DOING THE TIME WARP WITH ELEMENT DISPERSION

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INTRODUCTION

Despite nearly 70 years of modern geochemical exploration and related research there is still much that we don't know about the processes of weathering-related element dispersion and the formation of secondary geochemical anomalies. Many questions relate to time and the history of geochemical anomalies. The following questions spring to mind:

- How fast are different target and pathfinder elements 'mobilised' under different weathering regimes and what is the flux?
- How long does it take to form (and destroy) a detectable secondary geochemical anomaly under different weathering conditions?
- Is secondary geochemical dispersion a continuous process or is it episodic?
- The geochemical anomalies that we find – when did they form and how have they been modified?
- How have changes in biota through time affected element dispersion?
- Are anomalies spreading at the present time?
- Mobile metal ions - do they effectively exist?

In areas with variably preserved old regolith, where there has been opportunity for multiple or continuous geochemical dispersion under a range of weathering regimes (i.e., most of Australia), answers to these questions could improve exploration success. For example, if the relative expression of a geochemical anomaly is markedly different under different weathering regimes, setting the appropriate anomaly threshold and recognising the appropriate multi-element association will depend on knowing when the anomaly formed and under what conditions. Understanding particular element behaviour under different weathering regimes and recognising these can also help predict the formation and location of important supergene and residual ore deposits.

Dating of regolith by various methods now provides time constraints on materials associated with element dispersion at a number of key sites. Detailed studies of the dispersion patterns at these sites can start to answer some of the fundamental questions listed above.

WEATHERING EPISODES AND LANDSCAPE EVOLUTION

Weathering profiles and their contained geochemical anomalies are preserved according to their position in the regolith and the history of landscape development, relative uplift, erosion and deposition (Figure 1). Different weathering features and episodes may be manifested and preserved in separate parts of the weathering profile if there has been erosional lowering of the land surface or burial of older profiles.

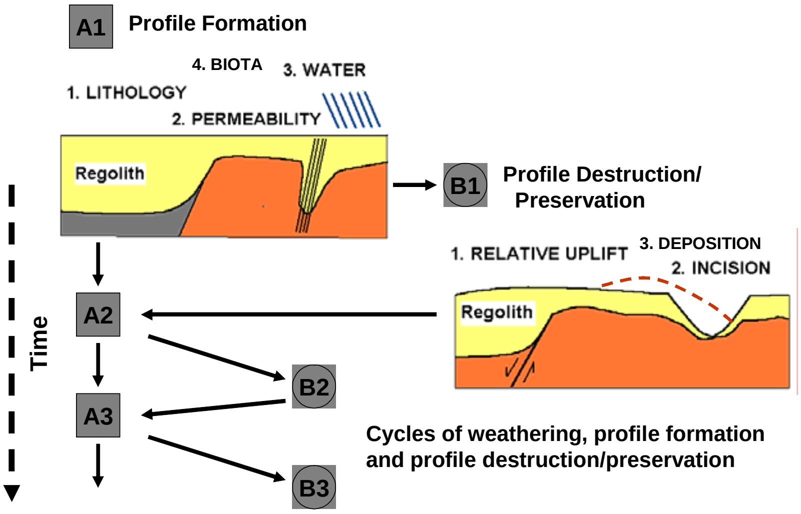

Figure 1: The basic controls on formation (A), destruction and preservation (B), of weathering profiles. Cycles of these processes can interact in different combinations through time and under different, climatic, hydrologic and biological regimes. Different geochemical regimes involving element dispersion, fixation and fractionation can accompany these changes.

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Alternatively, younger and older features may be superimposed if the land surface has been relatively stable. Each episode may be characterised by different geochemical dispersion and fixing processes, particularly if climatic, hydrologic and biological conditions have changed. In many cases the earlier dispersion patterns are overprinted by patterns developed during contrasting conditions. This combination can result in very low concentrations of many target and pathfinder elements over mineralised sites, particularly in the non-ferruginous saprolite (i.e., a double or multiple 'whammy' dispersion scenario).

Materials exposed at the surface (e.g. lag) undergo a range of transformations with time and changing environmental conditions. These include variable transport and physical degradation as well as chemical leaching and precipitation. This results in element fractionation by combined mechanical and chemical processes. The degree of fractionation will vary depending on the age or life cycle of the material and commonly there is intermixing of materials with differing maturity.

SOME SITES AND EXAMPLES

Ongoing work in the Cobar region of western NSW has established a framework of dates related to weathering processes. These include:

- Palaeomagnetic ages of major oxidation, ferruginisation and hematite fixation across the region including several ore deposits;
- Ages inferred from the latitudinal gradient, continental drift and δO^{18} values of kaolinite in weathering profiles;
- Ages based on stratigraphic relationships and radiometric dating of Miocene leucitite flows; and,
- Ar-Ar ages of manganese oxides (cryptomelane-coronadite) associated with gossans.

Results to date indicate two major periods of deep oxidation and ferruginisation in the Early Paleocene (60 ± 10 Ma) and Miocene (12 ± 3 Ma). These two periods are preserved at the McKinnons gold deposit in different parts of the profile. At other sites the two dates occur superimposed in the same mottled zone or are singly preserved at particular locations. Profiles buried and preserved by leucitite flows (dated at 17 ± 0.25 Ma, McQueen *et al.* in prep.) also show evidence of Miocene ferruginisation but with a slightly younger age. At the New Cobar open pit, palaeomagnetic dating of the top 40 m of the oxidised saprolite gives a Jurassic age (ca. 180 Ma; McQueen *et al.* 2002). Oxygen isotope studies of kaolinite in saprolite at several sites suggest ages consistent with the earlier (Paleocene to Eocene) period of ferruginisation (M. Smith *pers. comm.*). Manganese oxides in the upper part of the gossan at New Cobar yield Ar-Ar ages of 15.9 ± 0.5 Ma (Vasconcelos 2004).

As in many parts of southern Australia, the weathering history of the Cobar region has been strongly influenced by major climatic variations through the Cenozoic. In general terms this has resulted in deep chemical weathering under predominantly warm humid conditions (with high availability of organics) in the Palaeogene, and superimposed chemical weathering under increasingly arid conditions since the Neogene. In detail the picture is more complex with fluctuations to at least two cooler-dry episodes prior to the Oligocene (McGowran & Li 1998). Over this period humid conditions with high water table levels would have favoured hydration/hydrolysis reactions and mobility of reduced species, particularly Fe^{2+}. Groundwater pH conditions would have been neutral to acid, the latter particularly where sulfides were oxidising. It is also likely that high organic content would have favoured organo-complexing of many elements. Arid climatic conditions, with falling and fluctuating watertables, favoured oxidation reactions and a change to more complex groundwater compositions, particularly with higher salinity, increased activity of carbonate and sulfate and regional neutral to alkaline pH. Under these superimposed arid conditions the solubility and mobility of some elements, particularly Au, was increased where chloride and thiosulphate complexing occurred, whereas other elements, especially Cu, Pb, Ag, Ba and Hg became relatively fixed as insoluble carbonates, chlorides and sulphates. Marked pH gradients around sulfide deposits that continued to weather resulted in dispersion of elements such as Cu and Zn to form broad anomalies.

McKinnons gold deposit

The McKinnons gold deposit is a supergene-enriched, epigenetic pyritic-quartz veinlet style gold deposit. Exposures in the open pit and information from the regional landscape history indicate that the deposit has undergone prolonged weathering and some erosional stripping. The upper part of the preserved weathering profile across the deposit (top 25 m) is strongly depleted in Cu and Zn as well as minor Ni and Sb. However, Pb and As are retained and locally enriched in this zone (Tan 1996). The highest gold grades (> 1.3 g/t) occur in the top 50 m of the profile, with greatest enrichment in the top 25 m (Bywater *et al.* 1996).

Palaeomagnetic dating indicates that a Paleocene ferruginisation event is preserved in the upper part of the profile and a younger, Miocene ferruginisation occurs below this (25 m, Figure 2). Representative samples from the ferruginous saprolite from these two zones confirm major differences in their trace element contents (Figure 3). The older part of the profile has a significantly higher As/Fe ratio and significantly higher Pb contents. The zone of younger ferruginisation has a very low As/Fe ratio and low Pb contents, but the highest Cu contents. Hematite is the principle iron oxide in both zones and its bulk abundance is similar for both (Figure 3). Higher As and Pb in the older part of the profile may reflect early, intense weathering under humid or seasonal conditions with widespread release of these elements from the sulfides, enhanced mobility and subsequent accumulation in hematite during oxidation. Elements such as Cu and Zn were not accumulated by hematite or, if they were, they were not strongly fixed in this mineral (studies on ferruginous lag in the Cobar area confirm that these elements are not as enriched or as strongly bound in hematite as As and Pb (McQueen *et al.* 2004)). Low pH conditions would also have favoured greater mobility of Cu and Zn. Later weathering under drier or arid climatic conditions resulted in overall lower release of metals from already partly weathered sulfides but some local accumulation of Cu and Zn in hematite, possibly enhanced by neutral to alkaline groundwater conditions.

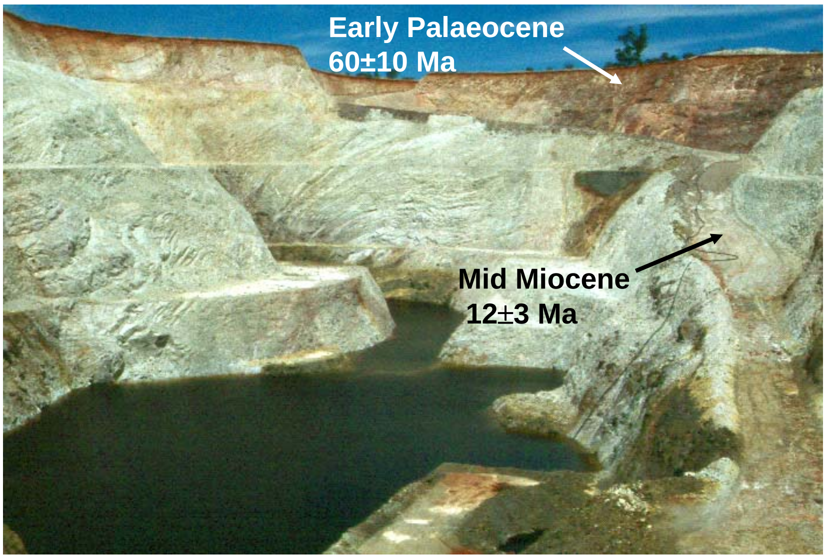

Figure 2: View of the McKinnons gold mine south of Cobar, looking southeast. Two episodes of deep oxidation and hematite fixation (identified by palaeomagnetic dating) are preserved at different levels over the deposit, (older regime has Cu-Zn leached and As-Pb concentrated).

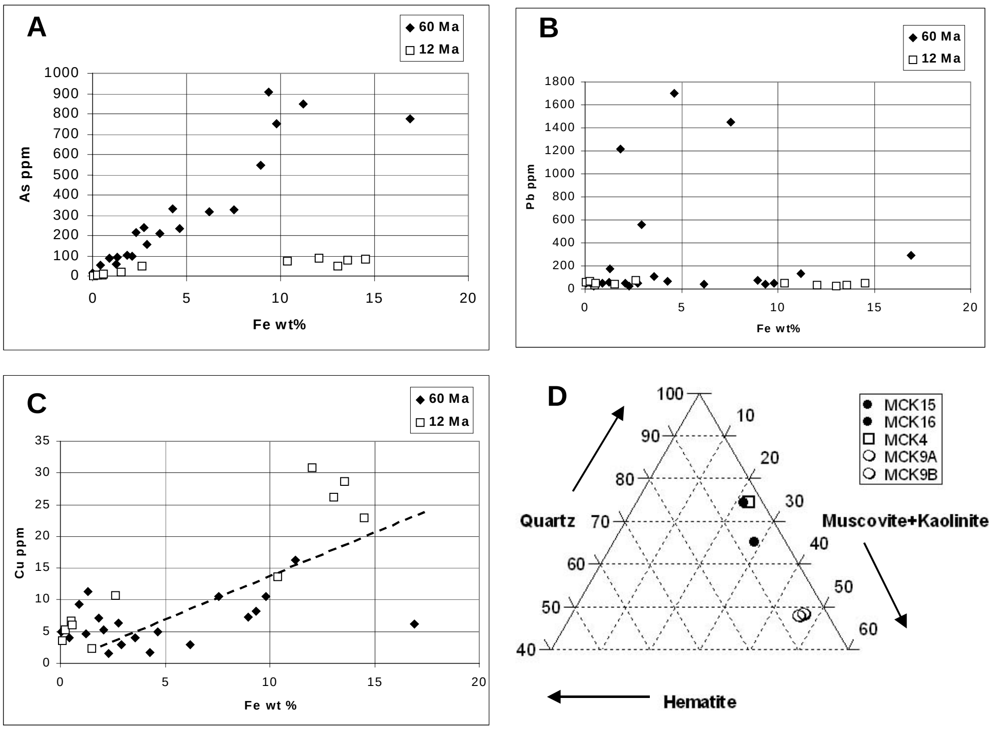

Figure 3: Geochemical and mineralogical characteristics of palaeomagnetically dated ferruginous saprolite from the McKinnons gold deposit near Cobar. A, B, and C show concentrations of As, Pb and Cu against total Fe extracted by aqua regia digest from individually dated samples (continued overleaf…)

(Figure 3 continued…) (analysed by inductively coupled plasma-optical emission spectroscopy; Smith 2001 and McQueen new data). D shows the major mineral compositions of bulk samples collected from the two main dated zones (quantitative X-ray diffraction by SIROQUANT^{TM}). Open symbols are for the 12 Ma (lower) site and closed symbols for the 60 Ma (upper) site. There is no detectable goethite in any of the samples. Gold content of the bulk samples is MCK15 (30 ppb), MCK16 (10 ppb), MCK4 (20 ppb) MCK9A-B(10 ppb). Fresh sulfide mineralisation contains 20 ppm As, 104 ppm Pb, 60 ppm Cu and 0.5-2.5 ppm Au.

New Cobar copper-gold deposit

The New Cobar deposit is a structurally controlled, vein-style polymetallic sulfide deposit with exploitable gold. It crops out as a small hill in an erosional terrain, shows weathering to approximately 130 m depth and is strongly oxidised to 75 m (Figure 4). Samples collected down the top 40 m of the weathering profile have yielded consistent Jurassic palaeomagnetic ages. Within this zone there is strong depletion of Cu, Co, Ni, and Zn as well as depletion of Ag relative to Au. Gold is depleted in the top 10-15 m, but it is preserved or relatively enriched below this. Lead, and to a lesser extent As, are preserved in the upper part of the profile. Anomalous Pb levels, particularly developed with hematite/goethite in low-angle fractures, define a 70 m wide halo around the deposit. In the lower part of the oxidised zone (yet to be dated) lead and copper arsenates persist. Covellite and native copper occur in the upper part of the supergene zone above the present water table. Coronadite-cryptomelane and lithiophorite are common manganese oxides in the upper part of the profile, typically forming coatings on gossanous hematite and secondary silica. The cryptomelane has been dated as Miocene, indicating precipitation significantly later than initial weathering and oxidation of the sulfide mineralisation in the Jurassic. This later stage precipitation of manganese oxides is probably related to strong oxidation or local pH changes following mobilisation of Mn at a period in the Miocene of high rainfall and leaching in the presence of organic acids (Vasconcelos *pers. comm.*). Rare earth element (REE) carbonates are also a feature of the upper weathering zone. Textural evidence (including infillings in partially weathered pyrite) indicates that these have precipitated under very dry, high pH conditions at a late stage of the weathering and dispersion history. The REE were residually concentrated by early intense chemical weathering under acid conditions that effectively removed Ca. Later introduction of carbonate-enriched groundwater caused precipitation of REE carbonates (the best available cations) and also malachite in the upper part of the profile. This was probably coincident with calcite and dolomite precipitation to form calcrete in areas away from the deposit. There is more to learn about the history of element dispersion at this deposit but clearly there has been multistage dispersion under different chemical regimes over a 180 My time span.

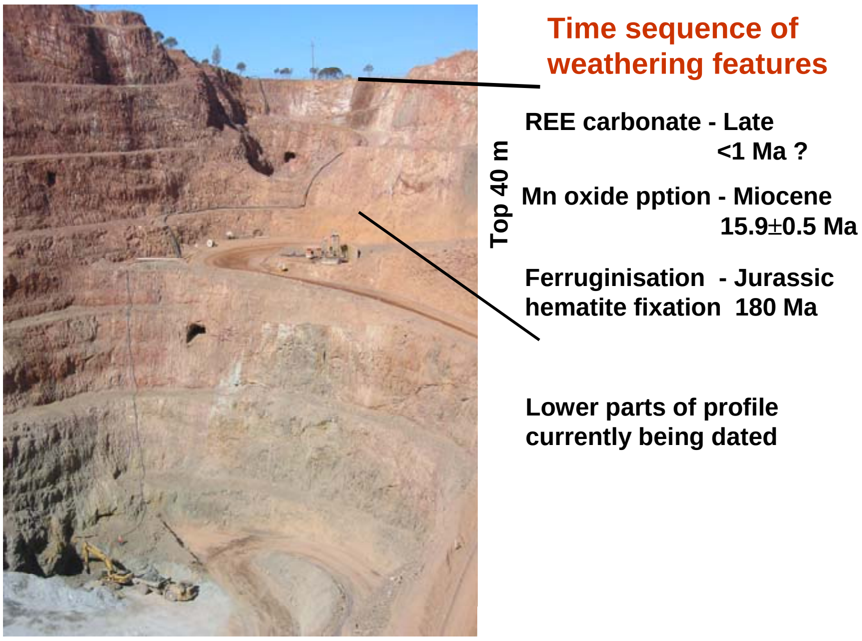

Figure 4: View of the south wall of the New Cobar open pit near Cobar. A number of ages of different weathering-related features at this deposit indicate a long history of weathering and element dispersion under varying climatic regimes.

Regional dispersion features

Geochemical investigation of the regolith across the Cobar-Girilambone region has identified a number of regolith-related element associations (McQueen & McRae 2004). The important associations include:

- An 'evaporitic' association of Ca-Mg ± Au, in some cases with Ba-Sr, related to regolith carbonate and sulfate accumulation in the near surface regolith and at the base of palaeochannels and transported regolith;

- An association of Mn-Co-Zn ± Ni-Cu-Au developed in redox boundary accumulations of manganese oxides/oxyhydroxides (particularly lithiophorite), commonly at around 20-30 m in thick regolith and also at the present, deeper water table;
- An association of Fe-Cu-Zn with goethitic accumulations at various levels in the regolith; and,
- An association of Fe-As-Pb ± Sb ± Bi with hematite, particularly in ferruginous lag, palaeochannel sediments containing ferruginous lag and in hematite-rich mottles in the upper saprolite.

The timing of these associations is not yet established. The 'evaporitic' association is related to the development of aridity but the timing of initiation and duration of this episode are not known. The manganese oxide association reflects a period when Mn was able to escape deposition with Fe in the upper part of the oxidised weathering profile and precipitate separately and deeper by oxidation. Given sufficient Mn in solution this could occur if conditions became more oxidising after iron oxide precipitation. Alternatively, separation could occur if the ground water pH became more alkaline promoting Mn oxide precipitation at Eh conditions where Mn was still in solution but Fe oxides had already precipitated higher in the profile. Concentration of manganese oxides at a broadly similar depth, significantly above the present water table across the region, suggests that it could represent a water table highstand formed in the Miocene. Iron oxides/oxyhydroxides show a wide distribution in the weathering profile, but a strong concentration in the top 20 m. There have been multiple stages of iron oxide/oxyhydroxide precipitation under a range of climatic conditions, but the details of associated element uptake from background under these different conditions is yet to be established.

CONCLUSIONS AND IMPLICATIONS FOR EXPLORATION

Initial studies utilising various regolith dating methods have confirmed that in regions subjected to prolonged weathering there are significant differences in element dispersion patterns formed at different times, reflecting different environmental conditions. Depending on the landscape history, different patterns are separately preserved or in some cases superimposed (Figure 5).

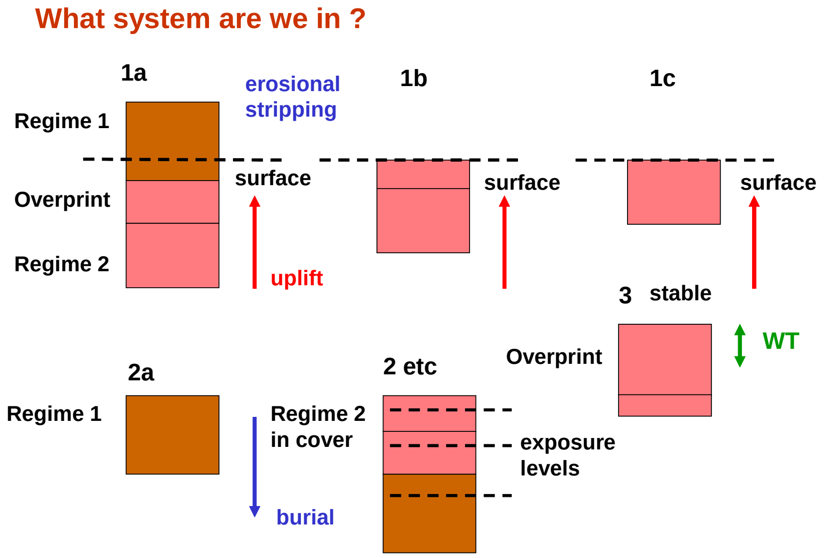

Figure 5: Interaction of multiple weathering regimes and some possible resulting regolith profiles. Profile 1a shows two partly overprinting regimes; profiles 1b and 1c show the effects of later progressive erosional stripping (the McKinnons profile would be an example of 1a). Group 2 profiles show the effects of a single weathering regime subsequently buried with later weathering and dispersion into the cover (these profiles may then be exposed at different levels). Profile 3 shows the effects of overprinting regimes in a relatively stable environment, possibly with changing water table levels (the New Cobar profile would be an example). Timing of exposure to the weathering front the prevailing climatic-chemical regime/s and hydromorphic versus mechanical transport critically affect element dispersion. Position within the regolith evolutionary model is therefore important for determining the geochemical expression of contained mineralisation.

Geochemical exploration programs generally take a 'one size fits all' approach to setting thresholds and pathfinder associations for a particular style of mineralisation in known terrains with similar regolith and bedrock type. It is also important to know if element dispersion behaviour has changed with time and what episodes of dispersion may be represented at different sites and levels in the landscape. To understand geochemical anomalies properly we need to know what system we are in.

Different systems formed at different times can result in different anomaly patterns around similar deposits. Superimposed effects over prolonged periods may explain the effective removal of some anomalies. Particular temporal weathering regimes or systems may be more conducive to element dispersion and/or fixing or more favourable for supergene ore formation. Identifying these systems and understanding where they might be preserved in the landscape and regolith can help make geochemical exploration more predictive and successful.

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