liquid decanted and analysed by ICP-MS for Ag, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Pt, Sb, Se, Sn, Te, Th, Ti, U, W, Zn and Zr.

**0.25M hydroxylamine (0.25MHH):** The residual solid from the 0.1M hydroxylamine extraction was then mixed with 90 ml 0.25M hydroxylamine hydrochloride in 0.25M HCL at 50°C for at least 30 minutes. The mixture was then centrifuged and the liquid decanted and analysed by ICP-MS for the same suite of elements as for the 0.1M hydroxylamine extraction.

**Sodium dithionite:** The residual solid from the 0.25M hydroxylamine extraction was then mixed with 0.3M ammonium citrate at pH 7 with multiple additions of 0.5 g of Na₂S₂O₄(H₂O) to remove crystalline Fe oxides. The mixture was then centrifuged and the liquid decanted and analysed by ICP-MS for the same suite of elements as the 0.1M hydroxylamine extraction.
RESULTS

Eloise

Introduction

The most promising geochemical target is the Proterozoic-Cretaceous unconformity, marked by a thin, discontinuous layer of gravelly sand and conglomerate, sealed in by a thick mass of semi-pelitic to pelitic sediments. The basal, high-energy sediments developed on and from the basement might be expected to retain down-slope dispersions from any parts of the Eloise deposit that were exposed in Cretaceous times.

Paleotopography

The paleotopography of this unconformity was obtained from mine and broad-scale (>1 km) water bore drilling (Figure 9). The Eromanga Basin deepens to the NE. The gradient of the unconformity, close to the mine (Figure 9A), is slight (1:1250) but there appears to be a much steeper slope (1:100) about 3 km NE, suggesting a scarp (Figure 9B).

The local paleotopography (Figure 9A) is well controlled by mine drilling. Together with the regional paleotopography it is clear that there is an arcuate gully to the E and NE, draining towards the upper edge of the scarp. Dispersion from the mineralization that outcrops at the unconformity N of the Median Fault would have been largely carried E, down the scarp. However, some leakage from the Median Fault could have dispersed W to the arcuate palaeodrainage (see arrows in Figure 9A). Geotechnical drillhole ENG2 is the nearest to the fault; drillhole ENG1 is more distant. The point where the decline intersected the unconformity is more distant still and is probably up-slope of any point where mechanical dispersion from the Eloise mineralization or from the Median Fault subcrop could have entered the paleodrainage.

Geochemical investigation

Mesozoic sediments below the concrete casing of the mine decline and core from the two geotechnical diamond drillholes (ENG1 and ENG2) were sampled. Near the mine, coarse, high-energy Mesozoic sediments are anomalous in Cu (75 ppm), Au (90 ppb) As (125 ppm) and, weakly, in Sb (0.7 ppm) at or very close to the unconformity in diamond drillholes ENG1 and ENG2 (Figure 10). There are no anomalies in the decline or in the upper parts of the Mesozoic stratigraphy (Figure 10). Backgrounds are typically <5 ppb for Au, 20 ppm for Cu, 10 ppm for As and 0.2 ppm for Sb.

Three km from the mine, there is a small Cu anomaly (80 ppm) at the upper surface of the basal sandstone in diamond drillhole 1TT about 2.5 m above the unconformity. There are very weak Au anomalies in 2TT (57 ppb at the sandstone base and 26 ppb in a thin conglomerate 0.3 m above the unconformity). Arsenic and Sb anomalies (102 and 1.5 ppm respectively) also occur in drillhole 4BTT in sandstones and conglomerates 1.3 m above the unconformity. The remainder of the Cretaceous stratigraphy (largely pelitic) was at background concentrations for these indicator elements. Typically, interface or basal sediment anomalies are weak and subtle and require well-controlled analysis for reliable detection. However, they provide a much larger target than the far stronger anomalies found in the top of the basement.
Microscopic investigations

The basement rocks are fresh, consisting of an assemblage of quartz, sericitic plagioclase, green chloritized biotite and granules of ilmenite that have been shattered and veined with calcite, closely associated with crystalline pyrite and minor chalcopyrite (Figure 11A, B). Some of the quartz contains accessory rutile and monazite. In basal conglomerates and grits proximal to mineralization, clasts of the basement assemblages are common and are remarkably fresh. Contained sulphides are unweathered (Figure 11C). Other clasts are largely round to subangular grains of sandy to silty vein quartz in a brown, sericitic, silty clay-quartz matrix (Figure 11C). Bits of this material are found clinging to clasts of metamorphic basement. There are a few grains (3-5 µm) of pyrite in the clay matrix.

In similar rocks distal to the mineralization but down-slope, sulphides occur both in clasts of fresh basement rocks and as replacements of cell interiors in fossil organic matter (Figure 12). The cell walls appear to be carbonaceous (grey, weakly reflective; brown to black in transmitted light; Figure 12C). Re-examination of slides from the proximal locations showed that the pyrite clusters, noted above, were also associated with carbonaceous material and were probably from highly macerated fragments of organic matter, so much so that the cell structures are unclear, but their sizes are consistent with this interpretation. Pyrite patches within individual clusters are relatively uniform in size. These size ranges are similar to those reported by Wilkin & Barnes (1997) and Paktunc & Dave (2002) for frambooids occurring in both modern sediments and sedimentary rocks.

Lancefield south Au deposit

Physical properties

The pH, EC and concentrations of selected elements (Ti/Zr, Si, Al, Fe, Mn, Au, Au/Fe, As, As/Fe, Cu, Cu/Fe, Zn and Zn/Fe) are shown in Figure 13. At the base of the profile, in saprock, chlorite and talc are alkaline (pH 7.8-7.9), decreasing to 6.5-6.8 in saprolite (Figure 13). Kaolinite and Fe-oxide-rich materials within the uppermost 20 m of transported cover have a pH of 6.5-7.8, and are slightly less in Permian sediments (6.5-7.3). A slightly greater pH in Tertiary sediments may be due to minor calcite. The pH (5.9-6.0) gradually decreases towards the surface in the silicified colluvium and alluvium.

Electrical conductivity varies from 27 to 7560 µs/cm. The greatest ECs (5370-7560 µs/cm) occur in the saprolite where very small amounts of jarosite and alunite occur. Permian sediments have a greater EC (65-1070 µs/cm) compared to the overlying Tertiary (50-100 µs/cm) and Quaternary sediments (27-342 µs/cm). Alunite and jarosite were not detected in the Permian sediments.

Total geochemistry of regolith units

The mean concentrations of selected elements of the main regolith units over mineralization and background are given in Table 1. Magnesium (not shown) is abundant (5.5-22.7% MgO) in saprock, reflecting primary talc and chlorite. It decreases sharply (0.1-0.6%) in saprolite and transported cover. However, two samples of basal Permian sediments contain MgO up to 1.6% associated with smectite. Calcium, Na and K contents are very low (0.5%) in all the regolith units with the exception of greater K contents (up to 1.7% K₂O) in the basal Permian sediments. Potassium is hosted by muscovite which has a greater resistance to
weathering than feldspar. The occurrence of K and Mg in the basal Permian sediments implies slightly less weathering.

The distribution of Si, Al and Fe is controlled by Fe segregations. Greatest concentrations of Si occur within the Permian sediments and Quaternary silicified colluvium and is associated with quartz and opaline silica (Figure 13). The distribution of Al largely reflects the abundance of kaolinite. Iron is enriched in saprolite and in sediments. The greatest concentration of Fe occurs in the mottled sediments as hematite and goethite. Three samples of transported cover show very high concentrations of Fe (31-35% Fe₂O₃), reflecting well-developed authigenic ferruginous hematite-goethite mottles in Tertiary and Permian sediments and detrital ferruginous hematitic clasts in silicified colluvium. The basal part of the Permian sediments has the lowest concentration of Fe (3-4% Fe₂O₃). Iron is largely enriched in the saprolite, due to residual concentration by leaching of alkalis and alkaline earths. Some of the Fe in the transported cover may have been concentrated by oxidation and precipitation of laterally migrating Fe²⁺. Manganese concentrations are much greater in saprock and saprolite of the basement (mean 0.18% MnO) and decrease significantly in the overlying transported cover (mean 0.01-0.06%).

Gold concentrations range from 2-345 ppb, with the greatest in saprock and saprolite (to 345 ppb; mean 124 ppb). Gold decreases in abundance from saprock to saprolite (Figure 13). Overall, the Au content of most of the Permian sediments is well above local background (Table 1). It varies from 2-125 ppb (mean 38 ppb) against a background of 10 ppb and is concentrated in the upper ferruginous unit. Gold is not anomalous in the overlying Tertiary and Quaternary sediments, where it ranges from 4–40 ppb (mean 15 ppb) in Tertiary sediments against a background of 12 ppb. The majority of the samples are close to background concentrations, with one sample reaching 40 ppb towards the basal sediments. Lowest Au abundances (4-10 ppb; mean 6 ppb) occur in Quaternary colluvium near the surface against a background of 3 ppb. Because of the variable ferruginization of the sediments, data were normalized against Fe, which has improved the signal (Figure 13). It clearly shows two clusters of Au in Permian sediments; one at the base of the clay-rich sedimentary column and the other near the top of mottled Permian sediments. Basal Tertiary sediments are also weakly anomalous.

Arsenic concentrations in saprock and saprolite range from 7 to 910 ppm (mean 245 ppm). It decreases in concentration from base to the top of the transported cover with greatest concentrations in Permian sediments (17-550 ppm; mean 200 ppm) and the lowest in Quaternary colluvium (14-55 ppm; mean 30 ppm). Tertiary sediments contain 7-210 ppm of As with an average of 75 ppm. The concentrations in Permian and Tertiary sediments contrast with abundances of As in the background samples (Table 1). However, the As anomaly is much stronger in Permian sediments compared to the Tertiary sediments. The whole sedimentary column of the Permian sediments is anomalous, especially the middle to upper part whereas, in Tertiary sediments, the strongest anomaly occurs at the base. The majority of the Quaternary colluvium is close to background. Normalization of the data to Fe has significantly enhanced the anomaly in clayey basal Permian sediments (Figure 13).

The Cu distribution is similar to that of As but the concentrations are less (Figure 13). It ranges from 49-470 ppm (mean 180 ppm) in saprock and saprolite. Within the transported cover, Permian sediments have the most Cu (12-155 ppm; mean 90 ppm) followed by the Tertiary (19-65 ppm; mean 35 ppm) and Quaternary sediments (40-
Copper concentrations in most of the Permian and Tertiary sediments are well above the local background whereas, in the Quaternary sediments, Cu is only slightly above background. Due to association of Fe with Cu, normalization of the data to Fe has strongly enhanced the Cu anomaly in clayey basal Permian sediments and weakened it towards the top, in the mottled horizon (Figure 13).

The concentrations of Zn, especially in transported cover, are lower than those of As and Cu. However, Zn is anomalous in Permian and Tertiary sediments against a local background but not in Quaternary sediments. It varies from 80 to 450 ppm (mean 125 ppm) in saprock and saprolite, from 19 to 130 ppm (mean 50 ppm) in overlying Permian sediments, from 18-30 ppm (mean 25 ppm) in Tertiary sediments and from 14 to 35 ppm (25 ppm) in Quaternary sediments. The greatest concentration of Zn occurs at the base of the Permian sediments. Normalization of the data to Fe has further improved the contrast showing strong response at the base of both Permian and Tertiary sediments (Figure 13).

**Distribution of metals in iron-rich and clay-rich components**

Six samples of mottled Permian and Tertiary sediments were manually separated into Fe-rich and clay-rich components to determine differences in mineralogy and geochemistry. The Fe-rich component consists of hematite and goethite with small amounts of quartz and kaolinite; the clay-rich component is kaolinite and quartz with minor smectite and muscovite. The clay-rich component predictably has more Si (42-69% SiO₂) and Al (19-32% Al₂O₃) and less Fe (1-2% Fe₂O₃) than the ferruginous component (23-51% SiO₂; 12-20% Al₂O₃, 27-53% Fe₂O₃) (Table 2). The pH of the clay-rich component is greater (6.8-8) than the Fe-rich component (6.2-7.1). This is due to oxidation of Fe to goethite liberating H⁺ ions. Electrical conductivity shows the opposite trend.

Gold occurs in both materials. It is generally concentrated in the clay component in Permian sediments except for one sample (Table 2). However, the trend is opposite in the Tertiary sediments, where Au is concentrated in the Fe-rich component. Gold was not observed on SEM examination of either materials implying that it is either very fine grained or in a non-metallic phase or the concentrations are too low to be detected by SEM. In contrast, As (185-900 ppm), Cu (20-125 ppm) and Zn (20-125 ppm) are enriched in the Fe-rich components of the Permian and Tertiary sediments and the clay components are not enriched in these elements.

**Electron microprobe investigations**

An electron microprobe was used to determine mineral-element associations in (i) goethite pseudomorphs after primary sulphides, (ii) matrix minerals (kaolinite, chlorite-vermiculite and associated iron oxides) close to and distal from sulphides in saprock and saprolite, (iii) hematite-goethite mottles in Permian and Tertiary sediments, (iv) goethite-kaolinite cutans and bands in Permian, Tertiary and Quaternary sediments and (v) kaolinite, amorphous silica and Fe oxides of the matrix of Permian, Tertiary and Quaternary sediments. The data are presented in Figure 14.
and summarized in Table 3. The highlights of microprobe investigations are given below. Detection limits for electron microprobe are as follows: Cu (18 ppm), Zn (20 ppm), As (60 ppm), Fe (1000 ppm), Al (1500 ppm) and Si (60 ppm).

- Goethite pseudomorphs after sulphide are common in saprock but are rare in saprolite. They contain abundant As (mean 6140 ppm), and Cu (mean 5500 ppm) with lesser amounts of Zn (mean 105 ppm). Two grains of goethite pseudomorphs after sulphides were found at the base of the Permian sediments (Figure 15). These were recognized by traces of S and very high concentrations of As (to 12000 ppm) and Cu (to 7000 ppm). Goethite pseudomorphs in Permian sediments suggest that they are derived from the mineralized bedrock, which was almost unweathered at sedimentation. The kaolinite and goethite matrix analysed in the vicinity of a sulphide pseudomorph contains moderate amounts of As, Cu and Zn that increase with the goethite content. These concentrations are much lower than the goethite pseudomorphs.

- Hematite-goethite mottles in Permian sediments contain abundant As (mean 1260 ppm), Cu (mean 295 ppm) and Zn (mean 400 ppm). High concentrations of Zn in mottles are associated with the high concentrations of Mn oxides (Figure 14). Arsenic, Cu and Zn occur in significant amounts in mottles in the Tertiary sediments but with much lesser concentrations, despite having very similar mineralogy and Fe, Al and Si contents to those of mottles in the Permian sediments.

- Goethite-kaolinite bands and cutans in Permian sediments are highly enriched in As (mean 1530 ppm) compared to Cu (mean 90 ppm) and Zn (mean 55 ppm). Goethite cutans in Tertiary sediments also show a similar trend to those of Permian sediments but with much lower concentrations of As (mean 80 ppm), Cu (mean 120 ppm) and Zn (mean 10 ppm). Towards the surface in the Quaternary colluvium, goethite cutans are the major host for As (mean 60 ppm), Cu (mean 65 ppm) and Zn (mean 15 ppm) compared to the other materials.

- The kaolinite-silica matrix of each sedimentary unit has less As, Cu and Zn than the corresponding mottles and cutans. Although kaolinite is a major component of the sediments, it is also the mineral showing the least indicator element content. Kaolinite does not seem to inherit cations from its parent minerals and does not capture cations from its groundwater environment. The kaolinite structure allows little isomorphic substitution and, having a low cation exchange capacity (CEC), adsorbs little from solution (Le Gleuher et al. 2008).

Selective extractions

Selective extractions are used in the analysis of some sediments to provide information on the association of metals with particular phases. Three selective extractions of increasing strength (0.1M hydroxylamine, 0.25M hydroxylamine and sodium dithionite) were used sequentially to dissolve Mn oxide minerals, “amorphous” Fe oxides and crystalline Fe oxides, respectively from Permian, Tertiary and Quaternary sediments. The results are presented in Figure 16. Manganese, extracted by weak leach (0.1M HH), increases down the profile, whereas there is no significant extraction of Fe by 0.25M HH. Most of the Fe is extracted by the
strongest leach (sodium dithionite). These results suggest that there is no current active precipitation of Fe but Mn precipitation is still active. Arsenic, Cu and Zn are largely extracted by weak leaches in Quaternary colluvium, indicating its association with poorly crystalline Fe and Mn oxides. This is consistent with the electron microbe data, which showed that most of the As, Cu and Zn are associated with goethite in cutans. In contrast, As, Cu and Zn in Permian and Tertiary sediments are extracted by strong leach (sodium dithionite) suggesting its association with crystalline Fe oxides formed as mottles and cutans. Gold was only extracted by sodium dithionite, and only from older sediments, especially the Permian. This implies that Cu, Zn and As were introduced into the Quaternary sediments recently whereas, in Tertiary and Permian sediments, these metals were introduced much earlier during the formation of mottles, possibly in the Late Cretaceous and Early Miocene. However, cutans are younger than mottles, implying that there have been several periods of dissolution and precipitation of metals.

DISCUSSION

Eloise

This paper has contrasted dispersion mechanisms in two very different transported cover and environmental settings. At Eloise, the degree of weathering below the unconformity and transported cover is minimal so weathering-related dispersion in the basement and transported cover is also minimal. There is no dispersion into the upper parts of the fresh Mesozoic sediments. Apart from the mineralization itself as a target, the only useful dispersion is mechanical and is restricted to the Mesozoic sediments just above the unconformity. This is a thin and probably discontinuous layer of high-energy sediments developed on and from erosion of the basement. It appears to retain a down-slope largely mechanical dispersion from the Eloise mineralization that was detected in some of the drilling. Dispersion extends about 100 m from the mineralization or from mineralized faults and was strongly influenced by the topography of the unconformity (Figure 17B). Drilling 3 km distant from the mine also indicated some anomalies, notably just above the unconformity, at sites located directly down-slope from Eloise. These sediments may also have been derived from erosion of Eloise (Figure 17A) and are analogous to a stream-sediment dispersion train.

The very fresh nature of the sulphides in both the fresh metamorphic basement clasts and in the fragments of fossil organic matter in the clay matrix of the Mesozoic sediments seems to imply that Mesozoic erosion considerably exceeded weathering and the rapid marine transgression at this time was responsible for inclusion of large quantities of carbonaceous material in the sediments, resulting in a low oxygen content of the water. The very thin arenaceous rocks at the base of the Mesozoic sedimentary pile were probably rapidly sealed in by a thick succession of strongly laminated argillites and silts, allowing preservation of low oxygen contents in the pore waters of the sediments. This would preserve organic matter and allow the development of sulphides and their preservation. It is thought that sulphate, originally produced from the oxidative dissolution of pyrite, was reduced by bacteria in an organic-rich medium and formed H$_2$S and HCO$_3$$. The H$_2$S reacted with Fe oxyhydroxides to form frambooidal pyrite through amorphous FeS and greigite (Paktunc & Dave, 2002). Thus, it is likely that clastic movement of primary sulphides, down slope, away from the mineralization, dominated dispersion from
Eloise. However, this does not exclude some hydromorphic dispersion of elements that were trapped by carbonaceous materials and formed sulphides in the reducing environment under the sealing Mesozoic argillites.

Where the Mesozoic sediments and the Proterozoic basement have been weathered, as at nearby Maronan (Robertson et al. 1997), dispersion along ferruginized joints and fractures has been observed (Anand et al. 1997). Some most prominent anomalies of this type occur at the Osborne deposit and are thought to be due largely to weathering of sulphide mineralization that continued during submergence in a marine environment, with hydromorphic dispersion into the sediments as they accumulated (Lawrance, 1999). Further mobilization occurred during diagenesis and, following emergence, sub-aerial weathering. This has resulted in sub-horizontal zones of enrichment (Cu, Au, Ag, Zn, Mo, Co) at and below the present land surface, at ferruginous horizons representing redox fronts in the sediments, and at the unconformity. It is uncertain how widely this process has affected the region.

**Lancefield South**

The highly weathered and chemically enriched nature of the *in situ* regolith at Lancefield South presented an ideal situation for chemical dispersion to develop in the overlying transported cover over a long period. The interplay between Permian, Tertiary and Quaternary sedimentation and weathering have led to multiple profiles, a feature described in the voluminous literature on paleosols (Kraus, 1999). Paleo-magnetic dating of ferruginous weathering profiles from Lancefield South and data from elsewhere indicates three periods of hematite formation. These include:

(a) **Hematite formation in the Mid Eocene to Palaeocene (60-75 Ma)** with some evidence of earlier weathering in saprolite and the Permian sediments. Conditions were warm and humid from the Late Cretaceous to the end of the Early Miocene, with fluctuations to at least two cooler and drier episodes prior to the Oligocene (McGowan & Li, 1998), when the vegetation was dominated by conifer forests and woodlands.

(b) **Hematite formation in the Late Miocene (10 Ma)** in Tertiary clays in a seasonally drier and warmer climate (though rainfall was still more than at present; Martin, 2006), with consequent flora changes, as southern Australia drifted to lower latitudes.

(c) **Hematite formation (<1 Ma)** in Quaternary sediments under a semi-arid to arid climate with *Acacia* and *Eucalyptus* vegetation.

Thus, the three major episodes of hematite formation occurred under three different bioclimatic regimes. The different weathering conditions significantly affected geochemical dispersion processes through the Cenozoic. The formation of stacked weathering profiles in distinct sedimentary units favoured the transfer of metals across each weathering profile (paleosol) by hydrogeochemical and vegetation interactions (Figure 18). Based on the geochronology of weathering at Lancefield, three stages of dispersion of As, Cu, Zn and Au in sediments can be related to these weathering events.

(i) Permian sediments were deposited on residual soil, largely derived from mechanical breakdown of the basement, followed by limited weathering and pedogenesis (Figure 18A). In the early stages, there would have been physical mixing of residual soil containing fresh basement clasts and
sediments derived from this primitive soil as is implied by minor goethite pseudomorphs after sulphides in Permian sediments. This formed anomalous concentrations of Au, Cu, Zn and As at the base of the Permian sediments. However, strong dispersion (e.g., Au and As) not only occurred at the base but also at other levels, especially near the top of the Permian, largely associated with mottling which appears to represent paleoredox fronts associated with old water tables. Mineralized bedrock and the Permian sediments were weathered during the Mid Eocene-Paleocene when water tables were high (Figure 18B). This caused strong leaching of Mg, Ca, Na and K, oxidation of sulphides, retention of part of the Si, Al and Fe as hematite, goethite and kaolinite and accumulation of immobile elements such as Ti and Zr. Gold, As, Cu and Zn, released from the weathering of sulphides from mineralized bedrock and the basal Permian sediments, were dispersed hydromorphically and precipitated with hematite and goethite in the Permian sediments (Figure 18B). In past saturated environments, the dispersion occurred by developing a redox gradient between the water table and buried sulphide mineralization as proposed for electrochemical models (Govett 1976; Smeе, 1983; Hamilton, 2000). This resulted in a slight decrease of the pH in the Permian sediments which enhanced the mobility of As, Cu and Zn. Vegetation would have also played an important role in bioturbation and biochemical interaction. Indicator elements from the underlying mineralization have been incorporated into what is now crystalline hematite and goethite. Thus, the anomaly is detected after extraction only by strong reagents such as four acids, aqua regia and sodium dithionite. The adsorption of most transition metals onto synthetic and natural iron oxides and the binding mechanisms are well documented (adsorption of Cu (Balistrieri & Murray 1982; Kooner 1993), As (Pierce & Moore 1982), Pb and Zn (Businelli et al. 2003)). In recent years, extended X-ray absorption fine structure spectroscopy (EXAFS) has demonstrated isomorphous substitution for Fe by Cu, Zn and Cr in natural goethite (Manceau et al. 2000). The time required for anomaly formation in hematite and goethite in Permian sediments is many millions of years. Goethite and hematite provided the sink to retain and accumulate the indicator elements transferred from below, preventing the metals from being rapidly dispersed. Thus, a highly weathered sedimentary cover is likely to trap dissolved indicator elements more effectively than a fresh, unweathered sedimentary cover, such as at Eloise.

(ii) Post-depositional weathering and bioturbation of the Tertiary sediments has obliterated macroscopic features, such as cross bedding, laminations and channels, preventing facies analysis from indicating the depositional environment. Similar sediments, largely of kaolinitic clay and fine-grained quartz, were deposited in valley fill lacustrine environments on the Yilgarn Craton during the Early Oligocene-Early Miocene (Kern & Commander, 1992; Anand & Paine, 2002; de Broekert, 2002). These paleochannels were incised into pre-existing residual regolith and older drainage sediments. The climate was cool and dry during the deposition of these clay-rich sediments (de Broekert, 2002). Although water tables were depressed by drier environments of the Late Miocene, the rainfall was greater than today and initiated the formation of megamottles
(Figure 18C). Megamottles were formed by localized removal and reprecipitation of Fe oxides around tree roots (Anand & Paine, 2002) during the Late Miocene. The process of formation of megamottles resulted in bioturbation and biochemical interaction between the Permian and Tertiary profiles. This transferred indicator elements to the higher Tertiary profile, although much less for Au, As and Cu (Figure 18C). However, the role of groundwater movement in transferring indicator elements from the saprolite or the Permian cover to the Tertiary cover appears limited by the height of the water table or the height of the capillary fringe. Bioturbation includes animal burrowing and plant uprooting that collectively mixes the material of all or part of the cover to form the biomantle. This is followed by redistribution of metals during the formation of mottles and cutans. There appears to be two stages of hydromorphic dispersion of As and Cu; the first, during the formation of older hematite-goethite mottles and the second during the formation of younger goethite-kaolinite cutans.

(iii) Quaternary sediments were deposited by fluvial, alluvial and aeolian processes under semi-arid to arid conditions (Figure 18D). The change from oxide-dominated to silica-dominated weathering is consistent with a significant decrease in rainfall and the onset of the modern climate. Over time, in response to a drier climate, the water table has gradually dropped to its current low position 25 m below surface. Vegetation is dominated by *Acacia*. The dispersion of Cu, As and Zn is subtle in the upper Quaternary silicified colluvium but can be detected by careful *in situ* chemistry and mineralogy of goethite-kaolinite cutans. Since the Quaternary sediments were deposited, concealing mineralization, indicator elements from the mineralization have only been incorporated into the most labile of secondary minerals such as poorly crystalline goethite and kaolinite (in cutans). This is indicated by partial extraction analysis. Dispersion in the silicified colluvium is probably related to bioturbation and vegetation. Roots tapping into either the mineralized Tertiary or Permian sediments or the anomalous groundwater, may take up indicator elements, which are recycled into the soil. Copper, Zn and As were subsequently leached from the soil and trapped in secondary Fe and Al cutans in silicified colluvium. Recent work on plant-metal relationships in the Yilgarn Craton suggests that *Acacia aneura* takes up indicator elements from mineralization at depth through 5-20 m of transported cover (Anand et al. 2007).

CONCLUSIONS

The geochemical expression of any concealed mineralization is a function of the ore type, preservation of the underlying *in situ* regolith and the post-depositional weathering history of the transported cover and erosion. At Eloise, the degree of weathering below the unconformity is minimal so weathering-related dispersion in the basement and the overlying sediments are also minimal. Mechanical dispersion is the dominant process and dispersion is restricted to the basal sediments. Dispersion throughout the sedimentary cover can occur where there is substantial paleorelief of the mineralized area, as found in Tertiary sediments around Pajingo, NE Queensland (Robertson, 2003); basal concentrations are more likely in areas of subdued
paleorelief. Apart from the mineralization itself, the most promising geochemical target at Eloise is the Proterozoic-Cretaceous unconformity. Sampling to detect down-slope mechanical dispersion of Cu, Au, As and Sb in coarse sediments at the Proterozoic-Mesozoic unconformity seems a valid prospecting method in areas of unweathered or slightly weathered Mesozoic cover. It could be used conveniently and cheaply in conjunction with drilling of magnetic basement targets to detect a near miss. The paleotopography governs the direction of dispersion and needs to be thoroughly understood before meaningful interpretation.

At Lancefield South, the events that accompanied the erosion, deposition and subsequent weathering of the sediments have undoubtedly affected the distribution of indicator elements. Although regolith anomalies may have been weakened, especially in the Tertiary and Quaternary cover, by post-depositional processes over a long time, they still clearly remain. Element enrichments and associations that are evident both in the in situ regolith and the sediments indicate that geochemical anomalies are not caused by mechanical dispersion of sediment carrying an allochthonous geochemical signature. Successive generations of high paleo-watertables within the cover have allowed migration of indicator ions upwards into the cover close to the surface. Bioturbation and vegetation transfer moved the indicator elements to the Tertiary sediments and silicified colluvium from anomalous Permian sediments. Combining mineralogical and geochemical techniques optimizes interpretation of primary and secondary characteristics of the indicator elements and assists in the determination of their host minerals. This improves understanding of the pathways of geochemical dispersion and improves exploration models. In these environments, in addition to basal sediments or interfaces (Permian, Tertiary and Quaternary), higher anomalous horizons can also be investigated in weathered sediments by sampling specific ferruginous units. Detailed investigations could also be carried out to determine any dispersion in soil. This was not possible at Lancefield and Eloise due to surface disturbance by mining.

These studies attempt to unravel the complex challenges of exploring through regolith in areas of significant sedimentary cover. To explore the basin-covered areas, we need to combine all applicable techniques to optimize the interpretation of the geochemical dispersion pathways. Future studies on hydrogeochemistry, mineralogical and geochemical dispersion and 3D basin structure will offer considerable insight into the exploration potential of the margins of sedimentary basins of Australia. These studies are being done as part of the newly formed Cooperative Research Centre for Drilling and Exploration Technologies supported by the Australian Government and the mineral industry.

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Captions to Figures

Figure 1. Location of Eloise Cu-Au mine showing other mineral deposits and the Eromanga Basin.

Figure 2. Location map of the Eloise Mine in relation to outcropping Proterozoic rocks, current drainage and the Eromanga Basin.

Figure 3. Generalized section through the Eloise environment showing the weathered and fresh Proterozoic basement partly covered by a thick wedge of Mesozoic sediments, in turn partly covered by Tertiary and Quaternary fluvial deposits.

Figure 4. Location and surrounding basement geology of the Lancefield South Mine and its nearby environments (after Hronsky et al. 1990).

Figure 5. Block diagram showing the generalised regolith relationships for the Lancefield South Mine.

Figure 6. Mineralogy, regolith fabrics and interfaces (unconformities) of the sampled vertical profile at the Lancefield South Mine.

Figure 7. Scanning electron micrograph showing preservation of pyrite and chalcopyrite protected by quartz in otherwise highly weathered saprolite.

Figure 8. Photographs of transported cover at Lancefield South Mine. (A) Mottled Permian sediments showing hematite-goethite mottles and goethite bands. Bouldery sediments are horizontally mottled; the mottles accentuate bedding in the Permian sediments which is less obvious in the surrounding kaolinitic matrix. (B) Quaternary silicified sediments over megamottled Tertiary clay sediments. Note the near-vertical orientation of mottles in the Tertiary which are restricted to a sub-horizontal layer in the clay. (C) Close-up of megamottles in Tertiary sediments showing red hematite-goethite areas separated by bleached kaolinitic clay. It is suggested that the whole unit was once oxidised and red and that bleaching was a later event. The bleached areas may represent leaching around pre-existing roots. (D) Photomicrograph of a thin section of Quaternary silicified colluvium showing common amorphous silica and kaolinite and poorly crystalline goethite and kaolinite forming cutans.

Figure 9. Paleotopography of the Proterozoic-Mesozoic unconformity (m RL) as determined from drilling. (A) Detailed paleotopography around the Eloise Mine showing drill sites, sampled drillholes and the decline. (B) Regional paleotopography around Eloise and to the NE as determined from sparse water-bore drilling. The location of Figure 10 (A) is shown as a box in the southwest corner.

Figure 10. Copper, Au, As and Sb geochemistry and geology of the decline below the concrete casing, the geotechnical drilling (boreholes ENG1 and ENG2) and water bore drilling (boreholes 1TT, 2TT and 3TT). Depths in metres below surface except for decline (m RL). Indicator elements in ppm except Au (ppb).

Figure 11. (A) Fresh quartz-pyrite-ilmenite mineralization in basement just below Cretaceous unconformity. Crystalline pyrite and ilmenite surrounded by metamorphic silicate material. Polished section photomicrograph. (B) Same sample as A, showing detail of crystalline pyrite with some chalcopyrite lining voids. SEM backscatter image. (C) Clasts of metamorphic basement material (mica, quartz and ilmenite) and some mineralized material (fresh pyrite) in a clay and quartz matrix from basal Cretaceous sediments from a location proximal to the Eloise Mine. SEM backscatter
image. (D) Part of a metamorphic mineralized clast of fresh basement-related quartz-pyrite in a basal Cretaceous grit at a location distal from the Eloise mineralization. Polished section photomicrograph.

Figure 12. Evidence of fossilized vegetation in a reducing environment. (A) Distinctive cell structure of fossil wood forms a clast among pieces of quartz and metamorphic rock fragments in a quartz and clay matrix. Cell walls of carbonaceous material with cells filled with silica and, in one, partly filled with pyrite. Basal Cretaceous grit in a location distal from Eloise. Polished section photomicrograph. (B) Clusters of round pyrite with a remarkably cell-like structure, possibly representing cross sections of vegetation fibres, among quartz shards and clay in the matrix of a basal Cretaceous grit at a distal location from Eloise. SEM backscatter image. (C) Carbonaceous material wrapped around quartz grains in a basal Cretaceous grit distal from Eloise. Thin section in transmitted light. (D) Same as C but in reflected light, showing pyrite-filled cells in carbonaceous material.

Figure 13. pH, electrical conductivity (EC) and geochemistry of selected elements for various regolith units, Lancefield South Mine.

Figure 14. Electron microprobe data for various mineral phases from various regolith units, Lancefield South Mine.

Figure 15. Backscattered scanning electron micrograph showing goethite pseudomorph after sulphide preserved in Permian sediments, Lancefield South Mine.

Figure 16. Bar graphs showing extraction of Mn, Fe, As, Cu, Zn and Au by sequential selective extractions from regolith units, Lancefield South Mine.

Figure 17. Model of mechanical dispersion along the Proterozoic-Mesozoic unconformity and into the unweathered basal Mesozoic high-energy sediments at Eloise Mine, leading to proximal and distal anomalies.

Figure 18. Model showing progressive formation of anomaly by mechanical, bioturbation and hydrogeochemical processes, Lancefield South Mine.
REFERENCES


Table 1. Mean element composition of bulk samples over mineralization (Lancefield South Pit) and background

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<th>Cu (ppm)</th>
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Table 2  Chemical composition of Fe(FC) and clay(CC) components of the sample, Lancefield South Pit

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Table 3 Summary, electron microprobe analyses of important minerals phases, Lancefield South Pit

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BD=Below detection
A Pre-Cretaceous

- Residual weathering and dispersion in soil
- Deposition of Permian sediments followed by physical mixing with underlying soil and mineralization

B Late Cretaceous - Paleocene

- Weathering of Permain sediments and underlying mineralized bedrock
- Higher watertable favour redox associated migration of ions to oxidizing front
- Bioturbation

Palaeo water table

C Late Miocene

- Deposition of Tertiary sediments followed by bioturbation and ferruginisation
- Watertable lowered due to onset of drier environment, but biota still able to access palaeo redox front and transfer metals to Tertiary sediments
- Physical and chemical interaction between buried Permain and new Tertiary sediments

D Quaternary

- Deposition of Quaternary sediments followed by weathering resulting in transfer of anomaly (weak) to Quaternary sediments

Present water table