

MECHANISMS OF METAL TRANSFER THROUGH TRANSPORTED COVER WITH THE AUSTRALIAN REGOLITH: A REVIEW

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Mineral exploration programs in Australia are faced with multiple challenges when it comes to exploring across landforms underlain by “transported” and complex regolith, the main challenge being the successful application of surface geochemical techniques to identify buried deposits. A growing trend to make surface geochemistry effective in exploring across depositional landforms underlain by shallow to deep sediments is the use (and abuse!) of partial and weak selective extractions (SWE), gas analysis and biogeochemical surveys to delineate anomalies in depositional landforms (some of these techniques have been in application for over 30 years). However, these techniques have found mixed success in delineating buried ore bodies and not merely ‘anomalies’, especially in Australia, because the particular mechanism(s) and their effectiveness in transferring metals associated with mineralization upwards through the often complex transported overburden is poorly understood, thereby complicating and limiting the interpretation of datasets, and precluding the discrimination of negative and false anomalies. To address the lack of understanding of various upward metal transfer mechanisms through transported regolith (as opposed to the metal concentration in residual regolith), a review was conducted to evaluate the potential mechanisms effective in the Australian environment. In general, besides solid state diffusion, which is extremely slow for most metal cations except H⁺ (Smee, 2003), four dominant mechanisms with potential to transfer metals upwards through barren cover were identified (some covered by Cameron, et al. 2004): groundwater, gases, vegetation and bioturbation. Most of these categories have variants or sub-mechanisms, and may be influenced by microbial processes, and all are summarized below.

Groundwater in association with infiltrated water is the main agent of chemical weathering, and facilitates the dispersion of metals from the ore body. Flow directions, solution properties, aquifer heterogeneity, adsorption, complexation and inherent interactions and feedbacks between these processes influence the extent of *lateral and vertical dispersion* within the unconfined aquifer. Redox processes and formation of a possible stagnant zone at varying depths affect vertical migration and fractionation of specific elements (rare earths, Fe, Mn, V, As) at or within the fluctuating zone of the water table. *Capillary* forces at and above the water table can induce upward migration of solutes, with the rise being dependant on aquifer grain size and evaporation rates. Keeling (2004) has suggested capillarity as the main driver for dispersion Cu through 5-8 m of transported cover at Moonta, SA. *Seismic* or *dilatancy pumping* occurs in neo-tectonic active areas where faults and fractures act as conduits for upward transfer of mineralized groundwater (Cameron, et al. 2002). Earth tremors promote compressional stresses along faults and force groundwaters upward, with possible surface discharge resulting in a near surface anomaly. This mechanism is limited to low-rainfall and neo-tectonic areas that have regular seismic activity after overburden deposition. *Free convection* or buoyancy driven currents within the groundwater can arise due to density differences induced from point or diffuse heat sources. These can promote faster solute migration in a particular direction and the possible formation of irregular fronts. The oxidation of sulphides in an ore body is an exothermic reaction that produces heat and is capable of increasing groundwater temperatures and facilitating rapid increases of solute concentrations above ore bodies. The ability of convective flow to rapidly transfer solutes upwards up to the water table remains unexplored and has only been investigated via simulations and laboratory tests for point source contaminant transport. The formation of *electrochemical cells* around an oxidizing-reducing sulphide body within groundwater can provide excess cation concentrations at the oxidized upper edges of the sulphide body, and the proposed pattern of (“rabbit ear”) surface anomalies in regolith suggests its possible operation (Govett, et al. 1984). Another variant of the electrogeochemical model posits the onset of redox anisotropy between the buried sulphide body (reducing) and water table (oxidizing) after the deposition of sediments. Self-potentials arise and are maintained due to reducing conditions at the sulphide body front and oxidizing

conditions at the water table, leading to upward and outward migration of reduced species and their subsequent oxidation and formation of a reduced column above the ore body (Hamilton 2000). This model is considered to account for the rapid transfer metals upwards through thick (30 m) saturated cover (Cameron et al 2004). All the groundwater supported transfer mechanisms are limited to the upward limit to which groundwater rises or the water table (and capillary fringe), except that of seismic pumping. In the Australian environment dominated by Mediterranean, semi-arid, and arid settings, groundwaters are commonly more than 5 m below surface except in lower, discharge landform sites, and other, or additional, mechanisms are necessary to transfer metals from the water table upwards.

Gases migrate via molecular diffusion, advection and gas streaming (Hale 2000). Diffusion and advection appear to be the main sources of rapid upward migration of ore related gases (CO_2 , SO_2 , COS) and possibly of volatile metals. The upward *diffusion* of gases and volatiles that are produced as a result of weathering of ore body (COS, CO_2 , H_2S , Hg) has been experimentally shown to be viable mechanism of volatile metal transfer but has limitations in individual gas stability and tortuosity of the weathered and often cemented regolith medium. *Atmospheric pumping*, the depression front set up by large barometric pressure change, causes rapid upward migration of air present in pores and conduits, and has the capability to transport volatile (I, Hg) and radiogenic elements from nuclear blasts (Cameron, et al. 2004). Atmospheric pumping is restricted to fractured media, and whether it may operate in a connected heterogeneous sedimentary overburden needs testing. *Gas streaming* or bubble migration is the upward transfer of microscopic gas bubbles that form within the groundwater due to overpressure, and are then released from the water table. Specific metals (Cu, Zn, Pb, Hg, actinides) and ultra-fine particles (clays, oxides, bacteria) can attach to the surfaces of ascending gas bubbles (dominantly composed of CO_2), especially if the gas bubbles have an organic coating acquired from trace organics in groundwater. The bubbles can then be transported upwards to the near surface environments, where pressure changes are proposed to induce bubble instability and release metals. The stability of bubbles during their transfer from a saturated to an unsaturated medium as well as the fate of adsorbed matter on bubbles when the bubbles destabilize is unclear. In any case, most, if not all, studies of gas anomalies at the surface indicate rapid migration along conduits such as faults, fractures and shears, above which the gas anomalies are present, and this confirmation holds promise to at least accurately demarcate local structural features.

Vegetation or plant physiological uptake of elements from subsurface and their release to the surface via litter is a potential mechanism of rapid metal transfer. However, proof is required that plants tap into deeper water sources for their nutrient content, otherwise higher metal content in plant tissues merely may indicate recycling of a soil anomaly. The potential of plant assisted metal transfer from deeper groundwater comes from deuterium isotopic studies on facultative phreatophytes – plants having dimorphic root systems with laterals and sinker or tap roots (vertical), the latter roots acquiring water and nutrients from deeper groundwater source, especially during summer (Pate, et al. 1999). Recent work on plant metal relationships in Northern Yilgarn suggests plants do uptake ore related metals from groundwater at depth. Additionally, hydraulic lift – redistribution of deeper water acquired by sinker roots to near surface soil horizons to be used by laterals (Caldwell, et al. 1998) - is capable of rapid transfer of water and possibly metals within the overburden. Diurnal uptake and transfer of water groundwater to surface soil has been confirmed, but no data exist on ore metal transfer.

The depth of rooting is critical to the ability of vegetation in transferring water and possibly ore metals upwards. A global survey indicates that deep roots, especially sinkers, are ubiquitous with > 10 m depths regularly reached and confirmed in several climatic settings (Canadell, et al. 1996). Plants are known to take up mineralization associated metals that are essential micronutrients (Zn, Mo, Se) plus other ore metals (Au, Ni, Cu, Pb) and even potentially toxic metals such as As in significant concentrations (Meharg and Hartley-Whitaker 2002). Plant physiological processes biotransform specific metals within their tissues, thereby influencing the effectiveness of selective leaches and element mobility once the metals are released on the surface via litter. For example, gold absorbed by roots in the dissolved form can be converted into colloidal form within the plant tissues, and arsenic

and other elements are combined with phytochelatins to reduce toxicity. The subsequent release of these organo and colloidal species on the surface and their impact on partial or selective leaches needs further evaluation. Preliminary results point to the potential of phreatophytes and other specific plants to transfer metals from 10 m deep, current or paleo groundwater tables (redox fronts) or capillary fringes, but identifying the role of plant species, the rate and amount of metal transfer to the surface via particular plants and the regolith and groundwater environments (perched or permanent, saline or fresh) under which plant transfer is operative requires extensive testing.

Bioturbation within the biomantle is capable of moving huge amounts of soil material, and thereby bringing up anomalous material from depth to the surface. Ants, termites and earthworms are the main bioturbators in the Australian environment, but only ants and termites have the capacity to penetrate deeper into the transported regolith (> 1 m). These bioturbators, in combination with rainwash, are the primary cause of soil (and anomaly!) homogenization and lateral dispersion of surface anomalies over time. Although bioturbation on freshly deposited sediment begins within years with 1 m penetration achieved randomly, it is the development and evolution of the biomantle across the depositional landform that needs to be considered for anomaly homogenization and true anomaly detection, and the rate of biomantle homogenization varies from hundreds to thousands of years depending on the interplay between deposition rates on the landform and climatic/biotic factors. Furthermore, barring a few exceptions from the Kalahari in Africa, the effectiveness of bioturbation decreases rapidly downwards, with activity mostly ceasing at a depth of 2 m, which is likely to be the limit for uniform biomantle homogenization in most landforms.

The role of **microbes** in transferring metals upwards is restricted, but they affect most of the processes responsible for metal transfer. Microbial metabolism affects the kinetics of many hydrochemical processes, especially sulphide oxidation and other redox transfers (Edwards, et al. 2000). Microbial metabolism can impact on gaseous migration of elements by generating methanogenic, CO₂ and sulphur gases, and by generating volatile metal species via biomethylation (As, Se, Sb, Mo). They can influence the efficiency of metal uptake by roots via redox reactions, symbiotic associations and organic secretions. Microbes participate in intracellular and extracellular formation of minerals (and gold particles) within the saturated zone and soil, and can influence the efficiency of partial and selective leaches (Figure 3). Microbial induced biomethylation (with As, Sb, Se, Hg) can significantly affect the “loosely” bound metal fraction or the efficacy of selective or partial leaches. For example, recent studies demonstrate microbial role in biomethylation of commonly used pathfinders with some of the metal differentiating into volatiles (Craig, et al. 2003), possibly followed by demethylation. Microbial roles need to be investigated to address the question of whether the results of selective leaches or gas analysis are dependant on microbial populations and soil conditions rather than transfer mechanisms.

The vital parameter that influences the operation of the diverse mechanisms responsible for upward metal migration is the **nature** of the transported overburden (pre- and post- weathering) and its **depth**, both factors in turn affected by time and landscape evolution. Weathering of the overburden and formation of concomitant water table within the sedimentary overburden increases the possibility to transfer metals upwards via a combination of mechanisms such as vertical hydrogeochemical gradient and electrochemical effects, vegetation uptake and bioturbation, to form “incremental” anomalies over time. This has been shown to occur at a couple of sites in Western Australia. Alternatively, younger, fresh to slightly weathered sediments, even of shallow depth, will afford a much lesser opportunity for diverse mechanisms to operate, except mechanisms capable of rapid metal transfer such as gaseous diffusion and advection and possibly plant uptake, depending on porosity, anisotropy and hardness of the transported material. However, specific partial leaches, gas measurements and electrochemical techniques, rely on the principle of a rapid migration mechanism even in recent, fresh cover, and therein lies the need to understand the rate, extent and overall effectiveness of the mechanism(s) to mobilize ore metals upwards under different transported cover settings, so surface geochemical techniques can be efficiently and predictively applied, or discarded.

References

- Caldwell MM, Dawson TE, Richards JH (1998) Hydraulic lift: consequences of water efflux from the roots of plants. *Oecologia* 113:151-161
- Cameron EM, Hamilton SM, Leybourne MI, Hall GEM, McClenaghan MB (2004) Finding deeply buried deposits using geochemistry. *Geochemistry: Exploration, Environ., Anal.* 4:7-32
- Cameron EM, Leybourne MI, Kelley DL (2002) Exploring for deeply covered mineral deposits: formation of geochemical anomalies in northern Chile by earthquake-induced surface flooding of mineralized groundwaters. *Geology* 30:1007-1010
- Canadell J, Jackson RB, Ehleringer JR, Mooney HA, O.E S, E.D S (1996) Maximum rooting depth of vegetation types at the global scale. *Oecologia* 108:583-595
- Craig PJ, Eng G, Jenkins RO (2003) Occurrence and pathways of organometallic compounds in the environment - General considerations. In: Craig PJ (ed) *Organometallic compounds in the environment*, vol. John Wiley & Sons, pp 1-56
- Edwards KJ, Bond PL, Druschel GK, McGuire MM, Hamers RJ, Banfield JF (2000) Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. *Chem. Geol.* 169:383-397
- Govett GJS, Dunlop AC, Atherden PR (1984) Electrical techniques in deeply weathered terrain in Australia. *Journal of Geochemical Exploration* 21:311-331
- Hale M (2000) Genetic models of remote dispersion patterns. In: Hale M (ed) *Geochemical remote sensing of the subsurface*, vol 7. Elsevier, Amsterdam, pp 3-16
- Hamilton SM (2000) Spontaneous potentials and electrochemical cells. In: Hale M (ed) *Geochemical Remote Sensing of the Subsurface*, vol 7. Elsevier, Amsterdam, pp 421-426
- Keeling J (2004) Metal ion dispersion through transported cover at Moonta, South Australia. In *Regolith 2004 (Proceedings of the CRC LEME Regional Regolith Symposia 2004 – I. Roach ed)* 161-165.
- Meharg AA, Hartley-Whitaker J (2002) Arsenic uptake and metabolism in arsenic resistant and nonresistant plant species. *New Phytologist* 154:29-43
- Pate JS, Jeschke DW, Dawson TE, Raphael C, Hartung W, Bowen BJ (1999) Growth and seasonal utilisation of water and nutrients by Banksia prionotes. *Australian Journal of Botany* 46:511-532
- Smee, B (2003) Theory behind the use of soil pH measurements as an inexpensive guide to buried mineralization, with examples. *Explore (Association of Applied Geochemists Newsletter)* 118, 1-19.

Figures

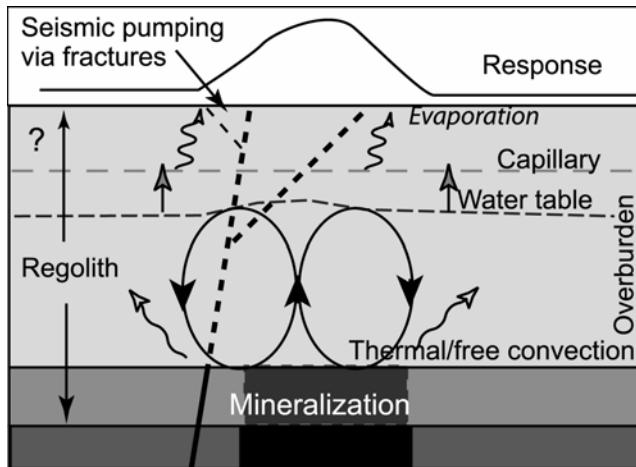


Figure 1. Some potential hydrogeochemical mechanisms for dispersion through transported regolith. The genesis and evolution of electrochemical processes within saturated transported cover are covered by Hamilton (2000).

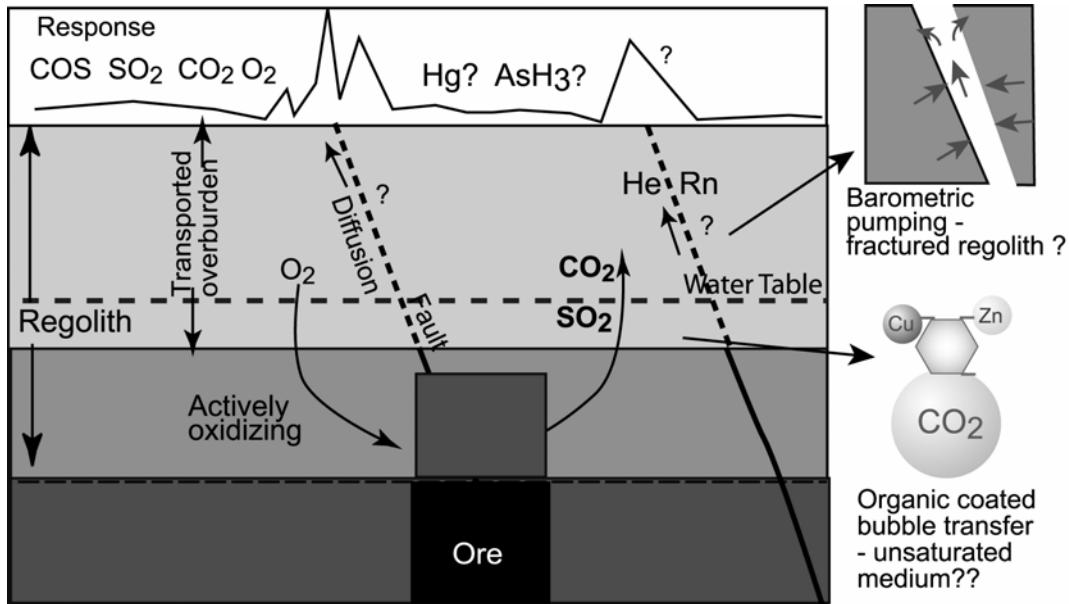


Figure 2. Illustration of potential gas based migration mechanisms through transported regolith.

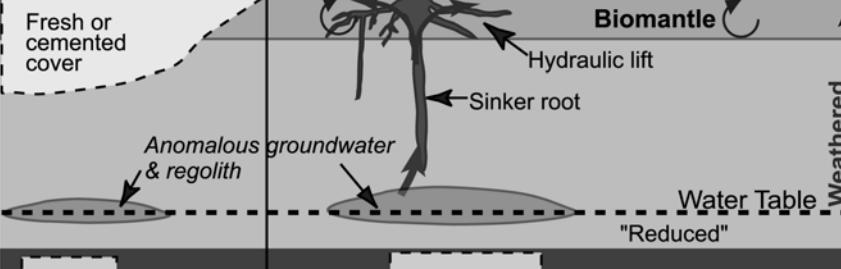
Fresh or cemented cover	Weathered cover. Possibly multiple profiles superimposed	Microbial processes
Possible mechanisms - Gas based	 <p>Potential mechanism - Gas based - Plant uptake from groundwater - Capillary and electrochemical at depth - Bioturbation near surface</p>	Impact on effectiveness of mechanisms and techniques Biomethylation $\text{As} + \text{CH}_3 \rightarrow \text{CH}_3\text{As}$
Fresh or cemented cover	 <p>Anomalous groundwater & regolith</p> <p>Water Table "Reduced"</p> <p>Weathered Transported Overburden</p>	Siderophores induced dissolution of oxides Biomineralisation $\text{Au(III)} \rightarrow \text{Au(0)}$ Reductive dissolution of oxides
	Weathered ore	- Sulphide oxidation - COS & CO2 generation - Possible biomethylation - As, Se, Sb, Mo volatile generation

Figure 3. Illustration showing the operation of potential mechanisms depending on nature of cover (fresh or cemented as compared to deeply weathered with minimal cementation) and influences of microbial processes.