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GEOCHEMICAL DISPERSION MECHANISMS THROUGH TRANSPORTED COVER: IMPLICATIONS FOR MINERAL EXPLORATION IN AUSTRALIA.

M.F. Aspandiar, R.R. Anand and D.J. Gray

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2nd Impression 2008)

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Addresses and affiliations of Authors:
M.F. Aspandiar
Department of Applied Geology
Western Australian School of Mines
Curtin University of Technology
PO Box U1987
WA 6845

R.R. Anand and D.J. Gray
Cooperative Research Centre for Landscape Environments and Mineral Exploration
c/- CSIRO Exploration and Mining
P.O. Box 1130,
Bentley
WA 6102

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Abstract

There is growing trend to make surface geochemistry effective for exploring across depositional landforms underlain by shallow to deep transported and often complex regolith cover using techniques such as partial and weak selective extractions (SWE), gas analysis and biogeochemical surveys. However, these techniques have found mixed success in delineating buried ore bodies, especially in Australia, because the particular mechanism(s) and their effectiveness in transferring metals associated with mineralization upwards through transported cover is poorly understood, thereby complicating and limiting the interpretation of geochemical datasets, and precluding the discrimination of negative from null results. A review conducted to address the lack of understanding of various upward metal transfer mechanisms through transported regolith as opposed to the metal concentration in residual regolith, found several potential mechanisms capable of achieving metal transfer through variable depth of transported cover. The mechanisms are classified according to two main processes: phreatic process accounting for groundwater flow, convection, dilatancy, bubbles, diffusion and electromigration, and vadose processes accounting for capillary migration, gaseous transport and biological transfer. However, most of the mechanisms have limitations that require to be addressed.

Phreatic processes are underpinned by groundwater as the main solute transfer process. Subsurface mineralized water can be transferred to the surface via faults due to s*eismic* or **dilatancy pumping**. The onset of compressional stresses along faults arising from earth tremors force the mineralized groundwaters upward, with possible surface discharge of water and their rapid evaporation resulting in a near surface anomaly. This mechanism is limited to low-rainfall and neo-tectonic areas that have regular seismic activity. An oxidizing sulphide ore body could act as a point or diffuse **heat source** resulting in buoyancy driven currents and possibly convective currents. The heat produced from sulphide oxidation can induce faster solute migration in a particular direction, especially upwards, with ions released from the ore body being driven upwards as opposed to along lateral flow. The ability of heat driven flow to rapidly transfer solutes upwards to the water table remains unexplored and has only been investigated via simulations and few laboratory tests for point source contaminant transport. **Electrochemical** processes involve the movement of charged ions within an electrical field and are considered to be efficient migration mechanisms because they favour rapid upward ionic migration. Electrochemical forces arising due to spontaneous potentials (SP) around an ore body are considered to result in excess cation concentrations at the upper edges of the sulphide ore with subsequent diffusion of cation along concentration gradient accounting for a near surface anomaly through cover. The resultant migration of H^+ to surface can modify soil conditions (lower pH) which can in turn mobilize specific cations within the soil. The proposed dual peak ("rabbit ear") pattern of surface cation concentrations in regolith is advocated as a case for the potential operation of the electrochemical cell mechanism. **Redox gradient** model for electrochemical migration posits the onset of redox anisotropy between the buried sulphide body (reducing) and water table (oxidizing) after the deposition of cover sediments. Redox differentials 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. *Gas bubble* migration is the upward transfer of microscopic gas bubbles that form within the groundwater due to overpressure or exsolution, 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 carrier gases - 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 remains unclear. All the phreatic processes are supported by groundwater and are limited by the height of the water table, except that of seismic pumping. In much of the Australian environment, 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.

The **vadose** zone processes are critical in transferring metals from the groundwater to the surface. **Capillary** or tension forces at and above the water table can induce upward migration of solutes. The

rise of solutes is dependant on aquifer grain size and evaporation rates with finer grain sized material and high evaporation rates at the root zone in dry climates causing high suction pressures which would transfer thin film of water and dissolved metals to the root zone. The effectiveness of capillary pull is limited by the variable regolith grain sizes and poor understanding of height to which interconnected water films rise in different textured materials. Weathering of ore body releases gases (COS, CO_2, SO_2, CH_4, Rn, He – depending on ore body type) and possibly metal volatiles (Hg, I, As, Se) that can migrate upwards from the oxidizing ore body and water table if the ore is submerged. The upward **diffusion** of gases has been experimentally shown to be a viable mechanism of volatile metal transfer but has limitations in form of temporal and geochemical stability of individual gases 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 ore associated gases and volatiles along structural conduits. Atmospheric pumping is restricted to fractured media, and its operation in a heterogenous weathered sedimentary overburden is difficult. Heat produced from oxidizing sulphides can set up **convective gas flow** where oxygen diffuses into the oxidizing ore body and released gases advect upwards. This transfer mechanism is limited by heat production (sulphide amount) and permeability of the ore body and cover. Mechanisms supported by gaseous migration have several limitations such as temporal stability of gases, excess contribution of gases from biological metabolism, temporal and spatial stability of bubbles and the channeling of gases and greater contribution via structural conduits.

The other critical vadose zone processes are biological: vegetation transfer or plant physiological uptake and bioturbation. **Vegetation** uptake of elements from subsurface and their release to the surface via litter is a long publicized potential mechanism of rapid metal transfer. Plants take up most ore associated metals (Zn, Mo, Se, Au, Ni, Cu) and even potentially toxic metals such as As and Pb, and have evolved novel methods to biotransform toxic metals, store and release them to the surface. Spatial and temporal water access by plants (determined via deuterium isotopes) demonstrates the ability of plants to seasonally access deeper groundwater via their sinker or tap roots and confirms the uptake of water and metals from potentially mineralized groundwater as compared to mere soil cycling. Additionally, *hydraulic lift* – redistribution of deeper water acquired by sinker roots to near surface soil horizons to be used by laterals is capable of rapid transfer of water and possibly metals within the overburden. Diurnal uptake and transfer of groundwater via hydraulic lift to surface soil has been confirmed for many species spanning diverse climates, but no data exist on ore metal transfer. The *depth of rooting* is critical to define the depth limits to which vegetation assisted transfer can operate. A global rooting depth survey indicates that deep roots, especially sinkers, are ubiquitous with > 10 m depths regularly reached and confirmed for several species in several climatic settings. 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 by myriad regolith mesofauna accomplish biomantle homogenization (homogenize anomalies brought to the surface via other mechanisms) and potentially transfer anomalous material from great depths beyond the biomantle. Material transfer from great depths (~5-50 m) by the main conveyor-belt organisms – termites and ants – has been documented, but reports of such deep burrowing activity are restricted, especially to parts of Africa. The effectiveness of bioturbation is limited mainly to the biomantle and decreases downwards, and further documentation of depth of bioturbation on a local to regional scale is required to make it a predictive metal transfer method outside the regions where it is documented to penetrate deeper.

The **microbial metabolism** affects the kinetics of many hydrochemical processes, especially sulphide oxidation and other redox transfers, and also impacts, negatively and positively, on the generation of gases throughout the entire cover sequence.

The vital parameter that impacts on the efficacy of the diverse mechanisms responsible for upward metal migration is the *nature* (depth, weathering degree, cemented, faulted) and *evolution* (multiple deposition periods, structural activity) of the transported overburden, both factors in turn affected by *time* and landscape evolution of the region. Weathering of the transported overburden and formation of concomitant water table within the overburden increases the possibility to transfer metals upwards via a combination of mechanisms such as electrochemical effects, capillarity, vegetation uptake and bioturbation, to form “incremental” anomalies over time. Alternatively, younger, fresh to slightly weathered sediments, even of shallow depth, will afford a much lesser opportunity for diverse mechanisms to function, 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. In specific cover situations, true surface geochemical anomalies don’t manifest on the surface, and it is vital to define the limitations of all mechanisms in addition to their potential merits, whereby surface geochemical techniques can be predictively applied or not applied.

Acknowledgements

The principle objective of the first part of CRC LEME metal dispersion mechanisms project was to conduct a literature review of the potential mechanisms, particularly those relevant to the Australian regolith and climatic settings, capable of transferring metals through transported cover. The outcomes of this review would provide a framework for the larger project of testing out the efficacy of different mechanisms at particular sites.

We would like to thank several CRC LEME and industry colleagues who provided valuable input towards the review. Dennis Gee provided constant support and publicized the value of understanding the mechanisms. Professor Gerry Govett, probably the first advocate for studying geochemical dispersion mechanisms in terms of its application to predictive surface geochemistry, wholeheartedly supported the project through its various stages and communicated his understanding and views on several mechanisms. John Keeling and Mel Lintern provided valuable information on particular mechanisms and discussion with Charles Butt's were important in evaluating the practical limitations of different mechanisms in addition to their advantages. We thank Stewart Hamilton for his comments on the original report, especially his suggestions on classifying the mechanisms.

We would appreciate reader's feedback on the review in general, and particularly on any case studies demonstrating proof of operation of one or combination of the mechanisms or the lack of operation (null result).

Mehrooz F Aspandiar
Project Leader – CRC LEME, Review of Metal Dispersion Mechanisms Project
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1. Introduction

The two overstated facts in the mineral exploration industry and associated research groups are "the inevitable push of mineral exploration into covered landscape regions" and "capability to see through cover", or being able to unambiguously detect mineralization buried under thick transported or in situ regolith cover. The early research arising from the need to look through weathered and shallow sedimentary cover (or transported or exotic overburden) where traditional geophysics provided mixed signals, was to improve the understanding of evolution of regolith and the landscapes in which the regolith occurs, the outcomes of which are visible in the successful studies of CSIRO Exploration & Mining (Anand and Paine 2002; Butt *et al.* 2000b). From the seminal work on "laterite" geochemistry (Smith *et al.* 1987) followed the widespread integrated benefits of understanding the distribution and evolution of regolith materials within landscapes via regolith-landform maps and geochemical analysis, and led to a more predictive basis to analyzing near surface geochemical data and anomalies via dispersion models. The different landform settings formed the framework for dispersion models and patterns and enabled judicious selection of sample media and sample spacing in specific landforms, which combined with conventional geochemical analysis aided mineralization detection.

After over a decade of exploration using regolith-landforms as the main framework, even the residual or insitu regolith and their associated landforms have been largely explored, and the focus is a shift to the spatially dominant transported regolith residing in a myriad of landforms, with most landforms being of low relief and underlain by complex regolith stratigraphy. The initial view advocated and implemented in the regolith-landform models and in senior exploration divisional decision meetings was to resort to drilling to either basement saprolite or buried lateritic residuum in the widespread depositional regolith-landform settings, an activity that is expensive considering the acreage required to be covered. However, specific regolith materials in the soil have proved successful even in transported regolith settings, especially the use of pedogenic calcrete for gold anomaly detection, with anomalies being detected through < 10 m of cover (Lintern 2001; Lintern and Butt 1993).

While the role of geophysics to make the transported regolith transparent is being increasingly championed and recognized, and geological modeling is being investigated to predict mineralization zones, the value of surface geochemistry as a penetrative technique in areas of > 5m of transported cover settings appeared to have reached saturation barring a few specific sample media. However, a number of sample media and geochemical techniques are being proposed (and recycled!) and applied to exploring under cover, the main being selective or partial extractions, gas or vapour sampling and analysis, biogeochemical and groundwater sampling and analysis, and electrochemical techniques. Table 1 summarizes the type and concepts of some of the selective and partials leaches and other similar methods available to explore in transported cover settings.

The past decade has seen a mushrooming of selective and weak (or partial) extractions (SWE) that use old and new digests on soils, and are increasingly being employed in exploration programs to detect chemical signatures of mineralization through transported overburden (Table 1). The routine use of these techniques in geochemical surveys has been aided by the rapid increases in analytical detection limits and lower analytical costs (Hall 1998). The partial and selective extractions work on the principle that bulk geochemical analysis do not provide as good a contrast from the background, and that partial extractions distinguish "recently" transferred metals from the underlying ore body because these metal ions are "labile" and "loosely" bound (as compared to the "tightly" bound metals existing within the sedimentary overburden), and therefore their extraction and measurement within a soil survey will provide a clue to the underlying ore body. Partial extractions and selective leaches are not new, and "mild" or cold leaches have been employed by exploration geochemists (and soil scientists) for over four decades. The partial and selective leaches in some case studies do show merit in improving the detection of buried mineralization (Cameron *et al.* 2004). Gas sampling and analysis has also been advanced as a method to detect anomalies (Hale 2000; Highsmith 2004a) with recent advances in the technique showing promise of its use in routine geochemical sampling programs (Highsmith 2004a). Geoelectrical methods such as CHIM and its variants where electrodes are placed into the ground to extract metals have also been proposed (Goldberg *et al.* 1997; Putikov and Wen 2000) and some surveys using the method have found its effectiveness through over 50 m of cover

(Wang *et al.* 1997). Lastly, hydrochemical sampling has been proposed as a viable method for regional sampling with a number of case studies highlighting its value (Giblin and Mazzucchelli 1997).

Table 1. The fundamentals behind different partial and selective leaches, gas and geoelectrical methods employed to detect metal signatures of buried ore. The list is not extensive and many other leaches and gas analysis techniques exist.

Selective/Partial Leaches		
Leach	**Selective Phase**	**Mechanism or Concept**
Enzyme Leach	Mn-oxides	Hydromorphic dispersion anomalies Oxidation anomalies Apical anomalies
MMI-A	“unbound” extracted – loosely held, ligand complexation	Rapid hydromorphic or gaseous transfer upwards results in “unbound” metals, while endogenic or with time become “bound”
Deionized water	Weak “surface” bound	Transfer from ore body to surface with “weak” and non-specific binding to solid phase
Ammonium 1M acetate at pH 5	Adsorbed metals via exchange and carbonates	
Cold hydroxylamine (HxMn) 0.1M NH_2OHCl	Mn-oxides	Transfer from ore body to soil with surface charge and grain size of Mn-oxides preferentially adsorbing/incorporating the metals
Hydroxylamine (HxFe) 0.25M NH_2OHCl in .25HCl	“Poorly crystalline” Fe-oxides	Transfer from ore body to surface and preferential association with “poorly crystalline” Fe-oxide phase
Gas Methods		
Gas Sampling - Collectors inserted in soil (time averaged) - Mobile collection	Gas or volatiles	Gases released from oxidizing ore body-assumed continuous supply of gases from ore
Soil Desorption Pyrolysis (SDP) and Soil Gas Hydrocarbons (SGH)	Gases adsorbed on clay sized minerals	Gases gradually released from oxidizing ore body adsorbed onto clay fraction in the soil or gases indirectly effecting inorganic or organic changes in the soil – time averaged
Geoelectrical Methods		
CHIM	“mobile” ions	Ions migrate from buried ore to electrodes in the soil – ionic migration in an applied electrical field

These surface geochemical techniques (except groundwater sampling) advocate success in detecting subtle geochemical signals arising from buried mineralization below >5 m of transported regolith, with some techniques proposing target detection through over 100 m of transported cover. Although the success of SWE’s over traditional soil analysis to detect surface expression of buried mineralization are documented in Canada (Hall *et al.* 2004), comparative studies in Australia have found mixed success (Gray *et al.* 1999), and raised the question of whether SWE add value to an exploration program over traditional soil analysis, BLEG or cold extractable metal analysis. The value or success of any of the surface geochemical technique rests on the premise that metals and gases transfer from the fresh or weathered mineralization through the barren transported cover to the surface soil or vegetation. Furthermore, the process that underpins the effectiveness of some SWE and gas methods is the rapid and often continuous transfer of metals from the ore body upwards through transported regolith. Therefore, there is a need to understand how elements are transferred upward through barren cover.

Understanding the mechanism(s) has implications for the effectiveness and success of the technique in detecting true anomalies, but importantly, in differentiation between negative (nothing there) and null (wrong technique applied, potential untested) results. Although there are many cases of false anomalies, the critical question is whether a lack of anomalous surface geochemical response can be interpreted as barrend ground below? An example of the value of understanding of whether metal signatures from mineralization are transferred upwards to the surface and are then detectable via surface geochemical techniques such as soil sized fractions, partial leaches, gases, electrochemical, is illustrated in Figure 1. Gold from the underlying mineralization has dispersed into the overlying older and intensely weathered sediments, but not within the thinner, but less weathered near surface sediments, and subsequently surface geochemical sampling provided a null result (Radford and Burton 1999). In this particular example, an understanding of the extent to which the anomaly is effectively transferred upwards and within particular regolith unit or material, would enable the judicious selection of sampling media and sampling method. The example highlights the lack of predictive capability of the surface geochemical techniques because of a dearth of understanding of how metals are transferred upwards through different cover and environmental settings. In comparison, the understanding of geochemical dispersion via the combined processes of chemical and physical weathering of ore bodies within residual regolith is well established with proven successes in Australian regolith settings (Butt 2005; Butt *et al.* 2000b).

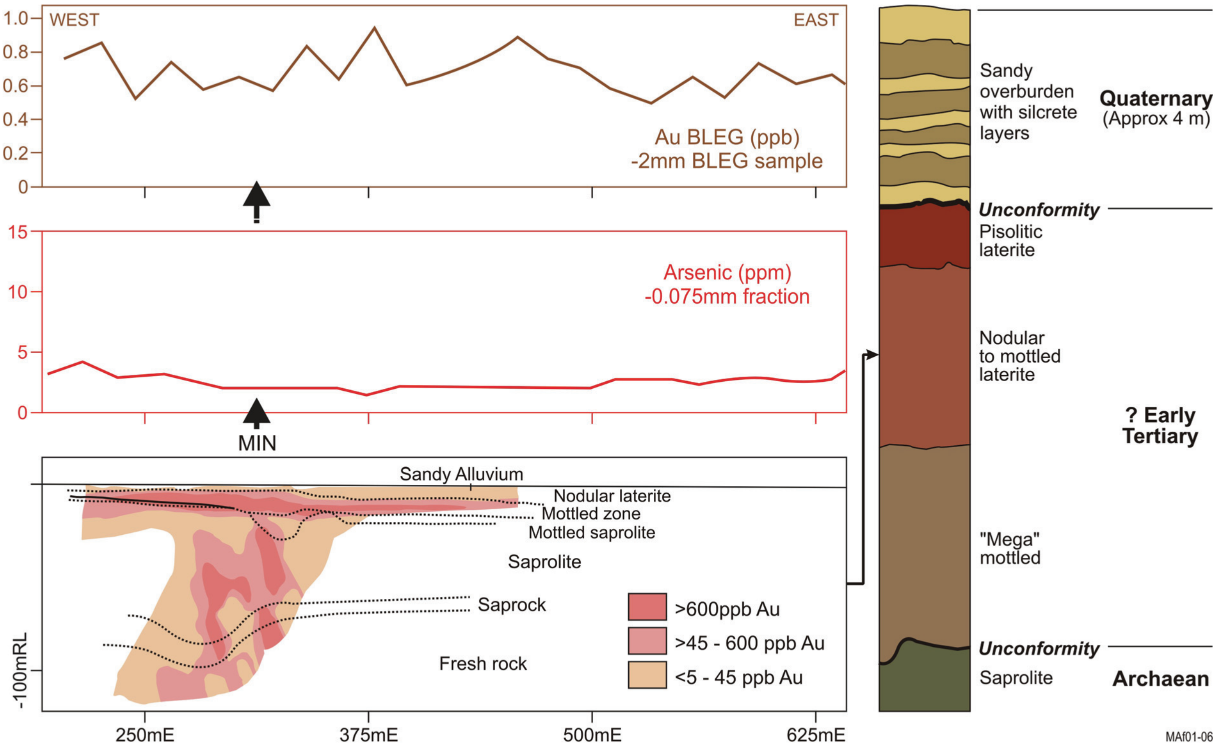


Figure 1. Gold concentration contours over regolith cross section from Big Bell. A magnified view of the regolith profile with interpreted unconformities is shown on the right. Part of soil geochemistry (Au and As) over the deposit from line 200 N is shown. The data and profile interpretation indicate dispersion into older deeply weathered transported cover but no detectable transfer into younger, fresh cover as indicated by a negative As and Au signal in soil (Modified from Radford and Burton1999).

This report attempts to address the lack of understanding of potential upward metal transfer mechanisms. The main objective of this report is to document the type, nature and operational extent of potential mechanisms by which metals transfer from the ore body upwards and laterally through unmineralized transported regolith, with an emphasis on the Australian regolith environment. Where there appears a linkage between the operation of different mechanisms and the effectiveness of selective leaches or associated surface geochemical techniques, the report alludes to the linkage, but the application of techniques are not extensively described nor explored. In view of the diverse mechanisms and their underlying processes, the report cites literature covering multiple disciplines.

A similar exercise to this was conducted as part of the CAMIRA project in Canada, the excellent results of which are published in Cameron et al. (2004) and this report borrows parts from that publication, especially on electrochemical and gas associated transfer mechanisms. The Australian regolith and landscape is unique although it does have similarities to other southern Hemisphere continents.

2. The Mechanisms

The mechanisms capable of transferring metals upwards can be grouped into two main categories based on whether they are within the groundwater zone (or saturated zone) or above the influence of the saturated zone (or vadose zone). This distinction is important for a dry continent like Australia because the groundwater table across much of Australia, especially the semi-arid and arid regions, is deeper and therefore the unsaturated zone processes and related mechanisms are critical to the upward transfer of metals. Further, previous reviews of metal transfer mechanisms have concentrated on the groundwater dominated processes with minor development of vadose based mechanisms. Accordingly, the mechanisms are classified under two main categories: **Phreatic** and **Vadose,** and the scope of individual mechanisms is illustrated in figure 2. Although most of the mechanisms described below have in the past been postulated to contribute to upward transfer of metals through the overburden, some have as yet not been proposed to achieve the same. The movement of ions and particles through transported cover is upwards against gravity, and therefore a **medium** (water, air, mineral particles) and **force** (concentration, electrical, temperature or pressure gradients) are necessary to drive the upward transfer via diffusion or advection. The major transfer mechanisms categorized according to the main processes are

Mechanism	**Force**	**Medium**
PHREATIC		
• Advective		
▪ Groundwater flow	Potential Energy	Water
▪ Dilatancy pumping	Stress	Water
▪ Convection or heat	Heat	Water
▪ Bubble transport	Pressure/buoyancy	Gas
• Chemical and electrochemical transport		
▪ Diffusion along concentration gradient	Concentration gradient	Water
▪ Electromigration		
▪ Based on spontaneous potentials	Self Pontentials	Water
▪ Based on redox gradients	Redox gradient	Water
VADOSE		
• Capillary action	Pressure/suction	Water
• Gaseous processes		
▪ Diffusion	Concentration gradient	Gaseous
▪ Atmospheric Pumping	Pressure	Gaseous
▪ Convection	Heat gradient	Gaseous
• Plant Uptake	Physiological/pressure	Water
• Bioturbaton	Animal metabolism	Regolith

Besides these main transfer mechanisms, two other factors or processes are also described, because they significantly affect the operation, scope and effectiveness of most of the mechanisms. These are

- Microbial induced reactions

- Time, climate, nature and evolution of the transported regolith

The above mechanisms, if effective, can cause a **direct** and **indirect** anomaly at the surface (Smee 2003). In the formation of a **direct** anomaly, the target metals (metals associated with mineralization) are transferred to the surface. For example, Au and/or pathfinder metals released on weathering of the ore body will be transferred upwards through transported overburden to form an anomaly at the surface. The formation of an **indirect** anomaly at the surface arises in response to another stimulus associated with the ore body. For example, the production of excess H^+ and Fe^{2+} because of oxidation of sulphides within mineralization will diffuse to the surface and cause a chemical change in the soil that is detectable and implies the presence of buried ore.

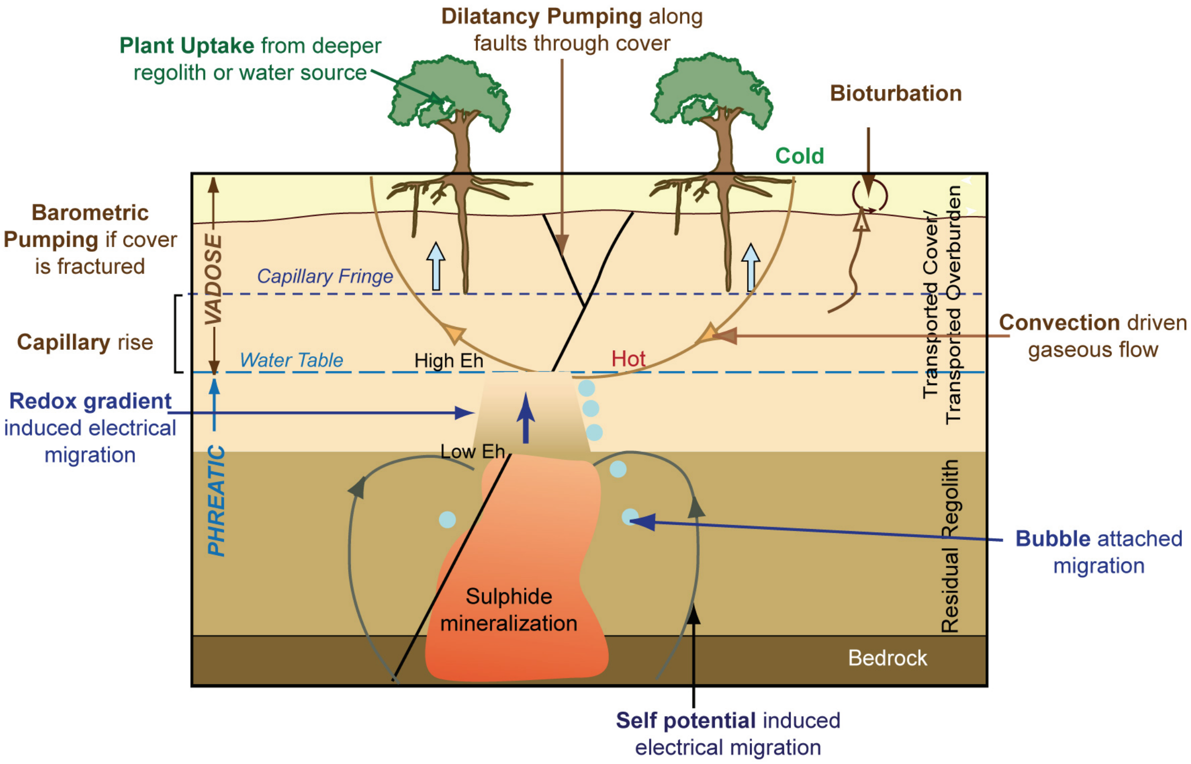


Figure 2. Illustration of the scope of the mechanisms within an idealized residual – transported cover setting.

3. Phreatic Process Based Mechanisms

3.1 Groundwater flow (hydraulic gradient)

Water is the main agent of chemical weathering and a medium for diffusive and advective transfer of metals in the regolith and deeper aquifers. Within the saturated parts of the regolith, groundwater in contact with rocks promotes dissolution or precipitation of aquifer minerals, but due to thermodynamic instability of primary ore minerals, groundwater mostly promotes the dissolution of primary or ore minerals with the release of the associated metals into solution and the migration of elements as solute species, as mineral particles (colloidal sizes) or adsorbed to colloids. The greater duration of contact of groundwater with the regolith and rocks offers a better opportunity for a chemical signal of the surrounding rocks to develop within the groundwater.

Table 2. Aqueous chemical reactions, processes and their effects on metal mobility.

Variable or reaction	**Process**	**Effects of metals**
pH (the master variable)	Affects solubility of minerals, metal species, hydrolysis, complexation and adsorption (via PZC of minerals)	Low pH increases solute concentration of cations, while neutral and alkaline pH decreases them.
Eh-pH (redox)	Affects mobility of metals with different redox states	Eh gradients cause migration and accumulation/loss of redox metals such as Fe, Mn, As, Au, S, Co, Cr
Adsorption/Surface reactions	Mineral surface process, mineral and pH dependant	Retard or increase metal mobility via surface adhesion or exchange. Low pH increase positively charged species migration
Major Ion Complexation	Presence of major anions that complex with specific metals	Some complexes at specific concentration increase metal mobility e.g. U with Cl^-, F, Au- Cl^-, I^-, CN^-
Colloids	Microscopic (< 4 μm) individual or mineral aggregate particles, sometimes in the nanometer range	Increase metal mobility by transferring adsorbed metals. Fine grain size and surface charge good at scavenging metals
Microbial Reaction	Intracellular and extracellular precipitation of minerals; electron transfer reactions (Dissimilatory Iron Reducing Bacteria –DIRB); organic secretions	Decrease (precipitation) metal mobility; Increase metal mobility by promoting host mineral dissolution (DIRBs) and organic complexing

Solute transport in the saturated subsurface proceeds through the collective processes of advection and mixing or hydrodynamic dispersion (Freeze and Cherry 1979), but can be affected by other gradients described below. Generally, hydrodynamic dispersion proceeds along the groundwater flow direction in a longitudinal form, but its exact geometry will depend on local and regional aquifer heterogeneity. Although advection and hydrodynamic dispersion affect the direction of solute and colloid flow, the composition of groundwater (solute composition) and therefore its metal composition is affected by chemical and biological reactions or mass transfer reactions, which are controlled by several aqueous chemistry factors: pH of the groundwater (the master variable), dissolution-precipitation, complexation, redox, adsorption and microbial influences (Drever 1988; Langmuir 1996; White 2001). The main processes and effects on metal mobility of these mass transfer reactions are summarized in Table 2. Most of these reactions are modeled via a combination of mass transport and equilibrium thermodynamic functions, and the modeling provides a predictive tool to estimate dispersion of specific metals if certain solid and solute properties of the aquifer are established. However, the understanding of the kinetics of the reactions between groundwater and aquifer minerals (dissolution, precipitation and adsorption), although actively researched, requires further quantification.

The lateral or longitudinal dispersion of ore metals within groundwater surrounding ore bodies occurs with extent of metal dispersion varying between meters to kilometers. Numerous hydrochemical studies around buried mineralization indicate higher metal contents in groundwater in close vicinity of ore bodies, with the metal type and content reflecting the chemistry of the ore body. Lateral transport and anomalous concentration of Au, As and Mo (Giblin 1997; Giblin and Mazzucchelli 1997; Gray 2001) Cr and Bi (Gray 2001), Cu and Se (Cameron *et al.* 2004) around ore bodies lying within the influence of groundwater have been documented. Isotopic and metal groundwater geochemistry studies using S, Pb and Sr isotopes demonstrate the dispersion of metals into the groundwater to varying distances with potential to distinguish the mineralization signature in groundwaters in shallow basins (de Caritat *et al.* 2005; Whitford *et al.* 1998).

Hydrodynamic dispersion occurs along a hydraulic gradient which is mainly lateral rather than upwards and therefore piezometric induced upward migration is limited. Other factors such as concentration gradients, heat or density gradients and electrical current gradients can promote upward transfer of metals, and in some cases at a rapid rate. These processes of upward metal migration mechanisms driven by groundwater as the medium are described in detail and illustrated in Figures 3, 4 and 5.

3.2 Dilatancy Pumping

One method of transferring mineralized groundwater from the subsurface to surface can be achieved with aid of earth’s internal energy released as a result of earthquakes. Several studies have shown the effusion of groundwater to the surface during and following earthquakes (Nur 1974). This process of groundwater pumping along faults and fracture systems in neo-tectonically active areas was referred to as seismic pumping by Sibson (1975). The theory behind seismic induced upward groundwater movement is based on the propagation of pre-seismic fracture in the brittle upper crust, resulting in the fractures acting as storage compartments and pathways for groundwater movement. The onset of compressional stress fields during earthquakes results in the closing of fractures with the subsequent forcing of groundwater along faults to areas of lower pressure at the surface. The result is the groundwater residing within fracture and fault systems is carried upwards to the surface through transported regolith. Furthermore, groundwater effusion at the surface is observed to continue for some duration after the earthquake event.

The role of seismic pumping as a mechanism of metal transfer to the surface through transported cover in arid and neo-tectonically active regions was advocated by Cameron *et al.*(2002) and Kelly *et al* (2003) based on their studies in arid, neo-tectonic areas where buried mineralization metal signatures were detected in soil via partial digests. Groundwaters in contact with an ore body have been documented to carry signatures of the ore and pathfinder metals from mineralization, and these groundwaters brought to the surface during and subsequent to earthquake activity will spread and flow, thereby depositing elements exotic to the near surface overburden (Figure 3). The high evaporation rates in semi-arid and arid settings result in the transferred metals being incorporated into the soils in close proximity to the mineralization, rather than widespread dispersion at the surface.

Support for this mechanism has been found at the Spence porphyry copper deposit in norther Chile which has a 50-100 m of transported Miocene gravel cover (Cameron *et al.* 2004; Cameron *et al.* 2002). The gravels in the area show vertical fractures that are interpreted to have formed in response to reactivation of basement faults. The chemical analysis of surface soils and those of underlying fractures above mineralization show anomalous Cu values while the soils and fractures distant from the ore body do not. The Cu anomaly in soils above the ore body is consistent with anomalous levels of Cu found in groundwaters within the vicinity of the deposit. These observations point to the pumping of Cu rich groundwaters to the surface via the fractures. Seismic pumping has also been proposed to explain the larger concentration of Rn around faults where micropulsations in the active fault zone induce greater radon transfer to surface (Panov et al., 1980 in Dyck & Jonasson (2000)).

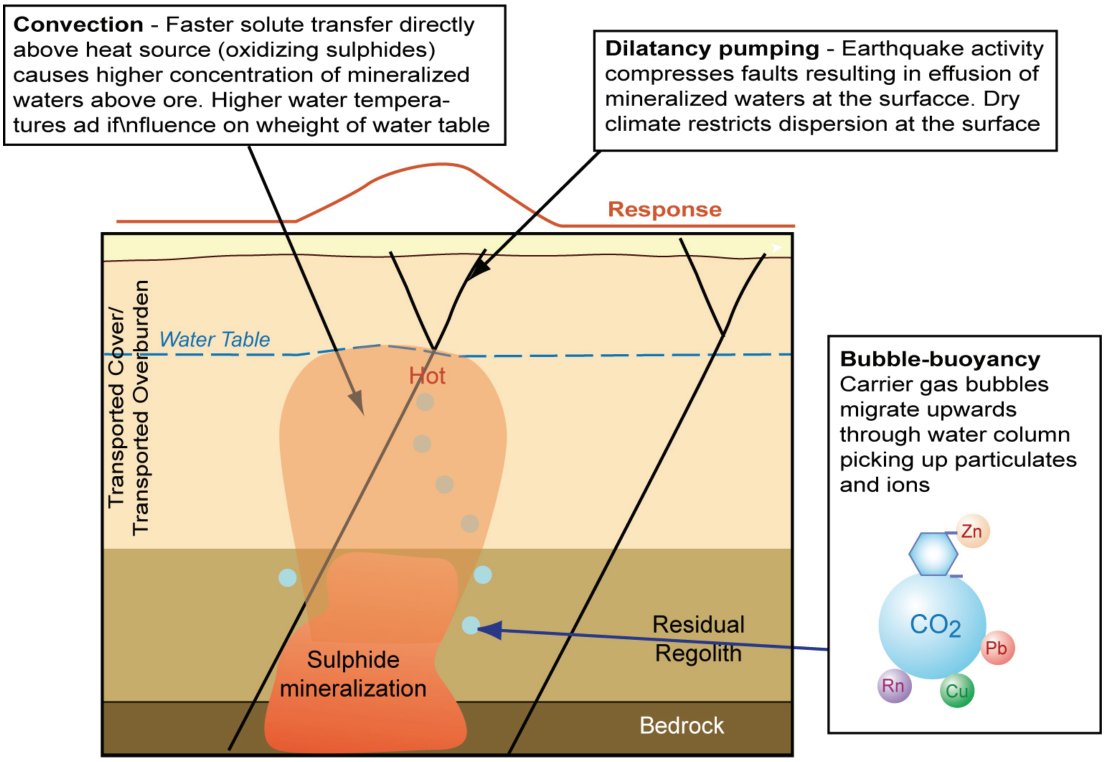
3.3 Convection – heat and density (buoyancy)

Convection in groundwater is considered to be the transport of heat, solutes or suspended matter. Two types of convection processes are considered to operate in groundwater systems: forced convection, which is transport via advection, where an external field forces groundwater to flow down-gradient because of water pressure or elevation differences, and free convection, where transport occurs due to density or buoyancy gradients caused by variations in the water temperature (thermal), salinity, solute, colloids material or contaminant plume (Domenico and Schwartz 1998; Freeze and Cherry 1979). In forced convection, Darcy’s law controls groundwater flow, while in free convection, buoyancy effects dictate flow. In addition to advection transport, free convection can become an important solute and heat transport process by creating hydrodynamic instabilities, which considerably modify transport behaviour and overall dispersion of solutes. Temperature or salinity changes or the increase in concentration of solutes due to contaminant sources, are the main causes of the density variations or occurrence of buoyancy in the groundwater. However, in areas of high density variations Simons *et al.*

(2001) suggest the operation of mixed convective groundwater flow systems, where hydraulic and buoyancy driven transport combine to govern solute concentrations in groundwater.

The onset of free convection leads to buoyancy driven convection cells or higher density currents of different geometries within the groundwater column, with common shapes of higher solute density being manifested as finger or lobe patterns. The solute transports driven by buoyancy gradient can result in movement of heat and solutes over larger distances and at faster rates as compared to diffusion alone (Simons *et al.* 2001). Experimental data and modeling results suggest the operation of free convection when denser fluids emanate from the surface with lobes of denser fluids migrating downwards (Simons *et al.* 2001). However, the lobes of denser fluids can be either ascending or descending depending on the position of the source inducing the density contrasts. The onset and growth of the instability fronts in heterogeneous systems rather than uniform sandy medium remains complex (Simons *et al.* 2001).

Most of the experimental, flow simulation and field studies on the buoyancy driven solute transport are conducted on saltwater-freshwater interactions at coastal zones, intrusion of denser contaminant plume solutes into fresh groundwater, salt lake hydrogeology, and thermal geological environments such as hydrothermal zones and deep sedimentary basins. The application of free convection in mobilizing solutes derived from an ore body upwards within shallow, non-hydrothermal groundwater environment remains largely unexplored. The ascending movement of solutes driven by convection within groundwater environments has important implications for upward movement of ions through the groundwater column because it i) increases the rate of migration of solutes in a particular direction and ii) it can influence the direction and geometry of the migrating front (fingers, curved fronts etc).



Convection - Faster solute transfer directly above heat source (oxidizing sulphides) causes higher concentration of mineralized waters above ore. Higher water temperatures ad if\nfluence on wheight of water table

Dilatancy pumping - Earthquake activity compresses faults resulting in effusion of mineralized waters at the surface. Dry climate restricts dispersion at the surface

Bubble-buoyancy Carrier gas bubbles migrate upwards through water column picking up particulates and ions

Figure 3. Illustration of principles behind dilatancy pumping, convection and bubble assisted transport mechanisms.

There are two potential effects by which mixed convection might play a role in upward migration of solutes from mineralization. The first is to do with increasing the groundwater density contrast by releasing extra “heavier” solutes to the groundwater. The ore body can be considered as the contaminant source releasing a higher concentration of solute species to the groundwater, resulting in the onset of possible buoyancy gradients in solutes. The flow of these solutes, however, will depend on groundwater gradients, which is predominantly lateral along flow directions. The second is via temperature contrasts produced due to oxidizing sulphides. The net sulphide oxidation reaction is exothermic, thereby producing heat (Nordstrom and Munoz 1985) with calculations indicating the release of 1409 kJ of heat for each mole of pyrite (Lefebvre *et al.* 2001). The oxidizing ore body, by acting as a comparatively higher heat source, can initiate and maintain buoyancy within the groundwater, and thereby induce faster migration of solutes upwards from the heat source (ore body). Mann et al. (2003) constructed experimental columns to simulate groundwater flow and noted the formation of convection currents over a heat source resulting in direct rise of solutes above the heat source. Based on calculations, Mann et al. (2003) also suggested that oxidizing sulphides were able to produce a subtle temperature contrast directly above compared to adjacent rocks. Cameron *et al.* (2004) noted the presence of a higher water table (~ 2m) and temperature above the ore body as compared to adjacent non-mineralized rocks. Wood and Hewett (1982) suggested the spontaneous formation and persistence convection cells in fluid saturated, sedimentary layers subjected to normal geothermal gradients, but the development of such convection cells in shallow sediment bodies remains complicated and unproved.

3.4 Gas Streaming or Bubble Migration

A potential gas and metal transfer mechanism arises due to the property of buoyancy (controlled by Archimedes' Law), where gas in the form of bubbles, migrate upwards through different mediums. Due to hydrostatic pressure changes, especially near the water table, gases dissolved in groundwater can separate into a gas phase forming bubbles of different diameters. The gases with sufficient concentration to form bubbles are referred to as carrier gases and are mainly two – CO_2 and CH_4 (Etiope and Martinelli 2002). The property of buoyancy induces gas phase bubbles to migrate vertically upwards in a liquid medium and escape or "burst" at the surface. The bubbles during their ascension can exchange gas with the surrounding liquid and collect particulates, and the attachment of metals to bubbles and their transfer with the bubble to the surface can potentially result in rapid metal transfer.

The micro bubble controlled transport of gases was proposed by MacElvain (1969) to explain seepages of hydrocarbons at the surface. Malmqvist & Kristiansson (1984) further advanced the bubble migration theory by proposing the formation of bubbles in the saturated medium via pressure gradients, and subsequent ascension of these bubbles across the air-water interface via mixing with air in the unsaturated zone to the surface driven by the pressure gradient created by the bubble stream. They also proposed that the bubbles acted as carriers of metals (Cu, Zn, Ni, Pb) and fine particulate matter that are attached to the bubble stream. The bubble stream migration theory circumvents the limitation of transferring non volatile metals (Cu, Pb, Zn, Au) using the carrier gas bubble as a conveyor of metals and other very fine particles. On a theoretical basis, the bubble migration velocity in saturated media is governed by Stokes Law and is dependant on bubble diameter, groundwater density, gas density and groundwater viscosity, while the bubble diameter is dictated by the porosity and grain-size of the medium (Etiope and Lombardi 1996).

Some researchers, via laboratory column experiments, have advanced the organic-bubble-metal relationship as a model for metal association to bubbles, a process that is used to clean up aquariums and separate minerals via flotation! Putikov & Wen (2000) describe the "natural ionic flotation" processes whereby presence of trace amounts of organic acids within groundwater (acetic and formic acids) act as anionic *surface-active agents*, which accumulate on the surface of the bubbles with the organics negatively-charged poles exposed to the surrounding water. Positively charged metals (cations) present in the groundwater are attracted and bond to negative poles of the organics on the bubble surface, and the bubble gradually picks up cations and particulates during its ascension through water column. The surface active agents such as anionic and hydrophobic non-anionic surfactants and natural organics aid the bubble transport of matter in saturated medium through a dual effect: they increase the temporal stability of the bubbles by reducing surface tension, and provide anionic surface for the attachment of cations, very fine particulate matter such as clay particles and bacteria (Lion and Leckie 1981; Wan *et al.* 2001). Laboratory experiments to visualize the effects of sorption of particles on the gas-water interface via micro-bubbles reveal the preferential sorption of colloids to the bubbles rather than to solid surfaces, with positively charged and hydrophobic particles showing maximum sorption (Goldenberg *et al.* 1989; Wan and Wilson 1994). Electrostatic forces are considered to be the main process driving the adhesion of particulates on the bubbles.

The support for the migration of metals with gas bubbles or aerosols comes from studies on the composition of marine aerosols and laboratory studies on short lived radioisotopes (Rn). Several studies on trace element geochemistry of bursting bubbles on the oceanic surfaces have found the bubbles to be enriched in specific elements compared to seawater, although the enrichment factors differ. Piotrowicz *et al.* (1979) found Cu, Cd and Zn to be enriched by a factor of 200, while Pb was enriched by over 2000 while Walker *et al.* (1986) found the marine aerosol bubbles to be enriched in actinides by a factor of 30-600 as compared to seawater. Studies examining the microbubble transport phenomena in saturated sand columns demonstrate the migration of radionuclides (Rn) and fine mineral particles via attachment to gas bubbles (Etiope and Lombardi 1996; Varhegyi *et al.* 1992).

The transfer of metals via gas bubbles can proceed based on the bubble stability and ascension capability within pore networks filled by either air or water. In the saturated medium the carrier gas bubbles can originate either due to overpressure (Malmqvist and Kristiansson 1984), due to oxidative weathering of sulphides or due to excess air brought in via recharge (Heaten and Vogel 1981; Ryan *et al.* 2000). Groundwaters are known to contain minor amounts of natural dissolved organic matter introduced via recharge (Aiken 2002), and these natural surface active agents present in the groundwaters can adsorb onto the bubble surfaces and in turn scavenge the cations released from ore bodies as well as fine particulate matter (clay layer silicates and Fe/Mn oxides or nanometer sized metal clusters based on electrostatic attraction). The bubbles can survive for sufficient duration (days to weeks) as the adsorbed organics would provide a stabilizing effect, and the buoyancy driven rise will carry the metals to water table, and beyond.

3.5 Electrochemical processes

Electrochemical processes involve the movement of charged ions within an electrical field. Accordingly, natural electrical gradients arising at or near the Earth's surface have the capability to set up electrical fields and transfer metals ions to the surface through transported regolith. Spontaneous polarizations (SP) which are described as natural voltage differences between two points in the Earth resulting in electrical currents within the Earth, have been demonstrated in association with sulphide ore bodies. Dispersion models have applied the SP concept to sulphide ore bodies and with suggestions of the resulting natural electrical force associated with the sulphide ore inducing upward ionic migration in residual and transported regolith. The main concept behind the proposed electrochemical models is the rapid upward migration of metals in solution or along the conductor, namely the sulphide ore. The upward force is generated by electrical or redox potential difference between the upper oxidized and deeper reduced parts of the sulphide body or redox differences between top of the ore body and the oxidizing conditions are the water table.

A similar principle is used for cleaning up metal contaminated soils via electrokinetics, where a dc electric field is applied across electrodes placed in the ground, which causes dissolved metal ions (or mobile ions) in the *saturated* soil to move rapidly under the action of the electric field. The metal transport occurs mainly via two processes; electromigration, which is the movement of ionic species towards respective cathode (cations) and anode (anions) (across an electrical potential), and electro-osmosis, which is the movement of water in a porous medium along a pressure gradient created by the electromigration of ions along a voltage gradient (Acar *et al.* 1995; Reddy and Shirani 1997).

The electrochemical models remain the most explored mechanisms for ionic migration in residual and transported regolith. The early electrochemical models for dispersion are strictly limited to residual cover or shallow transported cover with another mechanism such diffusion being invoked to account for ionic migration through saturated transported cover. Recent models based on redox stratification, are relevant to ionic transfer through the transported cover without the need for any other mechanism. Accordingly, the models are grouped into:

- Those having an electronic conductor within the basement with SP potentials. The effectiveness of these models are restricted to shallow transported cover areas because the electrochemical enhanced migration is restricted to the height or upper limits of the ore body.

- Those not having an electronic conductor and driven by redox gradients within a saturated transported cover. The effectiveness of this mechanism extends above the ore into the saturated cover.

There are several variants to these models and the main ones are described.

3.5.1 Spontaneous Potentials

Sato & Mooney (1960) proposed a model for the development of self-potentials associated with sulphide or graphite bodies in response to development of an Eh differential along the length of the sulphide body. In deeper areas (below the water table) of the conductive ore, oxidation of the reducing agents proceeds along the edges of the conductor thereby providing electrons to the conductor. The deeper oxidation reaction is matched by the reduction of the oxidiation agents at the near surface (above the water table). The simultaneous oxidation and reduction reactions give rise to an Eh differential between the near surface and deeper areas resulting in migration of electrons from the deeper parts to the upper parts along the conductor. The ore body does not participate in the electrochemical reactions and only acts as a conduit for electron transfer. To complete the electrical circuit, the movement of electrons along the sulphide ore needs to be balanced by movement of ions in groundwater. This is achieved by the net movement of cations to the cathode and anions to the anode (lower) via surrounding groundwater.

Govett (1973; 1976) and Bolviken and Logn (1975) extended the Sato & Mooney (1960) model by proposing ionic migration under an electrical self potential. They proposed the counterbalancing of ions with an upward flow of cations from anode to cathode and downward flow of anions to anode, thereby completing the electrical circuit (Figure 4A). Govett (1976) applied the SP model to account for dual peak or "rabbit ear" anomalies of H^+ and other cations at the surface through thin transported overburden (< 5m). The cathode edges around the oxidized sulphide ore served as high cation densities with a cation deficient zone in between. The accumulation of cations at the edges of the cathode subsequently diffused uniformly upwards to the surface resulting in twin H^+ responses at the soil surfaces.

Smee (1983) extended the model by proposing a two-stage process for migration of cations through transported clay overlying mineralization. The lower resistivity of clay rich overburden as compared to silicate bedrock forces the ionic current in basal units via sorption in the clay. The excess cations accumulated at the basal units diffuse upwards along the concentration gradients and collect in the soil horizons resulting in a soil pH change (Figure 4B). However, on theoretical basis, the rate of diffusion of cations through a saturated clay medium is very slow, with only H^+ having the potential to diffuse fast enough to manifest a signal through 20m of clay cover (Smee 2003).

A electrochemical migration model for deeply weathered regions with thick vadose zones is the model proposed for formation of gossans. Thornber (1975) proposed a electrochemical model to account for supergene alteration of sulphides that postulates the presence of reduced phase (deeper anode) and the oxidized phase (cathode). In the process of supergene alteration of sulphides in the ore body, the primary sulphides pentlandite – pyrrhotite are altered to violarite-pyrite in the weathering zone. The alteration of pyrrhotite to pyrite releases electrons that move up along the sulphide conductor towards the oxidizing environment (cathode) where they promote the reduction of oxidizing agents. The alteration of pyrrhotite to pyrite results in the release of Fe^2 from the pyrrhotite-pyrite boundary into the surrounding groundwater. The groundwater acts as an electrolyte. The charge carrying Fe^{2+} migrates upwards along the redox gradient to the water table and oxidizes, thereby precipitating as iron hydroxides and forming a gossan.

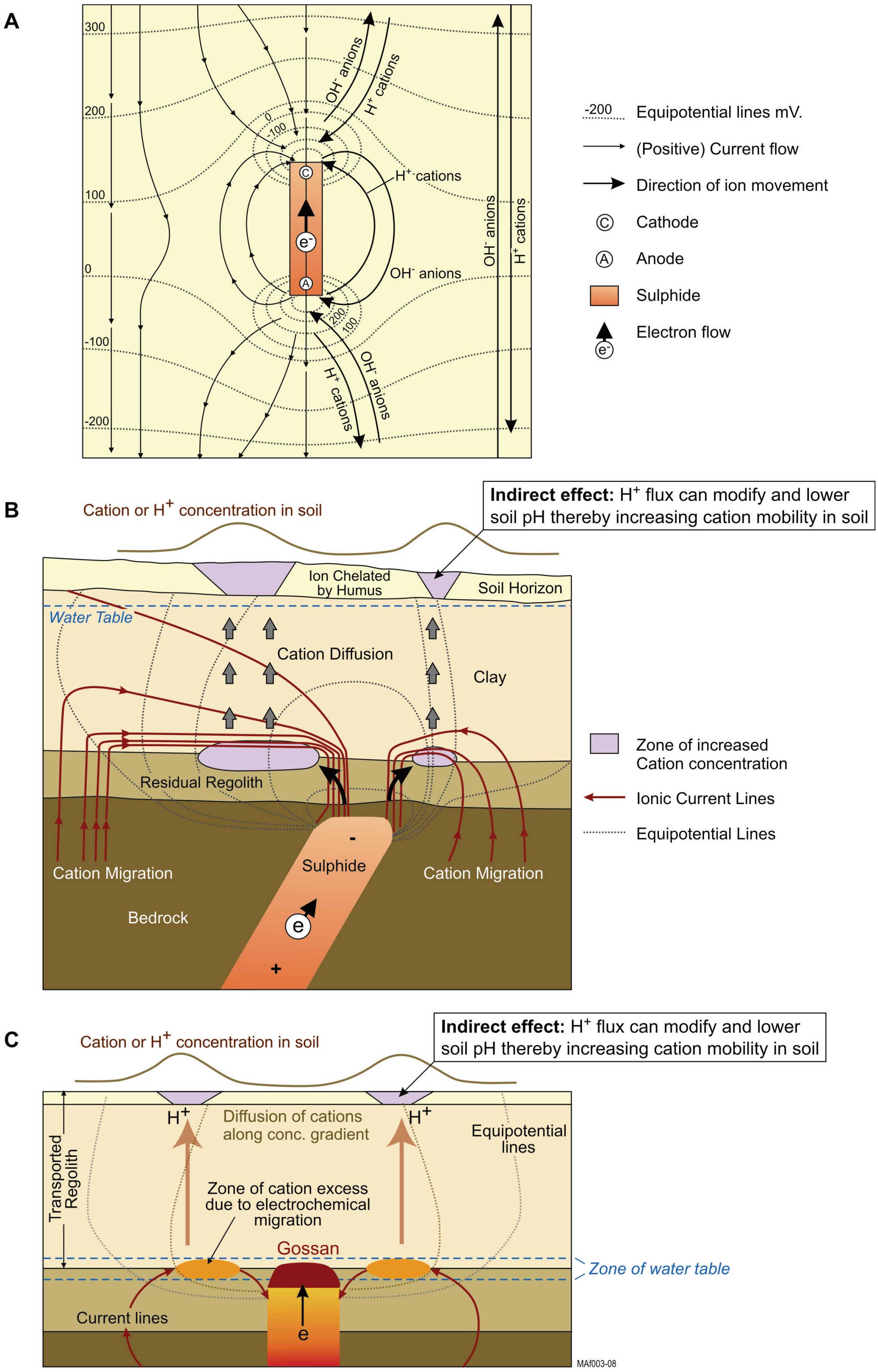


Figure 4. The various SP related electrochemical mechanisms. A. Cross-sectional sketch showing the movement of ions around an electronic conductor in bedrock (modified from Govett 1973). B. The electrochemical development of excess cations at high cationic current areas around a sulphide body. Soil anomalies (both direct and indirect) develop due to diffusion of cations from the high cationic charge areas at base of overburdent to surface. C. An electrochemical cell set up with generation of excess cations at the edges of the conductor (sulphide) and their subsequent diffusion through unsaturated cover. The diffusion results in excess H^+ within the soil which in turn affects mobility of exchangeable ions (indirect pathway) (modified after Govett et al. 1984).

A similar model was forwarded by Govett *et al.* (1984) to explain twin peak H^+ anomalies at surface for the deeply weathered regions in Australia. They proposed the development of excess cation density at the edges of the oxidized sulphide body present at the base of the water table in response to the electrical field around the conductor (Figure 4C). The cations concentrated at the flanks of the ore body due to convergence of ionic fluxes, migrated to the surface through the unsaturated zone via diffusion. The overall model postulated by Govett *et al*. (1984) is essentially a combination of two mechanisms; electrochemical in the phreatic zone and diffusion is the vadose zone.

The difficulty with the SP models is their recourse to another mechanism to transfer metals upward from the base of transported cover. The Smee and Govett models address the upward migration of ions, especially H^+ via diffusion (concentration gradient) and the efficiency of the diffusion mechanism is described later.

3.5.2 Redox Gradients

Hamilton (2000; 1998) forwarded a different electrochemical model to account for rapid upward dispersion of elements through saturated glacial clays (Figure 5). The model is based on the onset, development and continuance of a **redox gradient** between the water table and buried sulphide mineralization and requires a balance of availability of reduced and oxidized species within the saturated overburden. Therefore, the model is better suited to explain the ionic migration through saturated transported cover because it does not require the sulphide ore to act as the main electrical source.

The model posits the presence of a sedimentary overburden (glacial till) saturated via groundwater overlying sulphide rich mineralization. The onset of saturation conditions within the overburden (glacial till) leads to the formation of reducing conditions or a reducing front above the sulphide body as compared to oxidizing conditions existing towards the ground surface (top of water-table). The result is the development of a redox differential between the top of mineralization at base of the cover and top of water table near the surface. Reduced anodic species released from the sulphide body migrate upwards until oxidizing agents migrating downwards are encountered resulting in redox reactions and the release of charge. Subsequently, due to the limited availability of oxidizing agents within the groundwater column, the reducing front migrates upwards and outwards resulting in the development of a reduced column within the saturated overburden above the ore body. The lateral extents of the reduced column above the ore body depend on the balance of release of reduced species from the sulphide body as compared to availability of oxidizing agents at the groundwater table, with an excess of reduced species resulting in widening of the reduced front. With time, a steady-state equilibrium is reached between the supply of reduced and oxidized species, resulting in the redox equipotentials lines, which were initially horizontal, gradually becoming nearly vertical (Figure 5). In an ideal case of a fully developed reduced column, the current is focused at the flanks of the column due to the self-potential gradient being stronger towards the flanks rather than directly upwards (Figure 5). Such a mechanism was advanced to explain selective leach detected metal anomalies through transported clay in Canada (Figure 5). The resulting effect of the redox column is a “reduced chimney” which is a lower redox potential vertical zone within the transported cover directly overlying mineralization.

Similar effects to that postulated by Hamilton for the redox model have been noticed in the deeply weathered regolith profiles of Australia, Africa and South America, where the development of a water table within the deeply weathered rock or weathered surficial sediments sets up a redox gradient with oxidizing conditions prevailing at and above water table and reducing below. The water table associated Eh difference causes the reduced ions (Fe^{2+}, Mn^{2+}) released from the weathering front to migrate upwards and outwards until oxidizing agents are encountered. With time, the oxidizing agents in groundwater are consumed and a vertical and lateral redox gradient is established with oxidizing conditions at the water table and reducing column below it extending up to the weathering front. The oxidation and hydrolysis of Fe^{2+} species with iron oxide and hydroxide precipitation at or near the water table (oxidation front), results in operation of ferrolysis reaction with the generation of acidic conditions at the oxidation front (Mann 1983; Taylor and Eggleton 2001). The presence of grey, "leached" saprolites overlain by mottled zones and ferricretes in lateritic profiles are taken as evidence for upward and lateral migration of reduced ions (especially iron) to the oxidation front represented by the fluctuating water table. The emergence and evolution of a redox gradient associated with a surficial aquifer water table and its resulting effects occurs in deeply weathered lateritic profiles without underlying sulphide mineralization, and therefore the evolution of a "reduced column" may not be unique to evolution above sulphide mineralization. However, no oxidation reduction potential (ORP) measurements have been conducted on these materials to verify their redox state and therefore their origins may not be the same as advanced by Hamilton for younger saturated cover overlying sulphide mineralization.

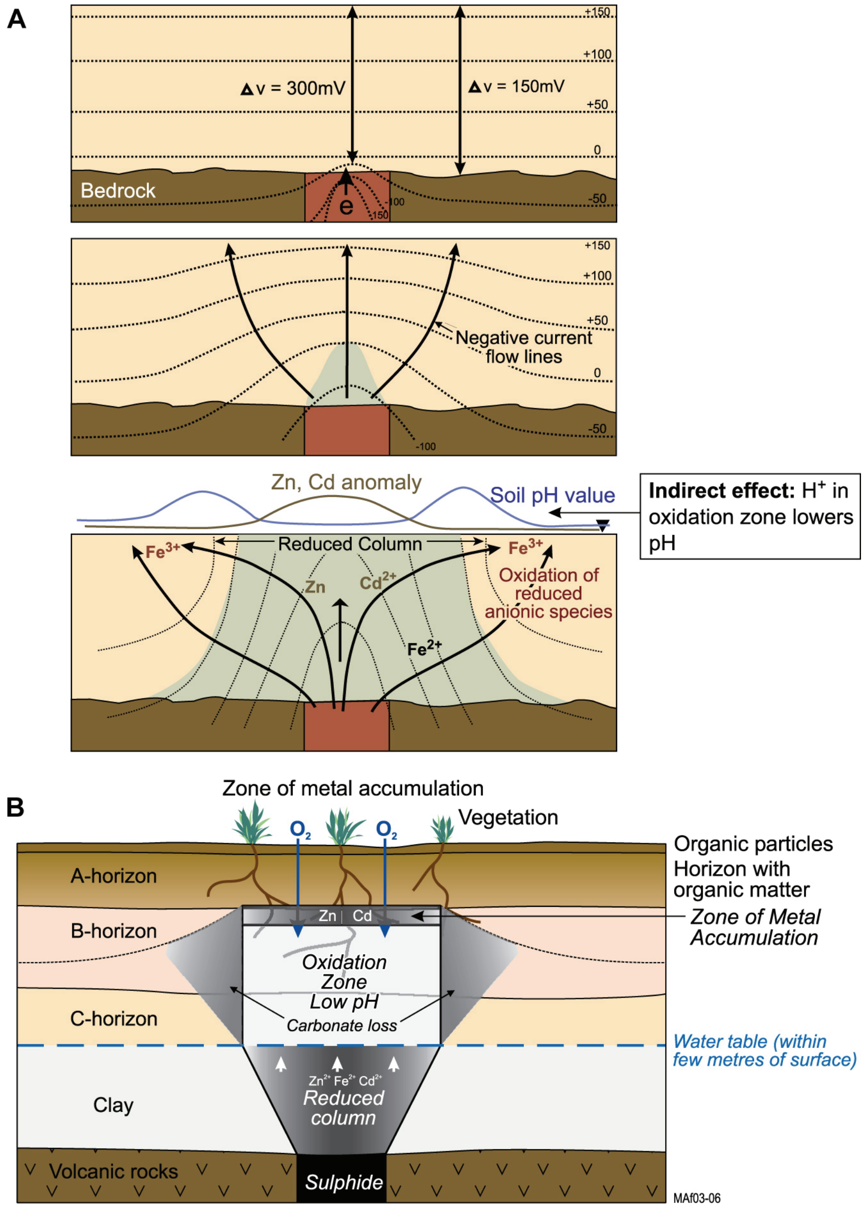


Figure 5. The redox gradient model. A. The stages in the eveolution of a "reduced column" and associated metal migration in a saturated cover sequence. The diagrams show the progressive modification of redox equipotential lines (after Hamilton 2000). B. A model for the development of soil anomalies through saturated transported cover at the Lake Cross deposit, Canada. Reduced metal ions are oxidized at and above the water table by infiltrating oxygen and thus produce H^+ ions which in turn dissolve soil carbonate (from Cameron et. al 2004).

Recent studies demonstrate the presence of a reduced column within saturated overburden overlying mineralization (Hamilton *et al.* 2004) and even over "Forest Rings" in Canada. Studies conducted on the Cross Lake VMS deposit in Canada, which is located under 30 m of clay, showed constrained Zn and Cd anomalies in the B horizons of the soils. These were explained by the formation of reduced column and possible upward migration of metals through the cover due to the redox gradient.

Several studies on regolith over ore bodies have inferred the presence of redox differences within the residual regolith and transported overburden, with the redox differences between the groundwater table and deeper weathering front affecting metal mobility and dispersion. Based on the gold grain chemistry, Mann (1984) advanced the reduction and complexation of Au in chloride rich groundwaters at the weathering front, the migration of the Au halide complex upwards to an oxidized front present at the mottled zone, and Au oxidation followed by precipitation of Au grains. Lawrance (2001) has advocated the mobility and adsorption of specific cations and oxyanions due to the paleo-redox fronts within residual and transported regolith, based on the presence and evolution of redox gradients governed by progression of groundwater tables. Therefore, redox induced mechanism and subsequent effects have been indirectly incorporated into exploration models and sampling media.

3.5.3 External Electrical Gradients

Many of the proposed electrogeochemical mechanisms to transfer metals upwards have the underlying conductive sulphide rich ore body as the main source of electrical or voltaic currents. In contrast to current being produced from below, Garnett (2005) suggested the extreme voltages generated by **storm cells** migrating across the landscape could provide short but intense currents to mobilize specific ions upwards from the deeper regolith. Storm cloud dynamics is still debated, but the general explanation is for the gradual polarization of charges within storm clouds with bulk of negative charge concentrating at the base of the clouds, which in turn links to the ground surface. The electrons on the Earths surface are repelled by strong negative charge on the clouds lower surface thereby generating a strong positive charge on the regolith surface. Garnett (2005) suggested that the charge imbalances could drive currents deeper and laterally on the surface and set up a local electrical gradient. The depths of current penetration could vary depending on the regolith material properties and its saturation. The electrostatic gradient generated could induce the mobilization of ions, with reduced species migrating upwards to become oxidized near the surface and in turn act as scavengers for other ions being mobilized from below. For example, the oxidation of specific reduced species, such as Fe^{2+} to Fe^{3+} with the loss of electron under the storm induced electrical gradient, could make the Fe^{3+} act as “traps” for other trace ions moving upwards, especially along the trailing negative edge of the storm footprint. This model is yet a thought experiment and no experiments have been conducted to study it.

The main advantage of the electrochemical cell models in effecting migration of metals upwards is the faster rate of transferring charged species as compared to diffusion (Hamilton 1998). Calculations conducted on various voltage settings, indicate the much faster rate of ionic migration through saturated clay subjected to an electrochemical gradient as compared to simple diffusion through the overburden. The faster migration of ions in an electrical field has been demonstrated and used in electrokinetic remediation of heavy metal contaminated sites where the processes of electroosmosis and electromigration operate between the inserted cathode and anode. Although electrokinetic remediation under specific conditions has shown dramatic ionic (cationic and anionic) transfer rates, intrinsic geochemical processes, such as metal hydroxide precipitation promoted by pH changes due to the ionic migration process itself, saturation state of the medium, soil mineral composition, pH dependant adsorption-desorption and oxidation reactions arising in response to the induced electrical currents can all affect electrokinetic functional efficiency (Acar *et al.* 1995). The soil mineralogy, ionic charge and initial metal species are important parameters affecting the efficiency of electrochemical migration of ions. For example, experiments by Reddy *et al* (2001) to evaluate the control of soil mineralogy and chemical species of the metals during electrokinetic treatment, found that in both kaolin and glacial till mediums, low migration rates occurred because the metals existed in “immobile” complexes and precipitates. Metals present initially in exchangeable form showed higher rates of migration, with anionic species (Cr(VI)) preferentially migrating to the anode and cationic species (Cr(III), Ni(II) and Cd(II)) to the cathode. The geochemical processes and metal speciation changes found to occur during electrokinetic remediation can also occur in ore body related redox gradients. Besides pH effected changes, there are factors functional in most aquifers likely to slow the operation of the electrochemical cell induced upward migration of ions, such as double-layer or "electro-filtration" (adsorption onto the clays) (Hamilton 2000).

3.6 Diffusion along concentration gradient and its effects in soil

Upward diffusion of charged ions along a concentration gradient within saturated (and unsaturated) overburden has been advanced as a mechanism but is grouped as part of the electrochemical mechanism described earlier. However, diffusion of ions is very slow and only specific ions can migrate upwards along a concentration gradient in the absence of another force such as heat or electrical gradient. According to diffusion calculations conducted by Smee (2003), he found that only H^+ can diffuse fast enough through saturated clay over a relevant time frame for young cover sequences.

The diffusion of H^+ upwards is suggested to work as follows. The weathering of sulphides generates an excess of protons because of process of sulphide dissolution and Fe oxidation. The excess protons generated collect at the base of the transported overburden due to SP pontentials (see section 3.5.1) thereby forming a concentration front in the overburden. The excess H^+, via diffusion and/or exchange on clays migrates along the concentration gradient to the surface and can be detected directly by measurement of pH.

This diffusion of H^+ mechanism also operates as an indirect mechanism, where over time the continuous diffusion of H^+ to the surface soil can induce a drop in pH inthe soil. The pH of the medium being the "master variable" exerts control on several important geochemical reactions such as adsorption-desorption, dissolution-precipitation and complexation (White 2001). In general, metal solubilities increase with decreasing pH and cation sorption is reduced at lower pH. Therefore, a drop in pH change will cause cations present in the soil to become "mobile" or exchangeable, and therefore become responsive to selective leaches. This mechanism has also been employed in the model of Govett *et al.* (1984) to explain "rabbit ear" anomalies in weathered regions, where H^+ diffuses upwards from the oxidizing ore body (Figure 4B,C).

Smee (2003) provided site examples of possible effects of the excess H^+ which result in either change in the extractable concentration of Ca contents in semi-arid to arid environments and Cu, Pb and Zn in wetter climates. The metals in the soil are not transferred from the underlying ore body, but are made more responsive to the SWE because of the indirect stimuli from the ore body below. The H^+ is generated at depth due to sulphide oxidation and over time forms concentrates at the base of the transported cover. This concentration front is proposed to set up an ion exchange based diffusion front and the ion diffuses to the surface. The H^+ has an advantage over other cations in clay mineral bearing overburden, because it can migrate comparatively faster via ion exchange on the clay surfaces. The gradual increase in concentration of H^+ over time in the soil could react with the ambient $CaCO_3$ in present in the soil and redistribute Ca (and similar charge/raddi ions such as Sr) within the soil and also make it more responsive to mild digests.

However, there are two observations that argue against upward diffusion of ions as a common mechanism in the vadose zone. Firstly, diffusion is a very slow process and the extent of its spatial operation within a dry, clay poor medium is questionable and not proved in the laboratory. Secondly, based on the H^+ diffusion model, the column through which H^+ migrates (the "chimney") should be acidic as well as the surface ("cap"). However, observations in Canada by Hamilton (2004) indicate that "chimneys" are basic with acidic caps.

3.7 Discussion of Phreatic processes

Of the mechanisms underpinned by groundwater as a medium, electrohemical mechanisms have been extensively invoked, explored and tested across a range of climatic settings to account for the surface geochemical response through cover. Most variants of the electrochemical mechanisms (except storm cells) have a strong predictive basis because they derive their electromotive force or an indirect response of excess H^+ from the presence of buried sulphide mineralization rather than an external source. However, the efficiency of electrochemical mechanisms needs to be evaluated in terms of the type or style of mineralization, saturation conditions, water table levels and mineralogy of the medium.

Sulphide poor ore types may not provide the initial self potential differential necessary to induce a large enough redox gradient to produce the “reduced” column or supply the excess of H^+. Alternatively, vertical redox gradients exist in many deeply weathered regolith profiles without an underlying ore body and the value of the reduced column as a singular product of conductive mineralization or otherwise needs to be tested. Is the voltaic force generated in response to evolution of the water table associated redox anisotropy or is it primarily driven by underlying sulphide mineralization or a combination of both? Another critical factor affecting the electrochemical mechanisms is the depth of water table and the related diffusion of H^+ ions and cations. If the water table is close to the surface and the oxidation of reduced species proceeds at the water table close to the surface as indicated in the redox model of Hamilton (2000), then resulting effects will have a likelihood of being transferred to the soil in the form of pH and subsequent increase in mobility or exchangeability of specific metals. However, if the water table is at greater depth (> 5 m), as is the case for most of the prospective regions of Australia, then diffusion of cations needs to advance upwards against gravity, mostly through dry, sometimes cemented medium with variable mineralogy (dominated by different proportions of quartz, kaolinite, illite, hematite and goethite), often against the downward movement of matter. Electrokinetic experiments demonstrate that the efficiency of the electrochemical process decreases markedly when saturation of medium drops below 10%. The efficiency of ionic migration within an electric field is also strongly affected by the mineralogy of the medium (kaolinite dominant vs till) and species of metals in solution (whether metals are tightly bound or exchangeable), and other competing species (Reddy and Shirani 1997; Reddy *et al.* 2001).

The generation and subsequent upward diffusion of H^+ from an oxidizing sulphide body need to be assessed on the merit of the source of H^+ and its migration through a dry, non-clay rich medium. Besides the sulphide rich ore at depth, parts of the upper regolith profile can produce localized zones of H^+ activity, especially semi-saturated units that have redox processes (manifested in mottling) operating within them. Evaluating the surface response of H^+ therefore needs to be carefully evaluated according to local soil conditions. Further, the extent to which upward diffusion of cations can proceed over meters in a dry medium remains unclear.

In comparison to the electrochemical mechanisms, other groundwater based mechanisms have been rarely invoked and tested to account for upward metal migration. But they do posses merit and require testing for specific ore styles and climatic settings.

The potential generation of heat because of an actively oxidizing sulphide body needs to be explored further because like the electrochemical mechanism, the source of heat or the driving force is the high sulphide bearing mineralization itself. Whether groundwater temperature differences are common over sulphide rich ore bodies as compared to adjacent rocks and the resulting temperature differential is capable of driving faster upward migration of solutes, needs to be field tested over a variety of sulphide rich mineralization styles. In the past, groundwater chemical parameters have been accurately measured and interpreted, but accurate temperature measurements and water table depth seem to have been less utilized. Although density driven flow can have a positive effect on the upward migration of solutes within groundwater as suggested above, density gradients are also known to attenuate signatures from the ore body. Carey et al (2003) noted the dilution of anomalies due to mixing of higher density unmineralized waters arising from denser salt lakes with mineralized waters. Possibly, the main factor to consider in heat or buoyancy related metal transfer is the competition between flow gradients and heat transfer processes.

Dilatancy pumping in neo-tectonically active areas located in arid climates, where the lack of rainfall aids restriction of metals transferred to the surface after earthquakes, remains the most probable mechanism to transfer metals directly to the surface. However, the intensity and spatial extent of neo-tectonic activity within the region is critical to the operation and viability of this mechanism. Although the Cratons and Fold Belts are considered tectonically “stable”, there have been recorded earthquake activity and associated faulting within the Cratons, but the effusion of groundwater at the surface after an earthquake event remains to be tested for this mechanism to be considered widely applicable. More data on effusion of groundwater following an earthquake is required for a region in order to evaluate the scope of this mechanism.

The drawback to any mechanism underpinned by groundwater as a medium are twofold; the degree of chemical mixing with unmineralized groundwater and the height of the water table. The degree to which physical and chemical heterogeneity of the subsurface will affect the flow and mixing of waters of different composition and density, and thereby reduce or negate the signal arising from mineralization, needs further qualification. An example of chemical heterogeneity is found in a study conducted by Carey *et al* (2003), where different waters mixed and attenuated the signal from mineralization. However, the study is from a salt lake environment where density driven flows could be a norm. Also, solutes disperse along the hydraulic gradient and flow direction and the lateral extent of metal species dispersion will depend on the mass transfer reactions (retained near ore body due adsorption or mineral precipitation, or dispersed due to redox and colloid mobility) and the physical parameters of the evolving regolith aquifer, dominantly heterogeneities in hydraulic conductivity. Deeply weathered regolith profiles display significant physical heterogeneity in the form of variable permeability and porosity that control flow paths (Acworth 1987; Johnston 1987), and this physical heterogeneity can negate or at least displace the upward movement of ions.

4. Vadose Zone Based Mechanisms

The role of phreatic zone mechanisms in transferring ions to the surface through cover, however, appears limited by the height of water table. Above this height, in principle, another mechanism needs to operate to transfer the metals to or near the surface. Even in the electrochemical models, ionic migration experiments and calculations are conducted in saturated and semi-saturated mediums, and operation of ionic transfer in physically and chemically heterogeneous dry medium due to electromigration appears difficult. The presence of high groundwater tables within the transported cover (0.2- 2 m below surface) and within reach of the bioturbation activity, will imply mechanisms reliant on groundwater as the medium as the main transfer mechanism of anomalies. If the groundwater lies well below the surface (> 3 m), especially beyond the limits of bioturbation and sometimes beneath the base of transported cover, then the scope of operation of hydrochemical mechanisms using groundwater as a medium is restricted to its present or past water table, and another mechanism needs to be considered to transfer metal upwards. Mechanisms operating in the vadose zone and capable of transferring metals from the groundwater table to the surface, such as capillary, gas dependant diffusion and advection, and biologically induced one, are considered and evaluated. Most of the mechanisms considered below require that the regolith or groundwater in the immediate vicinity of the ore is anomalous.

4.1 Capillary

The capillary rise phenomena can raise metal bearing waters several metres above the water table, and therefore is a potential advective mechanism of upward metal dispersion. Water at the water table is subject to an upward pull due to surface tension of the air-water interface. Immediately above the water table (pressure head $p = 0$ at water table), pores are saturated but pressure head is less than atmospheric ($p<0$). The negative pressure head or tension above the water table applies a suction that draws water upwards into the pores, and this rise of water will continue while the radius of curvature of pores is small enough to cause a pressure difference across the air-water interface (Gillham 1984) (Figure 6).

Although the upper limit of rise of the water due to capillary action from the water table is generally considered the capillary fringe (CF), the precise definition of the upper limits of CF differ (Berkowitz *et al.* 2004). Some consider the CF to represent the near complete saturated zone above the water table that is under negative tension, while others consider it the maximum height above the water table to which some pores remain connected via water to the water table. For example, in soil literature, the near complete saturated zone above water table where visual water rise is observable is referred to as the capillary fringe, and the part saturated zone above the fringe where water is not visible but connected to the water table is referred to as funicular zone. The CF is a critical zone where water can flow horizontally and vertically along hydraulic gradients, and solutes and even microbes can flow upwards (Berkowitz *et al.* 2004).

In soil science and vadose zone studies, the term matric potential is preferred to describe the state of water above the water table because the pressure of water in the soil matrix is a combination of capillary forces and adhesive forces. Water held between grains is due to capillary forces, while water adsorbed on mineral grains such as hydration envelopes is due to adhesion (Figure 6). In addition to capillary and adhesion water, there is hygroscopic water that is very strongly bound to mineral grains via molecular forces and is unavailable to flow or plants. Osmotic potential is present when solutes are such as salts are added to the water. The total water potential of the unsaturated zone is then given by sum of matric and osmotic potential.

The theoretical heights of water rise due to suction can be calculated via the capillary rise equation. The capillary rise equation was developed for the change in height of liquid in a cyclinder of internal diameter *d.* The rise is dependant on surface tension, fluid specific weights, contact or wetting angle between solid or grain surface and pore diameter. The capillary rise formula is

$$h = 4\sigma \mathrm{Cos}(\alpha)/\rho g d$$

where σ is the surface tension of the water, α is the contact or wetting angle of fluid with matrix, ρ is the density of water, g is the acceleration due to gravity, and d is the diameter of the cyclinder. Considering water in contact with silicate minerals has a contact angle close to zero so $\mathrm{Cos}(\alpha) = 1$, and substituting surface tension for pure water at 20^0C of 7.3×10^{-2} and $g = 9.81 \times 10^3$ N/m^3, the capillary rise equation reduces to

$$h(m) = 0.03/d_{eff}(mm)$$

where d_{eff} is the effective pore diameter in millimetres (Keeling, 2004).

Therefore, height of the capillary driven rise of water from the water table is dependant on the texture and structure of particular regolith materials, or the effective pore diameter of the materials. Keeling (2004) calculated rise in pore water above the water table for sediments with different grain diameters (Table 3). The calculations suggest the upward advective transport of solutes is possible over 10 m in fine silt (~ 4 μm) and even up to 37 m in coarse clays. The upward transfer of metals can be rapid as the main driver for metal migration is capillary driven (advection of solutes) with diffusion of ions accounting for minimal transfer as diffusion would be very slow. Studies measuring capillary upflow in clay loam soil cores to investigate the rise of saline water from the water table, found daily capillary rise between 0-5 mm (Prathapar and Meyer 1992).

Table 3. Theoretical height of capillary rise in sediments (from Keeling 2004).

Sediment	Grain diameter (mm)	Effective Pore diameter (mm)	Capillary Rise (m)
Fine gravel	5	2	.015
Coarse sand	0.5	.2	.15
Medium sand	.3	.12	.25
Fine sand	.15	.06	.5
Very fine sand	.075	.03	1
Coarse silt	.025	.01	3
Fine silt	.008	.004	7.5
Coarse clay	0.002	.0008	37.5
Fine clay	0.0002	.00008	375?

However, two grain size related parameters can limit the upward rise of water; low hydraulic conductivity and negative pore pressures. Water in clays is generally held hygroscopically and therefore advective flow is negligible (hygroscopic water is not available to flow or to plants). Accordingly, capillary rise in clay sediments would not be as high as indicated by the capillarity formula, and flow would be restricted to macro and micropores present in the clay matrix.With very high negative pore pressures, boiling point of water can be reached and water will tend to boil (embolism) and if any further metal movement will have to be gaseous.

Two parameters will affect the capillary driven rise of water above the anomalous groundwater; the grain size of the cover sediments and the vertical water potential gradient in the vadose zone, which in turn is related to the climate. The grain size issues are described above and finer grained sediments would be most conducive to a higher capillary rise. The moisture state of the vadose zone which is related to climate is important because it affects the water potential gradient (matric + osmotic potential) in the vadose zone and impacts on the high potential evaporation. In dry climatic zones, vadose zones are thick and the water potentials are very high near the surface just below the root zone with a gradual concave decrease (Scanlon *et al.* 2003) (Figure 6). Studies on conservative elements such as Cl and water potential measurements in arid vadose zones show a downward decrease in water potential from below root zone to the water table, which points to a strong upward driving force for both liquid and vapour (Scanlon et al 2003). In these arid vadose zones the strong upward flux from groundwater is important for upflow of solutes. The semiarid and arid climates that prevail across much of Australia are important in aiding the development and maintainence of the water potential gradient in the vadose zone because deep drainage is minimal due to scarce surface water input as the potential evaporation exceeds precipitation.

In arid to semi-arid climates, capillary suction can combine with dry climate adapted vegetation to transfer metals to the near surface and a similar mechanism to that described below was postulated by Mann et al. (2005). The driving force for the upflow of water and vapour from the water table and possibly the limits to capillary rise in fine grained sediments is the drying front or the evaporation front, often located in or below the root zone (Figure 6). The high loss of the water from the the root zone and just below due to evaporation and evapo-transpiration creates a drying front which can gradually move downwards. The evaporation front results in low water potentials with a gradual increase towards the water table. The low water potential maintained by the evaporation front within or below the root zone will result in consistently high negative tensions in the drying soil matrix and subsequently pull more water along mineral grains with a connection to the water table. Also, the evapo(trans)piration loss of water at the top of the drying front would increase the solute concentrations in capillary water and result in precipitation of metal salts, sulphates, phosphates and chlorides and adsorption of metals on soil minerals within the evaporation zone. Furthermore, vegetation will be able to uptake the metals from the capillary water and transfer metals upwards, and these two processes could work in tandem to transfer metal upwards to the surface through a greater distance than capillary alone (vegetation uptake and transfer is described later). An example of evaporation front causing the precipitation of salts from water brought up from capillary upflow is documented for salt crystallization in soils with shallow groundwaters and demonstrated in the experiments conducted by Mann *et al*. (2005).

The depth at which the evaporation front develops and is maintained within the soil is dependant on the soil type, the vegetation type and rooting depth (Seyfried *et al.* 2005). The vegetation type and their rooting depths control the evaporation depth by extracting the soil water continuously via evapotranspiration and maintining a low water potential so suction is inturn maintained to pull water via capillary. Many plant types in semi-arid and arid zones have physiologically adaptations to maintain a low water potential in the rooting zone. The maximum rooting depths of plants is discussed later, but the maximum density of roots for plants adapted to dry environments vary from 1-2 m (Schenk and Jackson 2002). Furthermore, during drought periods where scarce surface water input is depleted, the deeper roots extract water and the evaporation front moves downwards. Accordingly, the precise depth at which the evaporation front develops varies within a profile depending on scarce annual precipitation and across soil and regolith types.

Mann *et al*.(2005; Mann *et al.* 1997) forwarded the capillary model and conducted laboratory experiments on capillary driven upflow of metal bearing waters in sand columns that were subjected to evaporation. Their experiments found the capillary rise of metal waters up to 1 m high within a short time frame. Mann *et al.* (1997) suggested that in finer grained sediments, the capillary driven rise could be higher and reinforced the importance of evaporation on driving the upflow. Sheppard et al. (1987)

studies on sandy soil cores subjected to capillary upflow from contaminated groundwater showed the capillary driven rise of specific metals through the core. Keeling (2004) suggests the formation of Cu anomalies through 5-8 m thick transported clay via capillary rise and evaporation leading to precipitation of atacamite ($Cu_2Cl(OH)_3$). Keeling (2004) suggested capillarity as a possible mechanism because the ore signature, expressed in the presence of atacamite, formed in transported clay sediments that overlie mineralized saprolite, but not where thin sandstone is present between the saprolite and the clay overlying similar mineralization and similar depths. Continuity of clay sized pores may have favoured a higher capillary rise in comparison to sands, with the evaporative loss at the surface driving the continuous pull from the water table and also favouring the diffusion of ions. Kelley *et al.* (2003) suggest the possible formation of anomalies in soil within a thin sedimentary cover facilitated by capillary rise of groundwater.

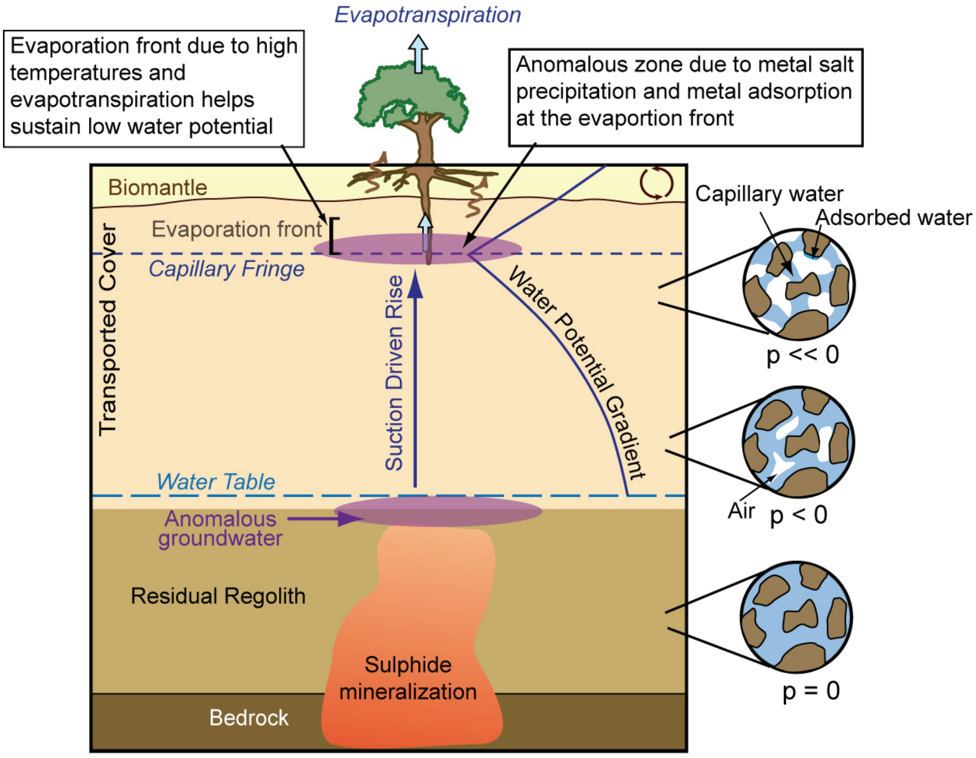


Figure 6. Capillary suction driven rise of mineralized water to the evaporation front. Drying at the evaporation front due to high temperatures and evapotranspiration will induce high suctions within the regolith matrix thereby maintaining the advective pull of capillary water from the water table. Increase of solute concentrations at the evaporation front will lead to metal precipitation and adsorption. Texture contrasts and grain size variations in the transported cover can preclude capillary suction over longer distances.

The difficulty in evaluating the role of capillarity in moving metals upwards is the height to which the capillary suction water rises is nature and thickness of transported regolith materials and adsorption of metals on clay minerals. The nature of transported regolith in Australia is important because it generally has texture zonation within it, which could impede capillary driven water movement across the stratified grain size materials. For example, Keeling (2004) provided an example where capillary rise may have occurred in clay sediments above basement, but not when clay sized sediments were separated by sands. Many of the capillary rise studies are conducted in 1 m or less column heights within uniform grain size materials, and the rise higher than 2 m through stratified textured materials needs to be evaluated.

4.2 Gaseous Processes

Gas is a ubiquitous medium and exists in minute pore spaces deep into the earth, trapped within minerals, in fluid inclusions, along mineral grain boundaries and as dissolved species in groundwater. Many elements of interest to the exploration and environmental geochemist, sometimes indicative of specific ore bodies, can exist as vapour and be transferred through the transported overburden via gaseous phase. Gas species have high geochemical mobility and are not greatly affected by gravity (Hale 2000). The high mobility of gases makes them an attractive transfer mechanism of ore related elements through barren cover to the surface soils (Highsmith 2004a), especially when a mechanism is required to transfer metals upwards from the watertable. Furthermore, in dry climates, vapour fluxes are generally larger than water fluxes (Kwicklis *et al.* 2006).

4.2.1 Gas Species and Generation

Gases and vapours exist as metal species in the near surface environments, and are broadly classified based on their origin into **primary**, those associated and emitted from the mantle and deep crust through volcanoes and faults, and **secondary**, those emitted as a consequence of interaction between ore bodies, water and biota (McCarthy and Reimer 1986). Secondary gases are important to dispersion mechanisms, because they carry a signature of the ore body, but not uniquely so, because they are also produced within the regolith and crust by other mechanisms, especially biological metabolism. The main gas species potentially released due to weathering of specific ore bodies (mainly sulphide minerals) and the factors affecting their upward transfer and their ability to manifest a mineralization related anomaly in the soil are listed in Table 3 and illustrated in Figure 5.

There are several gases and volatiles that can be produced due to weathering of ore bodies, and many of these are related to ore deposit style and composition. The main gas used to detect buried oxidizing **sulphide** bearing mineralization are the **sulphur** species (COS, SO_2, CS_2, H_2S) and **carbondioxide** with its antithetic relationship to oxygen. The reasoning behind use of these gases in mineral exploration is their generation via oxidative weathering of sulphides (mostly pyrite, but also chalcopyrite, galena and sphalerite) present in ore bodies. Oxidative weathering of sulphides results in the release of S. The S combines with H_2 and C (released from surrounding carbonates), leading to formation of a variety of sulphur gases depending on saturation, partial pressures, Eh and microbial conditions. Oxidative weathering of pyrite under dry, moist and saturated conditions has been demonstrated to release sulphur gases, mainly CS_2 (carbon disulphide) and COS (carbonyl sulphide)(Taylor *et al.* 1982) but also CO_2, SO_2 and O_2 (Hinkle *et al.* 1990). Considering the rates of generation, solubility and the Eh stability range of these sulphur gases, only H_2S and COS have the appropriate temporal stability required to migrate through transported sediments, but H_2S stability is further limited in oxidizing conditions (Oakes and Hale 1987). Therefore, COS, CO_2 and O_2 remain the most suitable gas indicators of sulphide weathering at depth. The presence of CO_2 and its antithetical relation with O_2 is interpreted as a product of reaction of sulphuric acid or protons released from weathering of sulphides with surrounding carbonates to form CO_2 with the consumption of O_2. Several studies have shown the elevated concentrations of CO_2 and COS with the depletion of O_2 above buried ore deposits, a gas expression interpreted to be related to oxidation of sulphides that releases CO_2 and COS with the consumption of O_2 (Hinkle and Lovell 2000; Lovell *et al.* 1983).

The gases – **radon** and **helium** - are formed primarily from the decay series of ^{238}U, ^{235}U and ^{232}Th (liberation of alpha particles). Of the three isotopes of radon - ^{222}Rn, ^{219}Rn and ^{220}Rn, only ^{222}Rn is generally measured because the others have half-lives of seconds and therefore can be used in uranium exploration. From ^{4}He and ^{3}He, ^{4}He is measured as the other isotope concentration is very small compared to ^{4}He (Butt *et al.* 2000a). Radon and He originate from a number of radioactive sources: uranium ore bodies, natural decay of uranium minerals in other rocks, geothermal sources, and have been used primarily to detect buried faults that act as preferential conduits for rapid dispersion, predict earthquakes and explore for uranium because the parent minerals in the ore body generate a higher amount of Rn. Both the gases are highly diffusive and so migrate rapidly, but radon migration is limited by its short half-live and therefore its detection merely confirms a source within 8m of sediment, if not less (Dyck and Jonasson 2000). Helium, in comparison is more stable and can accumulate, and therefore has a better potential of carrying a buried source signature to the surface. The usefulness of both the gases, however, is limited because of their natural production from sources unrelated to mineralization, and combined with their short-lives, limits their value as indicators of buried ore bodies (Butt *et al.* 2000a).

Specific ore bodies have been shown to contain varying amounts of **light hydrocarbons** having C chains of $C_1 – C_9$ and include methane, ethane and propane (Disnar 1990; Hulen and Collister 1999; Polito *et al.* 2002). Specific mineralization styles such as the Mississipi style base metals deposits and Carlin type gold deposits can contain trace amounts of "free" light hydrocarbons in wallrock and fractures especially the low temperature deposits. The genesis of these light hydrocarbons is considered to be thermal maturation of organic matter. Hydrocarbons, mainly methane and ethane, are also present in fluid inclusions (Hulen and Collister 1999; Polito *et al.* 2002). Escape of hydrocarbons from various hosts – wallrock, fractures and fluid inclusions- on weathering of ore bodies and their transfer upwards can manifest a light hydrocarbon signature at surface. The detection of hydrocarbon seeps and measurement of a continuous methane flux from petroleum basins demonstrates the transfer of these compounds from the deeper subsurface.

Table 4. List of gases that can potentially be generated from the ore body and the complicating effects in their use as buried ore body signatures.

Gas Species	Origin	Complicating effects	Reference
CO_2 & O_2	Oxidizing sulphides, deposit related carbonate reaction, consumption of O_2	Regolith microbial metabolism; Introduction into groundwater via recharge; natural degassing	Lovell (2000)
Sulphur: COS, CS_2, SO_2, H_2S, CH_3SH	Sulphides & oxidizing sulphides, especially pyrite	Regolith microbial metabolism generates similar gases; Temporal and oxidative stability very low for some gases	Taylor (1982) & Hinkle (1990)
Mercury: Hg	Weathering of sulphide minerals: Epithermal base-metals, VHMS	Microbial metabolism transformations to metal; adsorb within overburden matrix	Carr & Wilmhurst (2000)
Radiogenic daughters: Rn, He,	U & Th sources; mineral sands, kimberlites	Natural degassing from rocks; Rn very short-live; atmospheric interferences	Butt *et al.* (2000a) & Dyck & Jonasson (2000)
Light hydrocarbons: C_1–C_{10}	Hydrocarbons around specific base metal and Au deposits; Leakage from fluid inclusions	Biogenic production of most hydrocarbons, especially near surface; serpentinization of ultramafics	Disnar (1990)& Polito *et al.*(2002)
Organometallics: CH_3As, $(CH_3)_3Sb$, CH_3I, $(CH_3)_2Se$, CH_3Hg	Weathering of sulphides to release metal(loid) & microbial metabolism to produce organometallics	Many require reducing environment and/or appropriate strain and quantity of microorganism	Hirner *et al.* (1998)
Halocarbons & halogens: CH_3Cl, CH_3I, CH_3Br	Weathering of Pb-Zn sulphides; alkalynation of halides during oxidation of organics; fungi	High temperatures or organic matter and specific microorganisms required for volatilization – higher in soil	Keppler *et al.* (2000)
Volatile hydrides: AsH_3 (arsine), SbH_3 (stibnine), NiH_3	Weathering of sulphides - reducing conditions	Trace quantities produced & hydride stability in natural air limited to days	Klusman (1993) Turpeinen *et al.* (2002)

The ability and extent to which a metal can be volatilized from the solid state is dependant on its vapour pressure, which in turn is dependant on the temperature. Most metals related to ore deposits have low vapour pressures at normal temperatures and therefore cannot be easily volatilized as a result of inorganic weathering reactions within the ore body. However, **Hg** and specific metals such as **As, Se, Sb, I** and **Bi** may transfer to a volatile phase under specific geochemical conditions and as a result of bio-transformations or biomethylation. Mercury released from primary minerals (sulphides) can convert to vapour but it is also highly soluble in water. Mercury and other metals and metalloids – As, Se, Sb, I, Bi and possibly Au, can form organometallics via biomethylation activities of microorganisms (Craig *et al.* 2003; Hirner *et al.* 1998) (the formation of organometallics is described later under microbial processes). The halogens are also transformed into **volatile halogenated organic compounds** (VHOC) or halocarbons, either by microbial metabolism or by purely inorganic processes. Halide ions are either alkalated during oxidation of organic matter with Fe(III) serving as an electron acceptor (Keppler *et al.* 2000) or biomethylated by fungal metabolism (Redeker *et al.* 2004). Some metals can form metal hydrides under reducing conditions and become volatile at normal temperatures, an example being arsenic that forms arsine (Turpeinen *et al.* 2002) (Table 4). In view of many of the gases and volatiles being generated below the water table at the weathering front, Henrys' law explains the generation and subsequent stability of a volatile species in water. Generally, metal volatiles if present in water, have a tendency to move to the air-water interface or a nearby vapour phase (e.g. bubbles) and escape (get "stripped" from water) because their partial pressures in air are near zero. Although studies have demonstrated the formation of trace quantities of volatile organometallics in specific artificial and natural environments such as landfills, sewages, and swamps, and also arsine in arsenic contaminated soils (Turpeinen *et al.* 2002), but besides mercury, the generation of metal hydrides, volatile organometallics and halocarbons at the weathering buried ore bodies is assumed, and not yet proved.

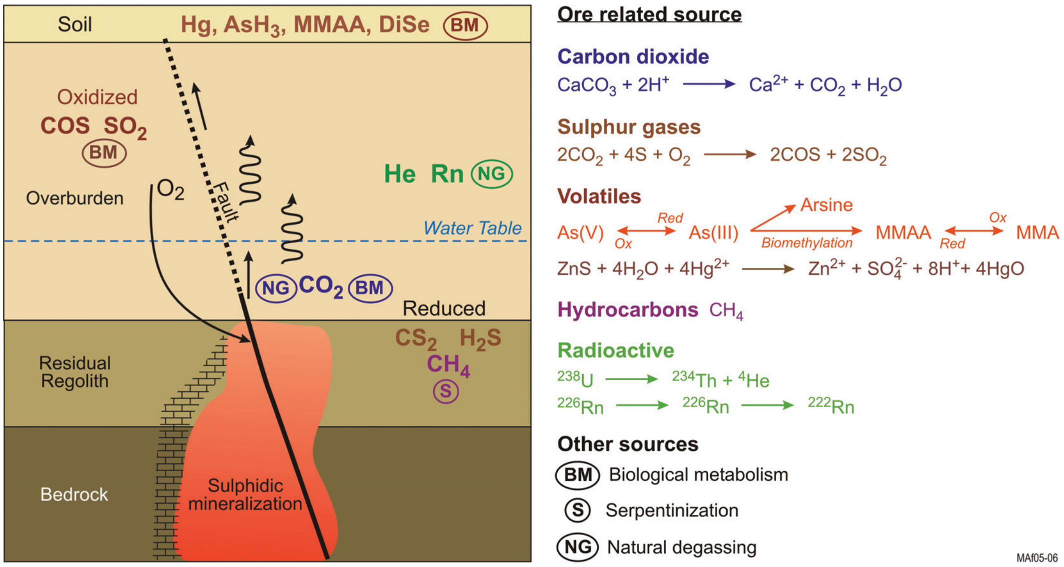


Figure 7. The source of different gases and volatiles whose concentrations are used as indicators of buried mineralization.

Dispersion of gases is dependant on the properties of the gas and the medium through which it travels. In theory, three transport properties affect the migration of gases: diffusion (concentration gradients), advection (pressure gradients) and buoyancy (or bubble migration) (Hale 2000; Ruan and Fei 2000). Bubble migration has been covered under phreatic processes and only its limitations, especially in the vadose zone will be described here. In the natural environment, all three migration mechanisms do not necessarily function separately, but with different intensities in response to different natural stimuli, which are described below and illustrated in Figure 7.

4.2.2 Diffusion (Concentration Gradient)

A common form of transfer of gases released from ore bodies is via diffusion. The molecular diffusion of gases occurs along concentration gradients. The diffusion of gases in isobaric and isothermal conditions is dependant on

- **Medium**, especially the density of the medium. Unlike open air, the regolith as a medium is made of materials having variable porosity with different grain and pore sizes, and therefore the gas molecules collide with each other and the surrounding medium. The factors affecting the direction

and velocity of gas migration are the shape, size, tortuosity and saturation conditions of the medium. These factors give rise to different types of diffusive fluxes which are employed to model and simulate gas diffusion. For example, Knudsen diffusive flux occurs where the gas molecule mean free path is much greater than the pore radius, and results in greater molecule-wall collisions than molecule-molecule collisions (Scanlon *et al.* 2002).
- **Diffusion coefficient** which is generally unique for different gases because it is dependant on the particular gas molecular weight, shape of molecules and their intermolecular attraction.

Gas emanating from a point source such as ore deposit, will diffuse through an overlying porous medium and form a hemispherical haloe within the overburden with the highest intensity of the gas species manifested directly over the source. The rate of diffusion is however dependant on porosity of the medium and diffusive nature of individual gases. In terms of medium properties, gases on encountering materials with different porosity will diffuse along paths of least resistance or diffuse through low-porosity materials at rates that are unable to manifest a haloe of sufficient intensity (Hale 2000). For example, simulations of gaseous diffusion through porous sand unit overlain by low-porosity clay unit, indicate the gas to diffuse freely with sufficient intensity through the sand. But on meeting the lower porosity clay, the gas diffuses along the boundary of the two units and then upwards where there is a change in porosity (e.g. fault). In contrast, for gas emanating from a ore body that is directly overlain by a low porosity material, the diffusion may be slow and the resulting haloe weak, and the signature from the source may not be expressed with sufficient intensity to be detectable even if a highly porous material overlies the low-porosity clay (Ruan *et al.* 1985). The main conclusion from gaseous diffusion experiments is that gases will diffuse rapidly along paths of least resistance such as contacts and structural conduits.

4.2.3 Barometric Pumping

Diffusivity of gasses occurs along concentration gradients under isobaric and isothermal conditions. The gas migration and exchange with atmospheric gases in the soil and unsaturated zone is also controlled by variations in a number of climatic variables such as pressure, temperature and rainfall (Klusman 1993), and all of these climatic variables impact on the efficiency of advective flow of gases. Of the climatic variables, the role of pressure gradients appears critical to the movement and exchange of gases within the unsaturated soil and rock, with measurements and simulations indicating the much faster transfer of gas (advective flux) due to barometric pressure fluctuations (Carrigan *et al.* 1996; Massmann and Farrier 1992; Nilson *et al.* 1991).

Barometric pressure is the pressure the air exerts on the surface and is measured in millibars (inches of mercury). Diurnal pressure changes arising due to thermal and gravitational effects produce pressure variations of a few millibars. In contrast, longer term, regional weather patterns cause cyclical variations or oscillations in barometric pressures to the tune of 10-30 millibars over few days. The oscillations and amplitude of the pressure curves varies according to the intensity of weather changes. The variable pressure changes induce the movement of gases into or out of the permeable subsurface. A fall in barometric pressure leads to an upward pull of gases from the permeable strata into the atmosphere, and a rise in pressure pushes air downward into the ground.

The influence of barometric pressure in facilitating the net transfer of gases into and out of homogenous medium would be minimal, because the small upward displacement of gases from the pores during the low pressures are balanced by the downward pushes during the high pressures. This near equal upward and downward gas transfer limits the volumetric expansion and contraction at the mixing zone between fresher air and gases emanated from the ore body. But in a heterogeneous medium, especially one bearing fractures or wide conduits surrounded by a uniform porous medium, a barometric surface high pushes “fresher” air into the fractures facilitating the mixing of the downward displaced air with gases originating from the ore body (CO_2, COS, Hg, C_4-C_9). During a low, the volumetric displacement of the gases from the pores are provided breathing space in the fractures and are channeled upwards through the conduits resulting in a net upward transfer of ore related gases. The upward extent of migration of the ore associated gases will depend on the volume ratio between the matrix and fractures (or the spacing between fractures) and the diffusivity of the gases (Nilson *et al.* 1991). Closely spaced fractures afford a smaller space for the release of gases from surrounding porous matrix to be channeled upwards, while larger spacings provide a better exchange space. But spacing densities higher than 10 m provide do not increase the upward migration efficiency of the gases because the air penetration is linked to the time between high and low barometric pressures that is to the tune of 100 hours. Further, the diffusivity of individual gases is also important in determining the rate at which a gas migrates to the surface. Highly diffusive gases will migrate upward slower than lower diffusive gases. The highly diffusive gases on upward migration tend to mix with air in surrounding matrix much more efficiently than lower diffusivity gases. This efficiency of mixing lowers their concentration within the conduits as compared to less diffusive gases, which are detectable at the surface earlier.

Support for the functioning of this mechanism comes from the detonation of nuclear devices 400 m below ground in fractured, bedded tuff. The detection at ground level of specific gases and volatiles (I_2) released with the blast after 50 days, or within years confirmed the migration of gases along conduits (Carrigan *et al.* 1996). This upward rapid transfer of gases and volatiles through tuffs can be explained by barometric or atmospheric mechanism coupled with minor gas diffusion (Cameron *et al.* 2004). The advective transfer of gases through stimulated barometric pressure changes gradients have been employed in the remediation of organic contaminants where artificially induced pressure changes force fresh air to be pumped into the ground and organic vapours to be pumped out. Although the barometric pressure induced advective gas flux is considered to be limited to fractured mediums, it can have an effect in heterogeneous, porous sedimentary regolith, especially when longer time scales are considered.

4.2.4 Thermal Convection

The other climatic variable that exerts influence on the flow of gases is temperature. The temperature differences between soil and open air induce changes in density of soil air that directly affects the flow of gas into or out of the unsaturated zone. The difference in temperatures between soil air and open air drives the exchange of gases within the soil and atmosphere but largely on inclined surfaces, such as hills (Rose and Guo 1995). Warmer air from the soil exits at the upper end of sloping surfaces and is replaced by colder air at lower end of the slope. However, if the atmosphere is warmer than the soil, the process operates in reverse with cold air discharging at the bottom and warm air entering at the top. Depending on a number of factors such as the inclination of the slope, temperature differences and permeability of the soil, the velocities of convection driven exchange can be high. Thermal convection process as described and modeled by Rose and Guo (1995), however, only operates effectively in sloping terrains or hills underlain by highly permeable soils such as sandy, gravel deposits, and therefore appears restricted to specific terrains and subsurface materials.

Thermal convection can also potentially arise in response to heat generated from oxidizing sulphides within the ore body. The role of heat released from oxidizing sulphides in accelerating solute migration has been previously described under phreatic zone convection mechanism, but the heat generated from oxidizing sulphides in drier environments can also raise the air temperature around an ore body. For example, temperature measurements in oxidizing open mines and mine waste heaps have documented temperatures reaching as high 60 ^{o}C (Harries and Ritchie 1981). The increase in air temperature around an ore body can result in a gas temperature gradient from the oxidizing sulphide body to the surface. This temperature gradient can establish gas convection currents that provide a driving force for advective air flow into and out of the sulphide body, irrespective of slope (Lefebvre *et al.* 2001; Lu 2001). The advective flow of gases is a more efficient gas transfer process than diffusion alone.
The role of convective currents established as a result of sulphide oxidation, although researched for mine wastes and dumps, has not been previously advocated to transfer gases and volatiles to the surface. The advective transfer can, however, operate in dry environments and is indicative of a buried sulphide rich source. For an oxidizing ore body exposed to air and thereby generating sufficient heat can result in emergence of convective gas currents which can rapidly drive oxygen into the oxidizing sulphides and release gases from the ore body upwards (COS, SO_2), potentially leading to fast and efficient transfer of gases from the ore body to the surface. The role of thermal convection in transferring gases is dependant on the presence of a high content of sulphides and permeability of the transported cover. Laboratory and modeling simulations indicate that highly permeable cover sequences are necessary for advective flow of gases to occur (Lefebvre *et al.* 2001; Lu 2001). A highly

permeable cover allows effective convective currents and favours advective transfer of gases, while in a low permeability cover sequence, flow of oxygen and other gases are limited to diffusion. Other factors affecting the onset and efficiency of convective flow are the saturation conditions around the ore body which will minimize heat transfer. Many of the air convection studies and simulations are conducted on uniform mine waste heaps and their cover barriers, which are not easily transferable to the natural ore body and cover heterogeneity.

4.2.5 Indirect Effects

The reasoning behind the formation of indirect anomalies at the surface as a consequence of gases is based on subtle modification of geochemical environment caused by the continuous transfer of gases from an ore body to the surface over time or the changes effected in microbial populations at the surface that in turn release specific gases. The continuous stream of gases could alter pH and Eh of surface soils, which in turn could affect the mobility of metals and/or alter particular mineralogical phase in the soil. Several studies report the unusual elevation of “mobile” or “extractable” metal concentration in surface soils over buried mineralization, and also the possible modification of specific minerals in the soil.

The gases with the efficacy to induce surface geochemical change are light hydrocarbons because their accumulation can produce a change in the Eh-pH state at the surface. The gradual efflux of methane as microseepages to the surface over hydrocarbon fields has been suggested to create a reducing environment in the soil directly above the gas field. The resulting reducing environment facilitates the reduction of Fe and Mn oxides and hydroxides in the soil, leading to the gradual migration of Fe and Mn to the edges of the gas field, and thereby manifesting a Fe-Mn aureole pattern over the gas field (Roeming and Donovan 1985). A similar indirect effect of gases was suggested for selective leach tests conducted on soils overlying nuclear blast sites. Hall *et al.* (1997) found a decrease in concentration of Fe extracted via hydroxylamine leach directly over the main fault over a nuclear blast, and they speculated the gases released from the blast could have modified the Fe bearing minerals.

Another source for hydrocarbons above the ore body is the presence of specific microorganisms in the soil related to the ore body. Increased microbial activity above an ore body can result from a geochemical effect related to the ore body such as the presence of the “basic chimney” due to redox gradients (section 3.5.2) providing extra nutrients or the release of specific sulphur gases. The rupture of the microbial cells on death, releases specific hydrocarbons which can be detected via soil gas analysis.

The cases documented for indirect effects are largely confined to non-metalliferous mineralization, such as petroleum fields and nuclear blasts. The magnitude of hydrocarbon efflux from a gas field is larger than one that would prevail from a base or gold mineralization, and the case reported by Hall *et al.* (1997) for detection of iodine and reduction in Fe minerals over gas efflux conduit is associated with a nuclear explosion. Nevertheless, it is important to consider and study the long-term influence of gases released from mineralization to the formation of indirect surface anomalies.

Response of major surveys shows anomalous concentrations over conduits which links with faster diffusive, advective and bubble migration velocities along paths of least resistance. The indirect pathway of a continuous stream gases affecting soil geochemical conditions will also be expressed above conduits.

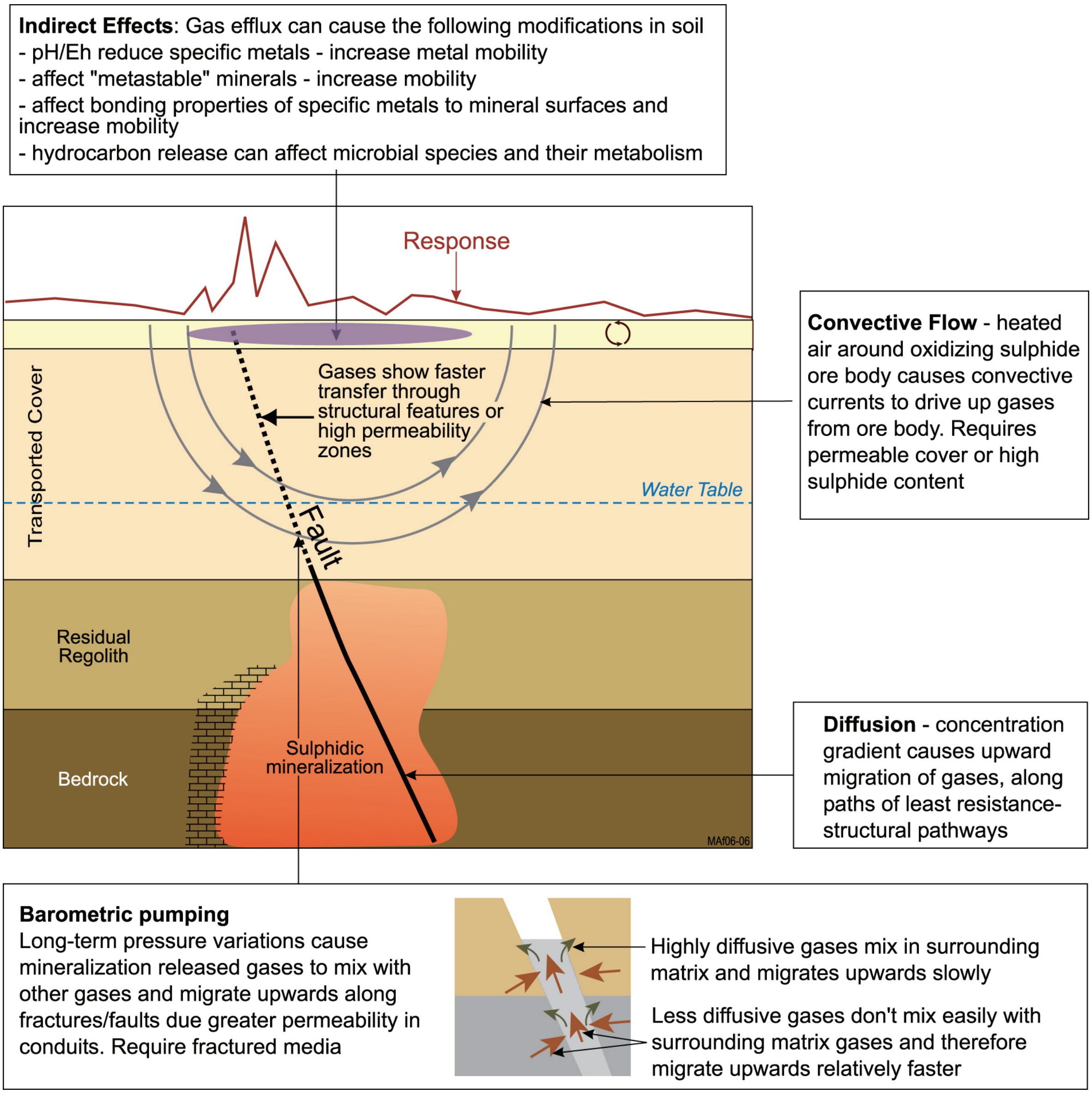


Figure 8. The gas based mechanisms of metal transfer from buried mineralization to surface. Surface gas surveys show higher concentrations of gases corresponding to subsurface conduits. This is likely due to faster diffusive and advective flow along paths of least resistance. The indirect pathway of anomaly formation due to gases will also be reflected above subsurface conduits.

4.2.6 Discussion on gas transfer

The gas based transfer of ore related metals appears attractive, especially because the natural pathway is mostly upwards and rate of transfer is rapid and continuous. However, studies demonstrate that there are several factors that affect the pathway and quantity of gas and volatiles during their transfer upwards from an ore body and within the soil, and accordingly impact on the value of effectiveness of gases as a buried mineralization indicator (Table 4). The important factors that need to be considered when evaluating gas transfer are:

- The formation, stability and contribution of volatiles and mineralization related gases (CO_2, COS, SO_2, CH_4, Hg) from natural processes unrelated to mineralization, especially biological metabolism
- The role of structural conduits to preferential transfer gases
- The processes of non-volatile metal transfer via bubbles above the water table.

Genesis and Stability

Gases emanate from the Earth due natural activity unrelated to mineralization (radioactive decay of U and Th producing Rn and He, and CO_2 degassing from various sources) or enter the groundwater through the atmosphere itself via recharge or infiltration leading to "excess" gases in the groundwater, a case being CO_2, noble gases and some sulphur gases. Biological metabolism within the soil produces substantial amounts of the same gases - CO_2, COS and CH_4 – that are used as indicators of mineralization and facilitates biomethylation of specific metals (Table 3) and therefore is one of the factors limiting the effectiveness of gases and metal volatiles as buried mineralization indicators (Highsmith 2004a). For example, Alpers *et al.* (1990) in their study of stable isotopic composition of soil CO_2 over a massive sulfide deposit, found root respiration contributed to most of the CO_2 generation in the soil rather than the oxidizing mineralization and weathering of associated carbonates. For organometallics, it is a question of their formation, the quantity generated and their stability. A few studies on extreme reducing environments such as sewages, landfills, swamps and contaminated sites demonstrated only a minor part of the total concentration of metals were biomethylated to volatile species (Turpeinen *et al.* 2002) and the biomethylated species were stable within a narrow temporal and redox gradient. The generation and stability of volatile organometallics at the oxidizing sulphide front needs to be studied and compared to the same occurring in the soil. The soil generally has a higher microbial count, but the type of microbial species may be different at the ore body weathering front and have a propensity to biomethylate and generate organometallic volatiles. (The role of microbes in biomethylation is expanded later). In summary, the generation of gases from a source not connected with mineralization can significantly interfere with the transfer of signal from mineralization.

Purely on the basis of measuring gases at the surface, the redox and temporal stability of the gases may constrain their transfer potential and utility as buried mineralization indicators. Reduced gases and volatiles (H_2S, carbonyl, metal hydrides, some organometallics, and hydrocarbons) are unstable in oxidizing conditions encountered in the many regolith environments, especially the unsaturated zone. The stability, and therefore the survival of these reduced species during transport through oxidizing parts of the regolith above the water table are questionable. The fate of a reduced metallic gas species on oxidation is unclear. And the temporal stability of the some gas species and metal volatiles, especially when they pass through groundwater-air interface and the time they take to travel through the transported regolith is very low. Besides CO_2 and COS, the other gases have short lifetimes (Oakes and Hale 1987). Furthermore, linked to the gas species stability is the interaction of gases with the atmosphere once they transfer to the soil/air interface. Gas exchange follows between air and soil and gases can escape to atmosphere rather than gradually collect in the soil, and the rate of soil-gas interchange will depend on climatic (pressure, temperature, precipitation) and soil aeration conditions at the surface.

Structural Pathways

The main inference from a synthesis of studies on gas transfer through residual and transported overburden is the correlation of gas anomalies at the surface with directly underlying presence of preferential migration pathways such as faults, fractures and shears (Etiope and Martinelli 2002; Fridman 1990). Some published studies on soil gas surveys that demonstrate a gas anomaly at the surface do not define structural elements of the underlying ore body or cover, and therefore it is not possible to objectively interpret the anomalous "spikes" or broad patterns on the surface for these studies. Most studies on gas measurements, where faults and other structural elements associated with the ore body were established, have noted the higher CO_2 (Etiope 1999; Highsmith 2004b; Polito *et al.* 2002), Hg (Carr and Wilmhurst 2000), CH_4 (Etiope 1999; Polito *et al.* 2002) and He and Rn (Butt and Gole 1985; Carr and Wilmhurst 2000; Carrigan *et al.* 1996; Pauwels *et al.* 1999; Rose *et al.* 1990) elevations above faults or shears. This strong correlation between preferential pathways such as faults and gas anomalies at the surface suggests the likelihood of contribution of diffusion and atmospheric pumping mechanism to transfer of gases rapidly via conduits to the surface (within days-years). However, what remains unclear is the nature of gas transport and extent of dispersion through structurally unaffected or non-fractured transported overburden, which in many cases manifests strong physical and chemical heterogeneity due to a weathering overprint. Volatile diffusion simulations indicate that the porosity of the medium will have a significant effect on the pattern and intensity of the resulting gas anomaly at the surface (Ruan *et al.* 1985), and therefore the nature and thickness of the transported material and interconnectedness of pores remains critical to effective gas transfer.

The question of whether anomalies are reflecting structural pathways only and not mineralization requires further study over buried ore bodies. For example, Etiope (1999) in a study comparing CO_2 and CH_4 emanations from two grasslands (similar soil conditions), one underlain by faulted substrate and another underlain by non-faulted substrate, found higher concentrations and flux of both the gases over the faulted substrates. The higher gas flux over faulted substrates was interpreted as extra gas from deeper subsurface (groundwater, natural degassing) contributing to the total gas concentration and flux as compared to natural biogenic gas flux or "background". The results of such comparative studies make it imperative to compare time averaged gas and volatiles data over faulted but unmineralized areas against adjacent faulted mineralization.

Bubble

The evidence for transfer of metals upwards above the water table via the gas bubble or "streaming" theory is not well substantiated, largely because of the lack of proof or documentation that the metals within the soil are not contributing to the gas associated metal anomalies, and because the poor understanding of fate of bubbles and attached metals below and above the water table. Dyck and Jonasson (2000) commented that data in support for gas associated metal transfer (Rn) from deep subsurface lack a critical component of the metal content in the surrounding soil. One study by Pauwels *et al.* (1999) used custom made activated carbon samplers to sample soil gas averaged over 3 months to reduce the climatic and soil process effects. They found the metal concentration on the gas collectors to be unrelated to the soil metal content, but were coincident with gas content of CO_2, Rn and He, which in turn were anomalous over mineralization that contained faults. These observations led them to suggest the transfer of metals (Ni, Cu, As, Co) was related to the carrier gas - CO_2 (bubble). Other recent studies using proprietary films inserted into soil to collect condensed gases, found the formation of 20-30 μm sulphate precipitates on the film. The spatial Cu content of the precipitates was "spikey" but revealed a correlation with deeper mineralization. In contrast, Cameron *et al.* (2004) in their study of time averaged gas measurements, found no metal enrichment above ore bodies. The main reason for difficulty in evaluating bubble associated transfer of metals is the poor knowledge of stability and behaviour of bubble or bubble "stream" above the water table within the unsaturated zone. The stability of the bubbles during transfer from a saturated to unsaturated zone has not been well established nor is the transport processes of the released particulate matter in a heterogeneous closed regolith medium, rather than open air or mines, where particulate or aerosols can be generated and disperse according to wind gradients. Bubbles prefer preferential pathway of upward migration such as fractures and faults where their transfer velocity is likely to be very high (Etiope and Martinelli 2002), and it is possible that even on bursting during their upward movement across a air-water interface, the attached metals will be released and migrate or "leak" upwards along conduits.

Gas transfer remains an attractive metal transfer mechanism because of its postulated rapid transfer rates and presumed ability to move metals upwards above the water table. However, further, well constrained studies are required to establish:

- The contribution of specific gases released from ore bodies as compared to that from biological metabolism within the transported cover.
- The generation of biomethylated volatiles at the weathering front and their temporal and spatial stability
- The contribution of structures to amount of gases in background sites as compared to mineralized sites and
- The stability and transfer of bubbles above the groundwater
- The source of gases which are large enough to form a large and continuous stream of gas below the water table.

The critical assessment of the ability to transfer metals via gases and volatiles to manifest an unambiguous detectable signal at the surface needs to start from the ore body itself and consider the scale and structural character of the ore body and overlying transported cover rather than drawing inferences from gas measurements in the soil.

4.3 Vegetation or Plant Uptake

Vegetation in its myriad forms remains central to the biogeochemical cycle of several life sustaining elements such as C, N, O, P and S, and contributes significantly to the continuous cycling of energy and matter (elements) at the interface of the biosphere, atmosphere and geosphere (regolith). The vegetation cycle as a mechanism for transferring specific metals from deeper mineralization to the surface appears attractive because of two demonstrated facts about plants: water and nutrient movement due to water potential differences between leaves and roots is upwards against gravity, and the trace metal content of vegetation often reflects the trace metal content of its substrate. The substrate – plant compositional relationship has been used as a justification for utilizing vegetation as a sample medium for delineation of specific rock types and identifying surface anomalies of buried mineralization (Brooks *et al.* 1995). On longer time scales, vegetation growth and decay remains a valid uptake system of metals from the subsurface to the surface, and its role as a conveyor of metals from deeper subsurface to the surface over time to create gold anomalies at the surface has been proposed (Andrade *et al.* 1991).

Similar to gases, there is a need to distinguish the role of vegetation as a sample media to that it being a mechanism of upward metal transfer from deeper regolith. Several studies demonstrate the coincidence of soil anomalies with that of vegetation, with sampling ease or wider anomaly in vegetation being the proposed benefit of vegetation surveys to that of soil (Cohen *et al.* 1999; Dunn *et al.* 1996; McInnes *et al.* 1997). These studies do not necessarily prove that vegetation taps into the deeper subsurface through the transported overburden to effect the metal transfer.

Much of the value and effectiveness of plants in supporting upward metal transfer is linked to three main plant characteristics and functions, which are part of several morphological and physiological adaptations the plant has evolved to cope with water and nutrient stresses. The adaptations critical to transfer mechanism and need to be assessed are

- Access and uptake of groundwater because metal concentration of groundwater is most likely to reflect the ore signal.
- Plants adapt to nutrient stresses and develop novel methods such as morphological adjustments and release of root exudates to access non-bioavailable micro-nutrients. What nutrient deficiency adaptations do plants show that enable to access and uptake non-bioavailable metals?
- The maximum and consistent depth of rooting. What is the maximum depth to which roots can penetrate on a regular basis across a climate (or biome) so the limits on depth can be predicted?

All the above factors regarding the role of vegetation in bringing up metals and water from the deeper regolith are considered next.

4.3.1 Phreatophytes and Groundwater Uptake

Bulk of the water and nutrient acquisition for plant metabolism are accomplished via root uptake from the soil, with the maximum rooting density being present in the top 50 cm. In terms of upward transfer of metals through > 1-2 m transported overburden, uptake via shallow roots does not appear to be a viable mechanism. However, many plants in water and nutrient stressed environments have evolved adaptations to cope with different water and nutrient sources available in the landscape. One adaptation, notably in water limiting environments, comes in the form of phreatophytes (often referred as “deep rooted” plants), plants that send their roots into the groundwater or capillary fringe to obtain water for transpiration and photosynthesis. The phreatophytes generally bear deep penetrating roots that reach the groundwater table and are therefore capable of exploiting the deeper water sources during drought periods or dry summer months (Canadell and Zedler 1995; Ehlerninger and Dawson 1992).

The root morphology of plants plays a critical role in water and nutrient uptake and plant survival in different nutrient, water and temperature environments. Plants are able to change their root architecture and depth according to external stresses (Feldman 1984). Many of the phreatophytes have dimorphic rooting morphology, with a set of laterals radiating out from the main root crown, and a main sinker or tap root, growing vertically into the regolith (Dawson and Pate 1996; Pate *et al.* 1995; Pate *et al.* 1999) (Figure 9A). There are variations in the dimorphic rooting morphology, with some species developing several tap roots instead of one, and others having obliquely descending lateral roots. The laterals are generally restricted to the top 50 cm of the soil profile, while the tap roots penetrate much deeper, with their downward reach being limited by the water table or hard regolith materials, which can vary between 2 to 30 m, or even more (root depth is described later). In specific species in Australia, mainly in the *Banksias*, the laterals also bear vertical cluster or proteoid roots which aid in acquiring insoluble nutrients such P. The main function of evolving a dimorphic root system in semi-arid, arid and Mediterranean climates appears to be necessity to exploit different water sources during an entire wet-dry cycle or droughts so a continuous supply of water to the plant is maintained throughout the year. Furthermore, the shoot growth (above ground tree mass) shows an increase once the sinker roots reach a permanent source of water (groundwater) so the tree has a consistent supply of water throughout the year (Pate et al 1999).

Hydrogen isotope (deuterium, δ^2H) signatures of soil and groundwaters allow inference of depth of water compartments accessed by plants. The isotopic composition of regolith waters varies with depth with water near the soil surface becoming enriched as compared that at depth because of evaporation (Allison and Hughes 1983). Studies utilizing the differences in stable isotopic composition of soil and deeper groundwaters, and comparing the isotopic composition of – rainfall (soil water), groundwater, sinker or tap roots, laterals and stem base, indicate the greater dependence of the stem on groundwater in the dry summer months (especially the end of summer) as compared to soil water (rainfall derived) during the wet and spring months (Dawson and Pate 1996; Pate *et al.* 1999) (Figure 9B). The use of deuterium in monitoring of water sources demonstrates the role of sinker roots in water and macro nutrient uptake from the groundwater (often salty) during dry season and droughts (Pate *et al.* 1999). Further, the hydraulic conductivities of xylems of the sinker roots were significantly higher (> 200%) than those of laterals and trunk, enabling the sinkers to draw water uniformly without resistance so as to maintain a constant supply during summer. Other studies in Australia have confirmed the dependence of specific plant species on groundwater during dry seasons with roots commonly penetrating to depths of 6 -12 m (Dodd and Bell 1993; Zencich *et al.* 2002). Studies in South Africa on root penetration and water extraction from a deeply weathered granite profile by *Eucalyptus grandis* found younger trees to extract water from 8 m while 10 year old trees extracted water from > 8 m depth (Dye, 1996 as reported in Le Maitre *et al.* 1999). These studies confirm that specific plants do tap into deeper permanent source of water and therefore have the potential to transfer metals from the groundwater to the surface via plant tissue and release to soil via litter.

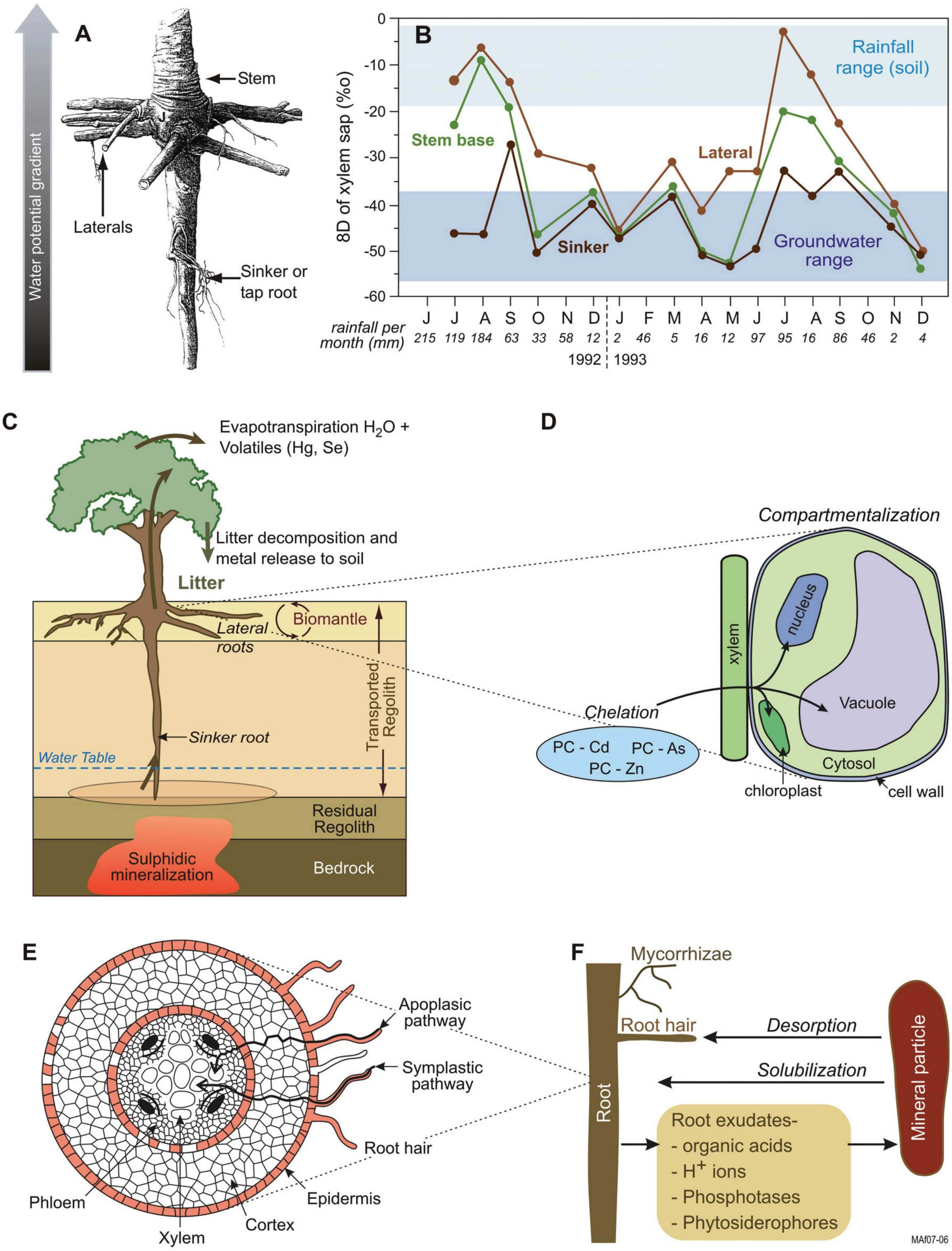


Figure 9. Plant water and nutrient uptake strategies that potentially can contribute to metal transfer from subsurface to surface. A) Illustration of root morphology of the *Banksia* with lateral and sinker roots. Water potential gradient from sinker to leaf results in transfer of water and nutrients from deeper subsurface compartments. B) Seasonal variation in deuterium isotopic composition of stem, sinker and lateral roots demonstrating uptake of groundwater by the plant via sinker roots during summer months (After Pate et al. 1999). C) Illustration of metal transfer process from deeper regolith and groundwater to plant tissues to relocation to above ground tissues (shoot, leaves) and eventual transfer to soil via litter. D) Strategies employed by the plant to detoxify and store high concentrations of specific metals within its tissues. E) Element transfer through roots to the xylem via the apoplastic (along cell walls) or symplastic (across cells) pathways. F) Illustration of physiological and biochemical metal acquisition strategies employed by roots, especially to acquire non-bioavailable metals associated with insoluble oxides and hydroxides.

The extent to which a species relies on groundwater as compared to soil water depends on the availability of permanent or ephemeral water sources. Some species utilize groundwater throughout the year with the total amount of water contributed by groundwater varying depending on season (Zencich *et al.* 2002). In other areas, especially along riparian zones in semi-arid settings of eastern Australia, *Eucalyptus* species were found to switch between soil water sources and deeper groundwater depending on the salinity and water availability (Mensforth *et al.* 1994). Another study in a similar environment found *Eucalyptus camaldulensis* to uptake variable amounts of groundwater depending on the plants distance from the stream. Plants with permanent access to streamwater obtained approximately 50% of their water from groundwater, while those plants of the same species away those distanced from the stream relied mostly on groundwater (Thorburn and Walker 1994).

The above studies demonstrate the ability of phreatophytes to draw water and macro nutrients from the groundwater, especially in water-stressed environments, rather than merely use soil water and nutrients.

4.3.2 Hydraulic Lift (Hydraulic Redistribution)

Related to the use of groundwater on a seasonal basis by phreatophytes, is the vertical movement of water from moist areas in the subsurface to dry ones, and the potential to carry metals via this movement. Hydraulic lift is the process of movement of water from relatively moist, high water potential soil layers to dry, low water potential soil layers, using the plant roots system as a conduit (Caldwell *et al.* 1998; Richards and Caldwell 1987). The transfer of water along water potential gradients occurs on a diurnal basis because differences in the rate of transpiration between day and night determine rate of water use by the plants. During the day, water available at all depths is taken up and travels through the plant in the transpiration stream to be lost to atmosphere from the leaf stomata through evaporation. During the night when the leaf stomata are closed and the water potential difference between the deep roots and shallow dry roots is high, water is brought up, but largely released to the drier soil layers, rather than taken up by the plant in the reduced transpiration stream (Figure 10). The water released to the soil is then absorbed by the shallow roots and transpired during the day.

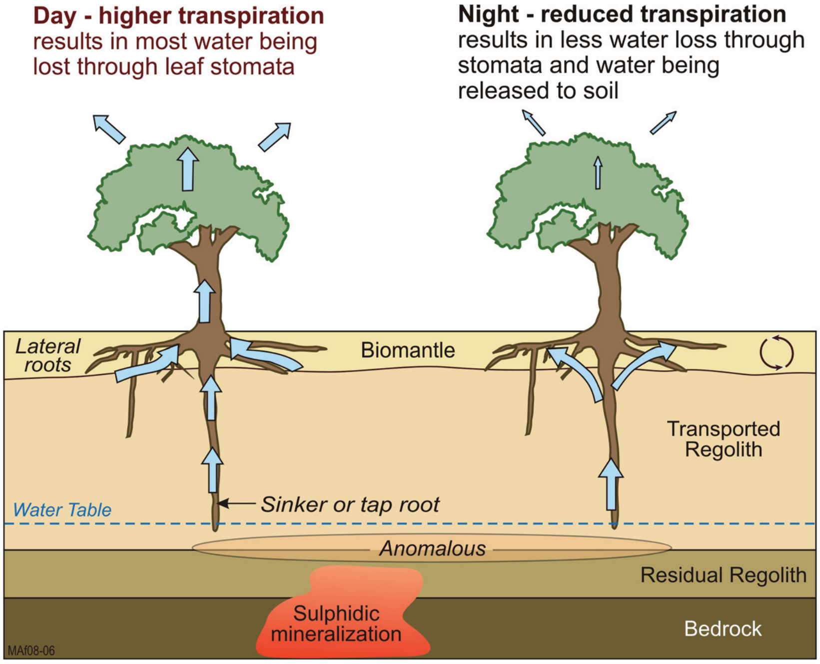


Figure 10. The concept of hydraulic lift. Water is taken from deeper compartments and transpired through the day, but at night when transpiration is lower, some water is lost to soil via the lateral roots. Potentially, metals could be moved to the soil from deeper water compartment. Inverse of this also works where soil water is transferred downwards.

The general direction of operation of hydraulic lift is from the subsurface to surface, following the pattern of drying commencing from the surface. However, inverse hydraulic lift, the movement of water through roots from surface layers to deeper subsurface drier layers also occurs (Burgess *et al.* 1998; Schulze *et al.* 1998). Burgess *et al.* (1998) in their study on laterals and sinker root sap flow and heat pulse experiments on *Eucalyptus camaldulensis* in the SW Australia found hydraulic lift operated via sinker roots during seasonal periods, especially during drier months. After the rains, inverse hydraulic lift operated transferring water from the upper wet soil horizons to the deeper groundwater zone. Therefore, the movement of water via the plant on a diurnal basis is recommended to be referred to as hydraulic redistribution.

Although initially the theory of hydraulic lift was questioned, deuterium isotope studies combined with heat pulse measurements have proved its operation, and over 50 species from Africa, North America, Australia and Brazil have been documented to display hydraulic redistribution. Even in the Pacific Northwest coniferous forests, Brooks *et al.* (2002) found the operation of hydraulic lift during the summer months, with hydraulic lift contributing 25-35% of the soil water used by plants. However, the magnitude of water lifted is unclear with estimates ranging from very little to over 100 liters per day. Also, the contribution of water lifted by tap root to the total flux of water through the plant can vary, with some observations indicating only minor amount of lifted water contributed to the entire flux for the plant (Moreira *et al.* 2003).

Although the ecological significance of hydraulic lift is as yet unclear, some suggestions have been forwarded. In accordance to plant communities, the water release via hydraulic lift into upper soil layers affords adjacent smaller plants of the understorey to utilize the water (Caldwell *et al.* 1998). Bringing water from deeper to drier, but nutrient rich soil zones may facilitate biogeochemical cycling by enhancing nutrient uptake and microbial processes.

In terms of metal transfer, there is no study to suggest the transfer of metals upward with the water from deeper zones (> 5 m), and therein lies its major uncertainty as a metal transfer mechanism. However, the main advantage of hydraulic lift is its dynamic and rapid operation (daily cycle), which may be able to continuously redistribute metals from the subsurface to the soil layers, possibly in dissolved form. If ore related metals are transferred (nutrient transfer studies have not been attempted as yet!), then the mechanism differs but supplements the traditional view of uptake to above surface and release via litter or volatilization, by releasing metals directly to subsoil.

4.3.3 Metal Uptake

Plant growth and survival is dependant on plants acquiring bulk of their water and nutrients from the regolith to create new plant tissues via photosynthesis. Plants require 13 nutrients (elements) to grow - K, Ca, Mg, P, S, Cl, B, Fe, Mn, Zn, Cu, Mo - and the availability of nutrients dictates plant growth rates and community structure. The macronutrients are involved in the build up the structure of proteins and nuclei acids, while the micronutrients are associated with the catalytic sites of specific enzymes. For ore metal transfer, the uptake of relevant micronutrients (Cu, Zn, Mo) is important, because a higher availability of these nutrients is likely to be expressed in the above ground plant organ content, as documented for numerous biogeochemical surveys (Dunn *et al.* 1996). Micronutrients and other trace metals acquired from deeper regolith at the groundwater table can be transferred to the surface via plant tissues and their subsequent release as litter, volatilized to atmosphere or possibly released directly into the near surface soil via hydraulic lift (Figure 9 & 10).

Besides the micronutrients required for plant tissue functioning, some plants do uptake and accumulate other elements proportionately depending on the metals availability in the substrate. An extreme example of metal uptake and storage in plants are the hyperaccumulators that have concentrations of specific metals in their shoots greater than a predetermined threshold value. Initially, hyperaccumulator status was based on metal concentration in their shoots greater 1000 μg g^{-1} on a dry mass basis for Ni (Brooks *et al.* 1977) but different thresholds have been applied to other metals such as Zn, Cd and Pb (Reeves and Baker 2000). The micronutrient amounts in plant tissues and hyperaccumulation thresholds for some documented metals associated with ore bodies are provided in Table 4. The list of hyperaccumulated metals indicates the involvement of plants in recycling micronutrients and other ore related metals (Ni, Cu, As, Zn, Pb, Mo, Sb, Se). Gold is acquired and concentrated in a variety of plants (Erdman and Olson 1985), although not to hyperaccumulator status. Even for a toxic metal like As (notable pathfinder), plants are able to uptake, tolerate and accumulate arsenic (Meharg and Hartley-Whitaker 2002).

Common native plants (tolerant species) adapt to high or low nutrient stress by evolving novel morphological forms and physiological processes such as higher root:shoot ratio, high leaf longetivity, release of root exudates and increase in root surface area, low nutrient uptake rates but high nutrient concentrations in their dry matter (Marschner 1995) and metal chelation and transformations within the tissues to facilitate the uptake and transfer of toxic metals such as As and Se. In many nutrient limiting environments such as those found across Australia, the roots may penetrate deeper and wider for nutrient access rather than water access. Similar to adaptations evolved to cope with water stressed environment, plant adjustments for nutrients has advantages for metal uptake and rooting depth, and therefore its understanding is important for the efficacy of metal transfer process.

Table 5. The average concentrations of ore related micronutrients in plant tissues and hyperaccumulation thresholds for other ore associated elements in plant tissue. Data from Marchner (1995) and Reeves & Baker (2000).

Element	**Average micronutrient amount in plant tissue (μmol g^{-1} dry wt)**	**Maximum threshold for hyperaccumulation**
S	30	
Zn	0.30	10,000 μg g^{-1}
Cu	0.10	1000 μg g^{-1}
Mo	0.001	
Ni, Co		1000 μg g^{-1}
Cd, Cr, Pb		100 μg g^{-1}
As		1000 μg g^{-1}

Root:shoot ratio and prolonged tissue life

Poorter & Nagel (2000) in their analysis of biomass distribution of plants between roots, stems and leaves based on stressed environments, found greater biomass allocation to roots only when nutrient limitations occurred. The root:shoot ratio becomes greater for nutrient limiting environments and accordingly roots tend to penetrate deeper and have an extensive subsurface network. This extensive subsurface network allows a greater access to nutrient sources and uptake of nutrients. Prolonged tissue life is also observed in natural communities growing in nutrient poor ecosystems. For example, plants loose their leaves much slower when growing in nutrient poor conditions (Chapin 1980).

Root hairs and root exudates

Metallic nutrients are either not available in highly leached regolith environments or where present are tightly “bound” to soil particles (minerals and mineral aggregates) i.e. not bioavailable. Plants have evolved novel strategies in the form of root structures and processes such as increase in root hair length and density, growth of special roots and release of special exudates to gain access to insoluble or non-bioavailable metals, which enables plants to acquire and uptake a range of ore related metals (Jones 1998), both essential micronutrients (S, Zn, Cu, Mo, Ni, Se) and toxic ones (As, Cr). The fine roots (root hairs) form a large part of the total root length and therefore able to access a larger part of the regolith. The root tips represent micro areas of intense chemical activity, releasing specific organic acids, protons and chelating compounds and thereby modifying the chemical characteristics of the rhizosphere in novels ways to access metals from regolith minerals (McCully 1999).

Some plants have adapted to the poor bio-available nutrient status of many Australian soils (and other similar nutrient poor environments) by evolving a specialized root structure, physiology and biochemistry, such as the cluster or proteoid root system. These dense array of short rootlets increase the surface area for nutrient acquisition and exude specific organic acids, namely citrate and malate, which enable the solubilization of non-bioavailable phosphorous, thereby facilitating P uptake (Dinkelaker *et al.* 1995; Neumann and Martinoia 2002). Roots in general also exudate a variety of organic acids that either stimulate bacteria to sequester nutrients or facilitate the complexation and solubilization of non-bioavailable nutrients in low nutrient environments (Dakora and Philips 2002) (Figure 9F). Although secretion of organic exudates has been demonstrated to facilitate major nutrient uptake (e.g. P), its influence on trace metal uptake has not been extensively studied, but is very likely considering the efficiency of metal uptake increases on application of chelates to the soil ("bound metals" become bioavailable) during phytoextraction studies (Salt *et al.* 1998). Another exudate released by specific plants to mobilize and complex "bound" metals are phytosiderophores, which are metal-chelating compounds such as mugenic and avenic acids. The compounds chelate and mobilize several cations such as Fe, Cu and Zn and subsequently transport them across the plasma membrane (Salt *et al.* 1998). The release of greater quantity of organic acids is partly in response to Fe deficiency, and the released organic exudates enable the complexing of Fe from insoluble iron oxides and hydroxides (Jones 1998). The organic acid facilitated dissolution of ferric oxides and hydroxides will also release tightly "bound" metals from the minerals and make them available for root uptake.

Some other roots have a symbiotic association with special bacteria or mycorrhizae to permit the capture of micronutrient from a larger area of the regolith (Figure 9F). Another symbiotic relationship is with nitrogen fixing bacteria that fix nitrogen from the air in their nodules in exchange for carbon compounds supplied by the root. The influence of mycorrhizae in the uptake of micronutrients at depth rather than the top soil is unclear.

Metal transport and transformations

The entire process of metal uptake from the root to the above ground tissues by plants is complex and only a brief overview is provided. The metal species enter the root through the root hairs, augmented by a myriad of root facilitated processes to uptake a "bound" metal from mineral particles. The metal can enter the xylem either through the symplast or the apoplast route. During the symplast route, the metals move across the plasma membranes of the root cortex and endodermis cells and finally into the xylem vessels. In the apoplast pathway, the ions move between the cells into the xylem. Once in the xylem, the flow of the xylem sap in response to transpiration transports the metals to the shoot and leaves. In the leaves, the metal will gain cross a membrane to be sequestered into the leaf. The metals acquired in dissolved form via the roots are transferred and stored in diverse plant cell types as different metal species.

The uptake of toxic metals require special mechanisms of detoxification and storage, and three general mechanisms employed by hyperaccumulators are chelation, compartmentalization and biotransformation (Salt *et al.* 1998). In response to toxic metal stress, plants produce two main metal-binding polypeptides: metallothioneins (MTs) and phytochelatins (PCs). These peptide ligands **chelate** with metals and reduce the solution concentration of free metal ions in the tissue and thereby limit damage to metabolic processes. The toxic metals and metal-chelates are subsequently sequestered into specific sub-cellular **compartments**, such as the binding to cell walls, cytosol and vacuole, with most chelated species being stored in the cell vacuole (Figure 9D). The dissolved metal forms can also experience **biotransformations** and be converted to inorganic (reduced), organic or colloid species within the plant tissue, mainly as a means to reduce toxicity of the metal (Figure 9D). Reduction in toxicity of a metal is important because many mineralization associated metals such as As, Cd, Pb, Se, Hg and Sb are considered toxic to plants. It is possible that most toxic metals (As, Cd, Se, Pb, Cr, Se) exist combined to organic complexes such as phytochelatins and thiols, and since the metals are immobilized by binding to the organic complexes (as opposed to free ions), the mechanism is considered to be one of detoxification. For example, arsenic in plants can be found in a number of species such as arsenate, arsenite, monomethylarsonic acid, dimethylarsinic acid, trimethylarsonium ion, arsenobetaine, arsenocholine and glycerol ribose. Generally, arsenic exists in more than one species in the plant tissue and it is likely that all the species are chelated with phytochelatins (Meharg and Hartley-Whitaker 2002). Another relevant example is of gold, which absorbed by Alfalfa and Wheat plants from soil solution as dissolved form (AuCl species) was converted to a 5-10 nm gold particle within the stem (Gardea-Torresdey *et al.* 2002). Another pathfinder but also a toxic metal at high concentrations, Se, is taken up by specific plants and bio-transformed into a non-protein amino acids, which enables the plant to cope with high levels of Se that are not bound to proteins.

4.3.4 Rooting Depth

Rooting depths of plants is critical because it limits the depths from which water and metals can be transferred to the surface. A general statement often used to advocate the deeper reaches of plants and to sell them as geochemical sample media is “root penetration can reach depths of tens of meters”. Precisely how deep and in which climatic and substrate conditions “tens of meters” can be reached so as to make rooting depth predictive was unclear. Few recent studies on global rooting depths, however, do supply valuable information and provide a framework for gathering more data to make rooting depths predictive.

Stone & Kalisz (1991) in their survey of the maximum depth for root penetration for various woody species, forest trees and shrubs found an amazing capability of roots to penetrate into deeper regolith. They suggested the need for plants to cope with water and nutrient stress environments as being the primary factors driving deeper root penetration. Most rooting depths are documented for the forests in northern Europe and northern America with depths up to 1.5 m, but this fails to consider rooting depths in nutrient and water stressed environments as well as different regolith factors in semi-arid and arid climates that show deeper root penetration. Stone & Kalisz (1991) found over thirty cases documenting the roots in contact with water tables at depths varying from 2 – 35 m. Another global survey of maximum rooting depth according to biome conducted by Canadell *et al.* (1996) found that over 50 species had rooting depths of greater than 5 m (Figure 11). The biomes commonly found in Australia and from which much of the data for Figure 11came from, show that rooting depth past 10 m are commonly achieved. Schenk & Jackson (2002) in their study on rooting depths from a global rooting depth database, found that 95% of all roots were confined to the upper 2 m, but deeper rooting depths were found in vegetation from water-limited environments and in shrublands as compared to grasslands.

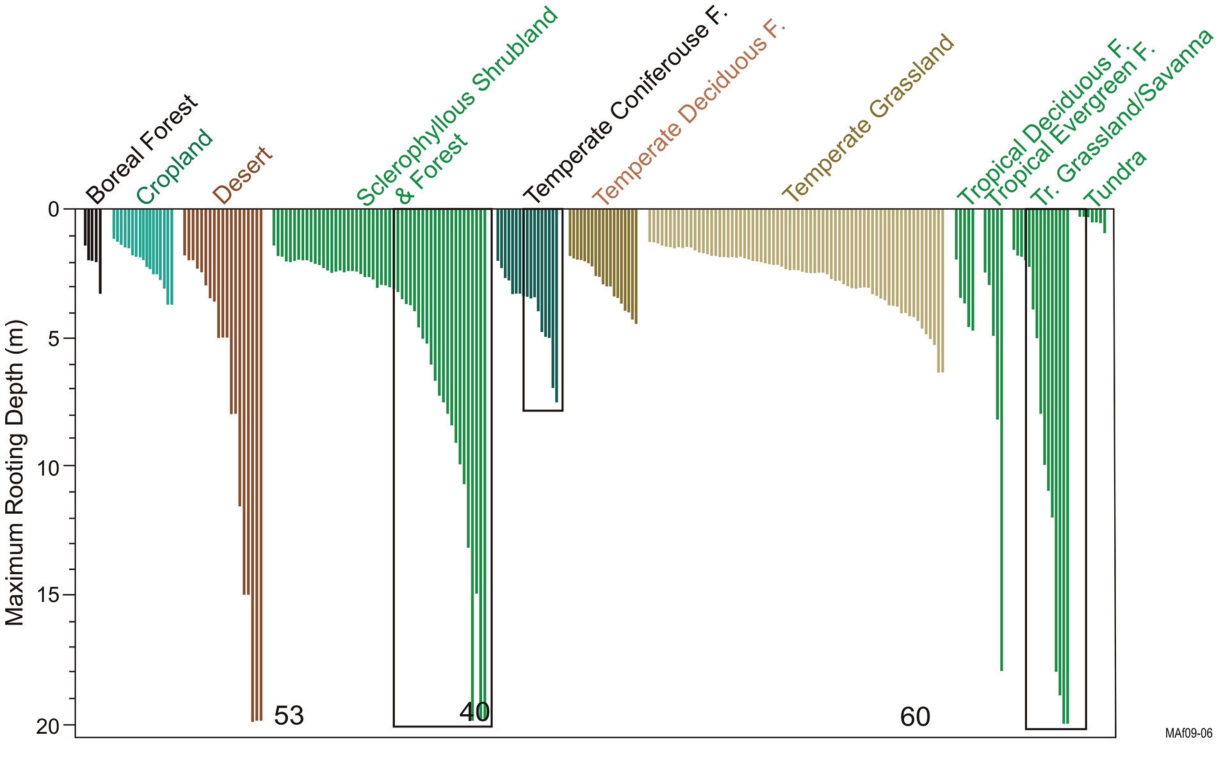


Figure 11. Maximum rooting depths (m) of reported species grouped according to terrestrial biome. Boxed areas are dominantly data reported from Australia. After Canadell et al (1996).

Two studies of rooting depths pertinent to Australia demonstrated the great depths and rooting habits of the Jarrah in the southwest. Kimber (1974) described that majority of the Jarrah roots terminated at the laterite surface at a depth of 1 m, but a few roots penetrated into channels or macrovoids through the laterite, and on reaching the water table at a depth of 15m the branched profusely. Dell *et al.* (1983) in their study on Jarrah forests in SW Australia reinforced the association of deeper roots and “channels” or conduits in 40 m deep bauxite profiles with deeper roots following conduits past the caprock (hard bauxite layer) into the clay rich pallid zone. They found large roots restricted to the conduits within the pallid zone and only fine roots (< 1 mm radius) penetrating into the clay matrix. They described common penetration of roots to the perched water table at 15 m but also found an unusual deep root at 40 m. However, the maximum intensity of rooting is confined to the top 1 m of the profiles.

Although the above information and that shown in Figure 11 may suggest that rooting depths of > 10 m are possible but not common, the reports used to synthesize the data may be biased towards the shallower rooting depths because of limited studies on deep rooting density and depth. The biggest impediment to constructing an objective analysis of rooting depths and their functions is the reliance on rudimentary techniques such as trenches, mine and road cuts to study rooting depth, root density and efficiency of deeper root nutrient uptake (Canadell *et al.* 1996; Stone and Kalisz 1991). New techniques such as root DNA sequencing to determine species of dependant root depths show promise to estimate rooting depths, but still are in their infancy (Jackson *et al.* 1999). All these factors regarding root depth suggest that roots, especially those in water and nutrient stressed environments, do penetrate deeper into the regolith, with common depths of most sinker roots being dependant on the depth of perched or permanent water tables.

The main impediments to terrestrial rooting depth are (Stone and Kalisz 1991)

- presence of hard soil layers or “pans”
- soil bulk density or hard rock
- permanent waterlogging
- chemical toxicity such as high bioavailable Al.

Most of the above are not always impediments, with the survey finding that in some cases roots exploited weaknesses in the “pans” and penetrated deeper. The above factors need to be objectively assessed in estimating regular rooting depths within a region across landforms.

4.3.5 Discussion of Vegetation Transfer

The role of vegetation as a pathway for upward metal transfer and recycling of metals has been appreciated and applied by exploration geochemists via biogeochemical sampling. Most of the micro nutrients will be continuously cycled in the soil, but stable isotopic data combined with trace metal uptake has demonstrated the capability of native tolerant species to tap the groundwater via sinker roots and over time to potentially transfer the deeper mineralization expression to the surface.

Besides accessing a great portion of the soil substrate for metals, plants do overcome some limitations of purely inorganic forms of metal transfer. Firstly, as demonstrated by the deuterium isotopic studies, plants are able to provide conduits to transfer water and metals from the water table and capillary fringe through unsaturated regolith to the soil and soil surface. Secondly, the rate at which plants transfer metals is much faster as compared to say diffusion within an electrical field. Smee (2003) calculated that amongst the cations, H^+ has the fastest diffusion rate through a saturated clay and may be centimeters per day at the most. In comparison, studies on the hydraulic lift mechanism in different climates demonstrate the upward movement of water over 1 m per day! Thirdly, employing active nutrient acquisition methods such as root exudates and rhizosphere microbial symbiosis, plants via their roots can solubilize and uptake tightly “bound” metals from insoluble regolith minerals (Fe-Mn oxides and hydroxides, clay layer silicates) that would otherwise be difficult to move on a purely inorganic basis. Fourthly, downward movement of material via infiltration does not necessarily impede upward ionic transfer via plants.

Plants, however, have their limitations and difficulties as predictive upward conveyors of metals, which arise mainly due to our poor understanding of plant functions within an ecological system, and are related to rate of metal transfer, the species density, its rooting depth and seasonal trends of metal uptake. The rate of metal transfer from the deeper subsurface to the soil is important and depends on the species, its density and soil processes. If the rate is too slow and the species density is low, then the metal transferred may not be expressed in the soil with sufficient contrast and uniformity. This factor may be relevant in vegetation ecosystems dominated by open woodlands, shrublands and grassland, where plant densities are low, and transfer rates via litter can correspondingly be slow. Cohen *et al.* (1998) in a comparative study of vegetation, soil and selective extractions to locate buried mineralization found that plant assisted metal transfer to soil was not adequately expressed in the soil, suggesting that plant based transfer from deep was not very active. A study by Hill (2005) found prickly wattles and mulgas to clearly express bedrock chemical signatures, but the surficial regolith not to do so, suggesting minimal active transfer of metals from plants to soil.

A larger number of stable isotopic studies of plant and groundwater uptake are required from different environments, especially semi-arid, arid and tropical regions to confirm or define limitations to seasonal metal transfer from subsurface to above ground plant tissues. Temporal water uptake studies need to be combined with multi-element metal content to estimate the cycling of metals on seasonally and on a longer term basis, from which transfer rates for individual metals and plant species can be estimated. For example, seasonal studies show less variation in some toxic metals such as As, and a greater variation in Au. The variability between metals can reflect a number of factors which need study such as better tolerance mechanism for specific toxic metals or a tendency for seasonal uptake of Au. The long debated question of the type of species and the particular tissue (bark, leaves, twigs, litter) that best accumulates metals to uniquely reflect mineralization remains pertinent and has to be addressed via regional and temporal orientation surveys. For example, Anand and Cornelius (2004) in a study of metal content of different tissues of plants found geochemistry of litter to provide the best expression of buried mineralization, and suggested that nutrient withdrawals or macro nutrient depletions as compared to trace elements within the leaves prior to fall was the reason. In terms of metal transfer through deep cover, it is important differentiate between species capable of rooting deep and transferring metals to the surface from deeper sources (reflect true anomalies) as compared to species (and their tissues) capable of storing the highest metal concentration but unable to tap a deeper nutrient source i.e. do not reflect the deeper mineralization.

The critical parameter that needs to be established for plant species so they can be predictively employed is the estimation of their rooting depth within a landform linked to groundwater depth. Despite the global surveys on rooting depths, our understanding of rooting depths of native species within prospective regions remains poor and needs further documentation. Furthermore, hydraulic redistribution of water, although promising, requires testing for the movement of metals with the water from depth to soil. If the metals are indeed transferred via passive water uptake through the laterals to the soil, is this rate on a yearly basis sufficient to express an anomaly within the soil over time?

Several biogeochemical surveys over mineralization, mostly in residual regolith settings, have shown the potential of native vegetation in carrying an ore signature, but there are only few reports where phreatophytes genuinely reflect the subsurface groundwater contamination or ore anomaly occurring at depth in their above ground tissues. Preliminary data from a study of native phreatophytes plants to adapt to contamination in arid environments shows promise. McKeon *et al* (2006) studied the uptake by native phreatophyte shrubs of nitrate released into the groundwater from a uranium mill site into groundwater. Using stable isotopic signatures and nitrate levels of leafs, McKeon et al (2006) found the native species to uptake nitrate from the groundwater at a depth of 10 m, with the nitrate content of leaf tissues being five times higher for plants growing over the plume as compared to those away from the plume. Recent biogeochemical studies in Australia, employing different plant tissues as sample media, demonstrate metal contents of particular plant tissues reflected mineralization buried under 5-20 m of transported regolith (Anand and Cornelius 2004). Detailed temporal geochemical surveys of river red gums have found the trace metal content of this species (has extensive tap and lateral root system) to be a suitable indicator of buried mineralization (Hulme and Hill 2005).

The role of vegetation, commencing with the roots and root hairs, metal bio-transformation and rate of metal transfer needs to be rigorously assessed, at least in areas where < 15-20 m of transported cover is present and where roots are likely to penetrate to the current groundwater or past water table limits.

4.4 Bioturbation

Bioturbation is the *biomechanical* process arising due to animal burrowing and plant uprooting that collectively moves material from the subsurface to the surface and vice-versa, and mixes the material in the entire or part of the soil resulting in the formation of the biomantle. The physical movement of material can transfer attached metals from the deeper subsurface to surface or near surface through the transported overburden and result in metal transfer over time. Bioturbation by soil mesofauna, especially termites, has been proposed as a method to transfer metals from the subsurface to the surface (Gleeson and Poulin 1989) and assumes importance as a upward metal transfer mechanism especially in tropical and savanna regions of Australia, South Africa, India and South America. Several prospectors in Africa have employed the “termite method” to explore for buried ore and although not explicitly stated, in Australia and South Africa, geochemical analysis of soil particle sizes and lag have been employed successfully to find buried and deeply weathered ore bodies with bioturbation underpinning the transfer mechanism. If prairie dogs and pocket gophers are keen to burrow through a meter of natural barrier to get to buried nuclear waste and bring radioactive material to the surface (Bowerman and Redente 1998), then bioturbation has something going for it!

Bioturbation is central to the formation and evolution of the biomantle and together with removal of fines downwards and laterally (sheet wash) is largely responsible for a number of soil characteristics such the formation of stone-lines and texture contrasts (Johnson *et al.* 2004; Johnson *et al.* 1990; Paton *et al.* 1995a). The main bioturbators and their functions are

- Invertebrates, mainly earthworms, ants, termites, and to a lesser extent cicadias, beetles, wasps, spiders and crickets. Earthworms consume soil, alter its particle size during digestion, and leave an organic rich, but often a nutrient poor cast (faces). These casts generally reduce soil decomposition rates. Ants are social insects, existing as large colonies that construct massive subsurface burrow networks. Similar to ants, termites construct huge subsurface galleries as well as large above ground towers.
- Vertebrates, such as birds and mammals. Mammals role in bioturbation can be classified according to those that disturb the soil via surface feeding (insignificant for soil turnover), those that disturb soil due to feeding and burrowing, and those that disturb soil due to their subterranean habits (search for food and mates). The last category is the most influential in deeper bioturbation and examples are wombats, gophers, mole and sand rats.
- Plants, due to their intrusion into the soil and deeper regolith via roots, and subsequent fall. An uprooted, fallen tree exposes the roots and the attached soil and an adjacent pit. With plant and root decay, the attached soil on the roots is released that gradually forms a mound on the surface. Sometimes, the slab of material attached to the root is detached on tree fall, rather than being gradually released.

The subsurface material excavated and uplifted on the surface is manifested as mounds or towers, and over time the mounds are subjected to the combined surficial processes of rainfall induced sheet wash and wind erosion during drier periods, resulting in the distribution of subsurface material on the surface. The entire process of mounding, removal of fines, gradual sinking of heavier gravel sized particles if present, shrink-swell processes and chemical reactions results in biomantle, and anomaly homogenization (Butt 1992). On the basis of accomplishing upward material transfer and soil mixing to homogenize anomalies, the bioturbators can be classified according to bioturbation process styles proposed by Johnson *et al.* (2004) (there are more than two but only relevant ones are described) and their processes in terms of metal transfer and anomaly homogenization are illustrated in figure 12:

- **conveyor-belt** organisms, mainly the termites, some ants and other invertebrates, responsible for accomplishing upward biotransfers of material from the biomantle and deeper, into the near surface biomantle and on the surface
- **mixmaster** species, comprise the moles, pocket gophers, wombats and other invertebrates, responsible for soil biomixing dominantly within the biomantle.

Factors critical to the role of bioturbation as vectors for upward metal transfer are:

- The rate and amount of material mixing via the mixmaster species, which will dictate the rate at which metals translocate upward and become homogenized so that the anomaly is uniformly representative on the surface. This has implications for other mechanisms because metals transferred via other mechanisms will also experience homogenization via bioturbation.

- The depth of burrowing activity of the conveyor-belt species, which defines the depth from which metals can be acquired
- Possible metal biotransformations that occur due to material transfer via the insects.

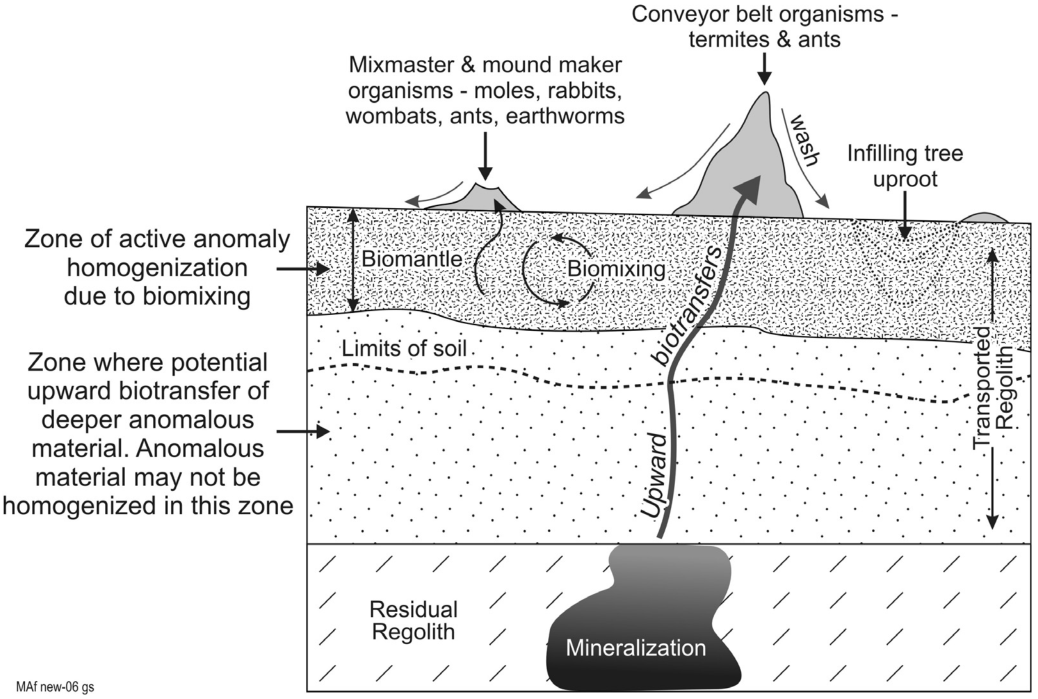


Figure 12. Different forms of bioturbation, their respective depth extents and role in anomalous material transfer from depth and material homogenization (modified after Johnson et al 2004).

4.4.1 Rate of Bioturbation and Homogenization

The rate of biologically induced material turnover or mixing is dependant on the species and density of the burrowing organisms, burrow depths, the nature of substrate, and the climatic environment. The contribution to bioturbation of the different groups of bioturbators varies across climate and landscapes (Paton *et al.* 1995b). In terms of rate of mounding, earthworms are the main bioturbators active in most climatic zones, but casting activity of earthworms is greatest in the wetter regions and reduced or negligible in dry regions. The influence of earthworms on bioturbation, however, is largely restricted to the topsoil or within 30 cm of the surface. In Australia, South America, Africa and India, ants and termites are the most widespread and active bioturbators responsible for biotransfers. Ants are active in nearly every climatic region. Termites in comparison in appear significant in tropical, sub-tropical and semi-arid regions.

Soil turnover or mixing by the mixmaster organisms can be considered as a guide to homogenizing part of the soil profile. Soil turnover is estimated by longevity of the nest structure and volume of soil hosted in the nest (Lobry de Bruyn and Conacher 1990). A review of near surface regolith turnover rates by ants and termites in a semi-arid region of Australia revealed that both the ants and termites turned over a similar magnitude of soil, but termite mounds hosted a larger soil mass than ants (Lobry de Bruyn and Conacher 1990). The longevity of ant and termite mounds at the surface is not well documented but varies between a few weeks (ants) to tens of years. At any one stage, the earthworm, ant, fossorial mammals and termite mounds may occupy only a fraction of the ground surface, but over millennia, their mounding activities tend to migrate across the particular landform and possibly across the entire landsurface, thereby homogenizing the biomantle. Ants rapidly turn over near surface material, with estimates of formation of a top 20 cm soil layer across a landform within 200 years. Studies of bioturbation activity of ants in semi-arid Australia have estimated the movement of total volume of topsoil across the landscape within 100-200 years (Eldridge and Pickard 1994; Lobry de Bruyn and Conacher 1994). Other studies have found similar time frames on top soil turnover by bioturbators, with estimates of a 20 cm thick A horizon being accumulated by erosion of termite mounds over 1000 years in North Queensland (Holt *et al.* 1980).

The surface expression of mounds may represent only a small part of an extensive underground gallery system that samples a larger subsoil area and facilitates rapid soil homogenization. Subsurface or subterranean galleries originating from the mound and traveling laterally and vertically are known to cover a larger subsurface area with some studies indicating gallery lengths up to 50 m from the mound (Lobry de Bruyn and Conacher 1990). Some subterranean termite species have construct galleries extending laterally 30 m from the central nest (Lee and Wood 1971).

Linked to the rate of bioturbation, is the rate at which a newly deposited sediment cover can be colonized and bioturbated by organisms. Studies on biointrusion of artificially constructed landscapes and waste barriers supply interesting information on depth and rate of bioturbation of freshly laid sediment. Biointrusion of various forms of barriers constructed over hazardous wastes indicate rapid bioturbation activity through the barriers, irrespective of the presence of hazardous waste composition (Bowerman and Redente 1998; Smallwood *et al.* 1998). Studies of disruption of the constructed soil barriers found the maximum effects of bioturbators was indirect through their alteration of soil bulk density and creation of an abundance of macropores that increased water access to the subsurface. Smallwood *et al.* (1998) found pocket gophers, harvester ants and other burrowing animals had burrowed up to a depth of 1 m within a decade into all the soil barriers constructed over waste repositories. Several experiments investigating ant penetration into barriers found ants tunneled to a depth of 1.8 m in 2 years, and in some other sites ants had penetrated to a depth of 2.4 m over longer periods. At the Hanford 300 site in the US, presumably in less than 30 years, ants had constructed tunnels to different depths, some as much as 2.4 m, with movement of soil of approximately 151 kg yr^{-1} and a volume of 0.13 m^3 yr^{-1} to the surface (Bowerman and Redente 1998). Harvester ants have been documented to burrow down to 1- 4 m depths, sometimes through gravel barriers, to hazardous waste and incorporate U and Cs into their mounds (Bowerman and Redente 1998). Studies on rehabilitation of bauxite mines in Brazil and Australia suggest the recolinization of disturbed land by ants progressed rapidly when native flora regrowths were present, with slower rates prevailing in drier climatic settings and also when no vegetation was present (Majer 1996).

The above examples of rates of bioturbation of freshly deposited sediment and artificial barriers demonstrate that mesofauna, and possibly vegetation, can rapidly transfer material upwards, but the material transferred to the surface is spatially restricted to a small area, and therefore extremely heterogeneous. It is only with time that subsurface material can be homogenized at the surface via bioturbation. The rate of homogenization can vary across regions depending on landscape, soil and climatic conditions.

4.4.2 Depth of bioturbation

The depth and rate of burrowing activity of the main conveyor-belt species - ant and termites- appears to be related to moisture regime, possibly climate and the species. The precise and predictive depths of penetration of conveyor-belt species in different landform and climatic settings are less clear, largely for the same reason as those stated for rooting depth: methods of studying the depth of ant and termite nests still rely on rudimentary techniques, mainly excavating a pit. In general, biomantle depths are greater in humid, pre-humid tropical and sub-tropical regions as compared to mid-latitudes (Johnson *et al.* 2004) but the depths can change across landforms, substrates and local moisture regimes.

Ants and termites are known to excavate and construct their galleries deep into the regolith, but such reports are limited. The main reason for termites to construct deep subterranean galleries is their search for a moisture source because most species require a high maintenance of humidity in their nests (Lee and Wood 1971). The source of nutrients, however, is closer to the surface and therefore in appropriate moisture environments, most nests and subterranean galleries are close to the surface. Therefore, in drier environments or where water sources are deeper (water table), especially during drought periods, deeper excavations by termites and ants are likely and predictable. Lepage *et al.* (1974) document a case of termites in Africa burrowing down to depths of 45 m during a period of drought.

There are several reports documenting great depths of termite galleries, especially in search of water, and some are reported in Table 5. Many of the deeper reports of termite galleries appear to be from environments mostly in Africa, often sand dominated settings. A statistically robust method to evaluate ant and termite depth was considered by Jensen & Hooten (2000) where the depth to which a percentage of ant and termite species burrow was reported. Jensen & Hooten (2000) in their review of burrowing depths of ants in a semi-arid environment found that most ant species would burrow to less than 1 m, but some species may burrow to a maximum of 5 m. A similar review of termites found 90% probability of termites burrowing to less than 1 m and 99% to < 5 m (Myles and Hooten 2000). However, their analysis was restricted to specific dry North American locations, and deeper depths may be reached in other regions.

Table 6. Extreme bioturbation depths recorded in specific countries.

Depth (m)	**Region**	**Reference**
70	Kalahari, Africa	Lock (1985)
70	Africa	Yakushev in Lee & Wood (1971)
45	Sahel	Lepage *et al.* (1974)
24	Zimbabwe	West in Gleeson & Poulin (1989)
10-15	Africa	Ghilarov in Lee & Wood (1971)
6	SE Australia	Davison in Lobry de Bruyn & Conacher (1990)

4.4.3 Metal transfer and availability

Transfer of material from deeper subsurface to near surface and surface is largely a mechanical process without any specific geochemical consideration, but some size sorting during upward transfer may be possible. Some burrowing organisms show selectivity to a specific particle size in the material transported to the surface. Some species of termites display a tendency to accumulate clay sized material (Lee and Wood, 1971). However, Lobry de Bruyn & Conacher (1990) in their review found that data on particle sorting by ants and termites during burrowing was contradictory with some cases showing particle sorting during excavation and others not. Jouquet *et al*. (2002) in a study of termite mounds in West Africa, found the termites use soil particle sizes selectively but suggested that size selectivity occurred in response to different ecological, physiological and behavioural needs of the termites. Therefore, grain size selectivity in biotransfers into and on the surface of the biomantle from depth varies and the impact on selective metal transfer may need to be evaluated for individual areas.

The passage of material through the mounds can be impacted by the metabolic activities of the mesofauna and therefore potentially affect metal mobility. For example, termites and ants are known to redistribute organic matter and affect and carbon/nitrogen ratio of soils. Lobry de Bruyn & Conacher (1990) in their review effects of termites and ants found that soil material affected by ant activity had increased levels of exchangeable cations as compared to the adjoining soils. Whether the increase of major exchangeable cations (Ca, Na, Mg) are also expressed by the trace ore related metals has not been documented.

There are reports of termite or ant burrowing activity resulting in a surface expression of buried mineralization. Lock (1985) advocated the transfer of diamond indicator minerals to the surface via termite activity in the Kalahari. Gleeson & Poulin (1989) found the termitaria (towers) to show a greater Au contrast than the adjacent soils in areas with thick soil cover. In areas of transported cover, results indicate similar dispersion patterns between termite mounds and adjacent soils (review by Butt 1992). The similarity in dispersion patterns is attributed to the erosion of mounds on abandonment resulting in distribution of particles and assimilation into the surrounding soils. Subsequently, any enrichment in mounds related to mineralization is passed on to the soil (Butt 1992). Bioturbation is considered one of the main process in bringing up ferruginous lags to the surface, and lag geochemistry has been successfully applied in geochemical exploration in the Yilgarn (Robertson 1996).

4.4.4 Discussion of Bioturbation

Bioturbation is largely a bio-physical material transfer and mixing process, which can result in the transfer of metals from the subsurface to the surface and within the biomantle. The established and predictive long term role of bioturbation is in facilitating homogenization via bio-mixing within the biomantle of metals brought up to the surface by any transfer mechanism. The rate of anomaly homogenization varies according to climate and bioturbation species, and can vary from a few hundred to over a thousand years. The biomantle depths vary, but are largely restricted to the top 1-2 m, with possible greater depths in restricted regions and landforms.

The value of bioturbation as a mechanism to accomplish biotransfer of metals from depths **beyond** the biomantle appears less predictive, because of the scarcity of data on deep burrowing activities of the conveyor-belt organism’s depths in different settings. Within a particular landform, only a few ant and termites burrows may penetrate to great depths beyond the biomantle. But considering the amount of material transferred to the surface and within the biomantle, a few deep burrows could be sufficient to carry adequate anomalous material into the biomantle for the anomaly to be subsequently expressed in the soil. However, prediction of depths of burrowing, especially to >2 m depths, remains difficult, and only water or moisture source appears a valuable guide to deep burrows. Deep galleries are mostly reported from where water sources are at great depth, but the reports are few and require confirmation from diverse environments.

Therefore, although bioturbation, via its influence on soil mixing processes, operates and influences the rate of anomaly homogenization widely, its role to transfer metals from deep subsurface needs to be properly assessed. There remains a gap in our understanding of the depth to which conveyor-belt organisms regularly or randomly burrow across different landforms and climatic regions. Furthermore, there is a lack of data on how the subsurface regolith properties, such as presence of variety of cretes (ferricretes, silcretes) within the profile, affect the depth of termite burrow penetration. This lack of data needs to be addressed so the potential or the limitation of bioturbation can be critically assessed as a metal transfer mechanism.

5 Microbes

Microbes (*Bacteria, Archaea* - and some Eucaryotes such as fungi and algae) are ubiquitous in the regolith and are now considered to influence, and sometimes directly control, biogeochemical cycle of most elements, with their influence established to exceed 2 km into the crust (Newman and Banfield 2002). Microbes have as yet not been advanced as sole mechanisms without the aid of another medium such as water, air (bubbles), plants in transferring metals upwards through barren cover. For example, there are no studies demonstrating or advocating the upward migration of gold laden microbes through sediment purely on a basis of these organisms accomplishing their metabolic functions - yet! Microbes, however, by virtue of accomplishing their metabolic activities in different environments at a variety of scales, exert positive and negative influence over the rate and efficiency of most metal transfer mechanisms, and therefore their role in influencing the effectiveness of each mechanism need to be evaluated and appreciated. Interestingly, they have not escaped exploration geochemists attention, but are largely referenced to account for data not easily explained by purely inorganic mechanisms!

The influence of microbes on metal mobility and upward transfer via other mechanisms within the regolith environment can be grouped into three categories:

- The uptake of metals with intracellular or extracellular precipitation of the metals and minerals - biomineralization (e.g. immobilization of Au)
- Aiding the dissolution of minerals increasing the rate of metal release and solubilization of specific metals (e.g. weathering of sulphides and oxidation of Fe and S).
- Biomethylation (and demethylation) of specific metals and nonmetals, thereby affecting the metals mobility and species (aqueous, solid and gas).

All the above reactions are mostly underpinned by the ability of microbes to accomplish redox reactions as part of their cellular functions. The dominant positive and negative effects of microbial induced metal transformations on the different transfer mechanisms are highlighted in Table 6 and illustrated in Figure 13, and their influence on reactions with examples relevant to metal transfer are described below.

5.1 Metal immobilization – biomineralization

Microbes assist in the precipitation of minerals - oxides, hydroxides, sulphates and metals – within the entire unsaturated and saturated regolith (Konhauser 1998) and thereby influence the mobility of specific metals during their upward transfer process. Biomineralization regulated by internal cellular mechanisms is referred to as “biologically controlled mineralization” (e.g. magnetotactic bacteria). The more dominant and diverse form of mineralization is external to the cell surface, resulting in formation of minerals due to the by-product of organism-surrounding environment or “biologically induced mineralization”. The microscopic size of bacteria, entails them with a high surface area to volume ratio, which together with the anionic surface charge on cell walls, enables bacteria to adsorb and accumulate a variety of metals from surrounding solutions (Beveridge 1989; Konhauser 1998). The nature and strength of immobilization of metals on cell surfaces is variable; some are tightly bound and accumulate to form nano-particles of minerals, while some are easily exchanged with the surrounding environment.

In addition to metal immobilization via intracellular-extracellular activity, microbes, especially in the deeper subsurface, regulate metal mobilization and immobilization via redox reactions coupled to the dominant energy source. These redox reactions exert a strong influence over the surrounding geochemical conditions and metal mobility. The metabolic activity of microbes involves a complex series of electron transfer reactions within the microorganism. The final electron transfer occurs from the cell surface of the microbe to an electron acceptor in the surrounding environment and is referred to a terminal electron accepting process (TEAP). There are several terminal electron acceptors in the regolith environment and the associated processes of these acceptors are: oxygen reduction (aerobic respiration), nitrate reduction, Mn(IV) and Fe(III) reduction, sulfate reduction, and CO_2 (Lovely and Chapelle 1995). The process of aerobic respiration, where microbes derive energy from the oxidation of organic matter coupled to the reduction of O_2 to release CO_2, is the most common microbial process. This process accounts for the generation of CO_2 in the soil, and can complicate, if not overwhelm the CO_2 signal arising from the weathering of ore body. In dissimilatory Fe(III)/Mn(IV) reduction, electrons are transferred to Fe(III) thereby reducing it. This reaction is catalyzed by microorganisms that couple the oxidation of organic compounds and/or H_2 to the reduction of Fe(III). The influence of this reduction reaction on metal mobility is described later. During sulphate reduction, sulphate is used as the electron acceptor to oxidize organic compounds, resulting in the formation of sulphides. The conversion of specific organic matter to CO_2 and methane (CH_4) is accomplished by methane producing microorganisms and proton reducing acetogenic bacteria. However, methane is strictly an anerobic activity. The general sequence of consumption of electron acceptors follows the trend of oxygen, nitrate, Fe(III), sulphate and methanogenic.

From a viewpoint of metal transfer where the metal mobilization, transfer and immobilization is important for spatial distribution of metals, the role of microbes in gold and some pathfinder elements serves as examples. Savvaidis *et al.* (1998) and Reith (2003) provide good reviews for gold-microbe interactions. Invitro studies on Au microbial interactions have demonstrated the capacity of a common soil bacteria, *Bacillus subtilis,* to take up mobile dissolved Au(III) ions and transform them into colloidal gold particles. Subsequent autolysis solubilized and reprecipitated the gold extracellularly as 20 µm, crystalline, pseudo-trigonal –octahedral gold crystals (Southam and Beveridge 1994). Other studies have demonstrated the ability of antinomycetes (filamentous or rod shaped bacteria) to precipitate gold nanocrystals, 5-15 nm in diameter on and within the cell walls without harming the bacteria (Ahmad *et al.* 2003). Numerous other studies have shown the ability of bacteria, algae and fungi to absorb gold (Savvaidis *et al.* 1998). The precise mechanism of gold uptake, reduction and precipitation remains unclear, but reactions on the plasma membrane are considered important in the ability of the microbe to bind gold.

Another pathway by which the microbes can affect metal mobility is shown by dissimilatory Fe(III) reducing microorganisms (sometimes referred to as Dissimilatory Iron Reducing Bacteria -DIRB) that reduce metals and metalloids, thereby affecting the mobility of redox trace metals. These bacteria are able to use O_2 or H_2 as the electron donors to reduce variety of metals from their mobile to immobile forms (Lloyd 2003; Lovely and Anderson 2000) and affect the mobility of several metals. Microbial reduction of redox sensitive metals pertinent to exploration, such as Au(III) to Au(0), As(V) to As(III), Se(VI) to Se(IV) have been demonstrated (Lloyd 2003), which suggests the microbial influence on metal mobility may be critical.

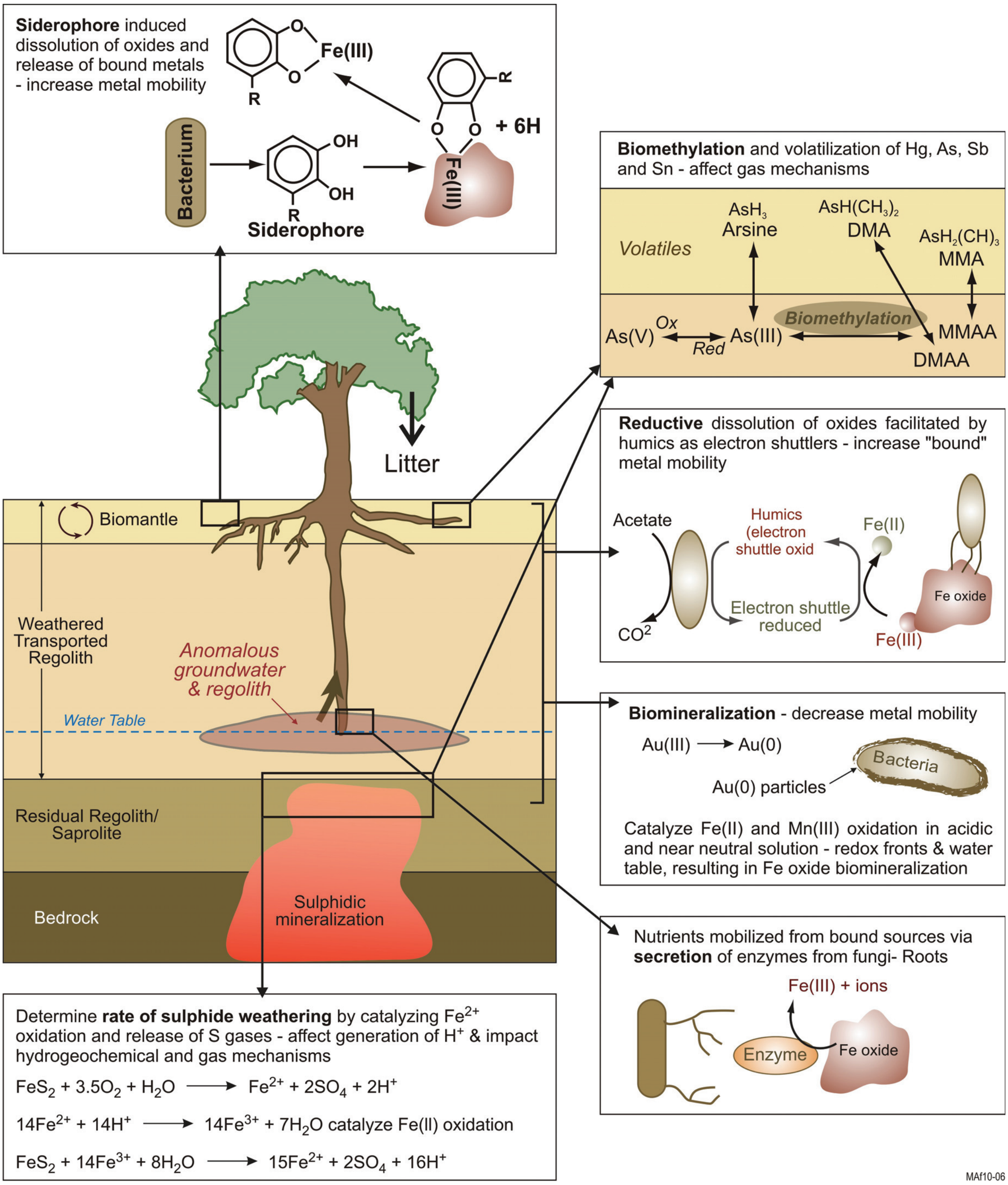


Figure 13. The various processes by microbes can affect metal mobility and migration efficiency across the entire regolith.

Microbial metabolism can potentially control metal mobility, but the reverse is also true: presence of high concentrations of specific metals can also influence the microbial community structure and activity. Some microbial species and community structures can potentially be linked to, and therefore indicative of “anomalous” levels of specific metals, and could possibly in future be a fingerprint to specific levels of metals. New genomic techniques such as total phospholipid fatty acid (PLAF) and terminal restriction fragment length polymorphism (t-RFLP) enable the assessment of microbial community structure in the regolith. Several studies on the effects of microbial community on application of toxic metals such as Cu, Zn, As and Ni have found long term changes to the soil microbial community structure (Giller *et al.* 1998), with variable reduction in microbial community and a gradual adaptation to the toxic metals (Turpeinen *et al.* 2004).

5.2 Mineral Dissolution

Microbes via their metabolic activities, directly and indirectly, affect the rate of metal complexation and dissolution rate of minerals. In view of the vastness of the subject of microbial induced dissolution, only the main mineral dissolution reactions relevant to metal transfer mechanisms and the effectiveness of different surface geochemical techniques are summarized.

The nature and rate of sulphide weathering within the ore body underpins several phreatic zone and gas based mechanisms. The role of microorganisms, especially the chemoautotrophs that acquire their energy from inorganic molecules, in catalyzing sulphide mineral oxidation and weathering, and thereby affecting the rate of cation and possibly gas release and transfer is rarely considered in the electrogeochemical models. The role of microbes in consuming O_2 via organic matter reduction, and thereby driving the expansion of “reduced columns” has been alluded to in the redox models, but the capacity of different microbes to catalyze the dissolution of sulphides, oxidize the released Fe^{2+} and/or oxidize sulphur or even reduce Fe^{3+} within saturated environments is less appreciated and studied.

The rate of oxidation and dissolution of sulphides is dependant on the availability of oxidants at the weathering front or the sulphide mineral surface. The common oxidants available around sulphide ore bodies are Fe^{3+} and O_2, but oxygen is considered to be a less effective oxidant than ferric iron. The main pathway for sulphide dissolution incorporates ferrous iron oxidation via oxygen according the reaction

$$14Fe^{2+} + 3.5O_2 + 14H^+ \rightarrow 14Fe^{3+} + 7H_2O$$

which is followed by reduction of ferric iron by sulfide

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Resulting in a overall reaction of sulphide dissolution of

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

For the above reactions, the rate limiting step is considered to be the ferrous iron oxidation by oxygen, which is slow at low pH (Nordstrom and Southam 1997). However, specific microorganisms that enzymatically oxidize iron and thereby increase the amount of $Fe^{3+}$to attack the sulphide surface will increase sulphide mineral dissolution kinetics (Nordstrom and Southam 1997). The mechanism of sulphide dissolution via enzymatic oxidation on the sulphide surface with direct microbial contact is still debated, but results do indicate preferential colonization of sulphides by specific microbes rather than other minerals (Baker and Banfield 2003).

The contribution of iron oxidizing bacteria and archea to the amount and rate of sulphide oxidation as compared to purely inorganic sulphide oxidation is important to assess the role of microbial diversity and activity on sulphide oxidation. Numerous studies have shown an increase in sulphide oxidation and dissolution rate in the presence of microorganisms. This increase in sulphide dissolution rates stems from the indirect pathway of microbes catalyzing iron and sulphide oxidation rather than dissolving minerals via surface contact. Studies in natural environments indicate microbial induced rate for Fe (II) released from sulphide weathering accounting for 75% of the total Fe(II) release (Edwards *et al.* 2000). The environmental variables, especially the number and level of activity of iron oxidizing cells is considered to determine the rate at which microorganisms enhance sulphide dissolution (Baker and Banfield 2003). Recent studies on the diversity of microbial communities within acid waters arising from sulphide mineral oxidation but removed from sunlight (chemoautotrophs) indicate a limited number of species of bacteria and archea flourished in the extreme conditions because of the restricted energy sources available in acid drainages (Baker and Banfield 2003). A variety of microbial niches are established around oxidizing sulphides depending on the evolution of physical and chemical regimes, such temperature, pH and ionic strength gradients. Specific microbial communities dominated in specific geochemical conditions surrounding sulphide dissolution that are favourable to mesophiles, such as *A. ferrooxidans* dominate in environments having > 1.3 pH and temperatures < 30 ^{0}C. Fluctuations in microbial community occurred according to rainfall, ionic strength and temperature, with cell populations being highest during summer months (Edwards *et al.* 2000). The diversity of organisms and their niches in the subsurface evolved to control the flow of iron, sulfur, nitrogen, carbon and energy according to temperature and pH regimes. However, the studies to date are from subsurface exposed mine environments, and the role played by microbial communities in weathering of sulphide ore bodies below transported regolith may be different. The contribution of microbes to increase the rate of sulphide dissolution and impact on the geochemical parameters such as pH and Eh could also directly influence other metal transfer mechanisms such as sulphur and CO_2 gas generation, metal hydride formation, electrogeochemical or redox gradient generation.

Another important pathway by which microbes enhance metal release and mobility in the regolith is via **reductive dissolution** of insoluble Fe(III) and Mn(IV) oxides and hydroxides, both of which are mineral groups established as excellent incorporators and adsorbers of metals, and oxide and hydroxide minerals groups are primary dissolution target for many surface geochemical techniques (Table 1). The reductive dissolution of insoluble oxides can be facilitated in both aerobic and anaerobic environments within the regolith, but the extent of reductive dissolution is still poorly understood. In aerobic environments, facultative microorganisms (bacteria and fungi) secrete a high Fe(III) specific bidentate ligand known as **siderophore**. The secretion of siderophores from the microbial cells is regulated by the microorganisms according to iron availability in the surrounding environment. The major siderophore compounds are hydroxamates or phenolates- catecholates. Both these compounds form high stability constant complexes with Fe^{3+} ions as compared to other low molecular weight chelators (Kalinowski *et al.* 2000). Furthermore, in the natural environment, siderophores are stable over a wider pH range than low molecular weight acids, especially at neutral pH. The microorganism takes up the siderophore-Fe(III) complexes into the cell envelope where the Fe(III) is reduced and released from the siderophore. The dissolution process is suggested to proceed via surface complexation and ligand exchange (similar to that used for selective dissolution of iron oxides!), with the coordination of the siderophore to an Fe(III) center at the mineral surface (Kalinowski *et al.* 2000). Some experiments show a significant enhancement of siderophore (desferrioxamine B, a common trihydroxamate siderophore) promoted dissolution of insoluble Fe and Al oxides and oxyhydroxides as compared aliphatic acids (root exudates) (Watteau and Berthelin 1994), while other batch reaction studies suggest the two-ligand system presented by siderophores and oxalic acids, both of which are organic molecules are likely to be present in soils, to be an effective mechanism for microbial induced Fe(III) oxide reduction (Cheah *et al.* 2003) (herein lies an opportunity to develop a new “enhanced” LEME leach or “E” leach!!).

The other mode of reductive dissolution arises in anaerobic environments where **dissimilatory** Fe(III) and Mn(IV) reducing microorganisms oxidize complex assemblages of organic matter (fatty acids, aromatic compounds) to CO_2 using Fe(III) as an electron acceptor, thereby enzymatically achieving Fe(III) reduction (Lovely 1997). Enzymatically driven reduction of Fe(III) oxides can occur via direct contact of the microorganisms with the oxide surface, or via Fe(III) chelators and electron shuttling humic substances that transfer Fe(III) or electrons from the oxide surface to cell surface (Lloyd 2003; Lovely 1997). Recent studies using the dominant Fe(III)/Mn(IV) reducing organism – *Geobacter* - have shown the employment of novel physiological adaptations by the species in facilitating the reduction of the insoluble Fe(III) oxides. *Geobacter* produce pili and flagella only when insoluble Fe(III) oxides are present, and not when soluble Fe(III) is available. Further, the pili act as nanowires enabling attachment to the oxide surface and facilitating electron transfer from the cell surface (Reguera *et al.* 2005) to the Fe(III) oxide surface and thereby eliminating the need for organic “electron shuttles”.

This mechanism is applicable in anaerobic and moderate to high organic matter environments, and possibly can operate in soil microenvironments that are periodically subjected to anaerobic conditions. The dissimilatory bacteria by achieving reduction and dissolution of insoluble oxides, facilitate the release of tightly bound metals from the oxide surfaces. Studies using dissimilatory reducing bacteria have shown arsenic adsorbed onto ferric hydroxides was released as As(V) when dissimilatory iron reducing microbes dissolved the ferric hydroxides even though arsenic was not reduced to As(III) (Cummings *et al.* 1999). In another study, Zachara *et al.* (2001) found the net increase in solution concentration of Co and Ni that were associated with metal substituted goethite, when Fe(III) reducing bacteria dissolved the goethite. Similar to pH, the role of reductive dissolution of Fe-oxides in soil environment and its contribution to the "mobile" or "labile" fraction of metals is unclear.

5.3 Biomethylation and demethylation

Microbial metabolism within soil (possibly in deeper zones provided organic matter is present) in anaerobic and aerobic macro and microsites can facilitate methylation of specific metals and metalloids, thereby effecting metal transformations, and importantly, generating metallic volatiles. Biomethylation is the process where organisms combine the methyl group (CH_3) to a metal or metalloid, thus giving rise to metal-carbon bonds (Craig *et al.* 2003). Since the identification of biomethylation of mercury to form the neurotoxin methylmercury, the role of biomethylation of other redox sensitive metalloids has increased, with methylated volatile compounds of Co, As, Se, Sb, Te, I and Pb being documented in natural settings and laboratory settings using selected microorganisms. Many of the volatile methylated metalloids have been measured in natural and anthropogenic locations such as sewage plants, geothermal environments, swamps, metal contaminated and landfill sites, but their presence and extent in uncontaminated environments and around weathering ore bodies needs to be established.

The main requirements for methylation are i) presence of the metal or metalloid, ii) availability of methyl donors or agents in the regolith and iii) suitable microorganisms to generate the methylated compounds (Hirner *et al.* 1998). In presence of metalloids, the three major coenzymes (organic molecules) capable of accomplishing the reaction are (Ridley *et al.* 1977): *S*-adenosylmethionine (known as SAM), *N*-methyltetrhydrofolate derivatives and methylcobalamine (vitamin B_{12} derivative). Of these, SAM is recognized as the main methylating agent in natural environments, but methylcobalamine is also pertinent, especially for methylation of mercury. For reactions involving SAM as the donor coenzyme, the methyl group is generally transferred as a radical ($CH_3\cdot$) or as a carbonium ion (CH_3^+) to the atom that must be nucleophile (able to donate electrons). In contrast, for methylcobalamine, methyl group is transferred as a carbonium to the atom that must be an electrophile (able to accept lone pair of electrons). The entire process from inorganic metal to the end biomethylated compound goes through a sequence of reactions with intermediate products.

The methylation of metal and metalloids pertinent to exploration geochemistry and studied include Hg, As, Se, Sn and Bi. **Mercury** is biomethylated in a range of environments, both anaerobic and aerobic, by numerous microorganisms. For mercury biomethylation, methylcobalamin is the methyl donor, and via a sequence of reactions results in the production of monomethymercury and volatile dimethylmercury. **Arsenic** is biomethylated to produce volatiles such as arsine (AsH_3), monomethylarsine (MMA), dimethylarsine (DMA) and trimethylarsine by fungi and bacteria, sometimes under both aerobic and aearobic conditions (Turpeinen *et al.* 2002). Studies on As contaminated areas showed that microbes contributed to the species transformation of As and the production of volatile As species, but the production of methylated volatile As compounds accounted for a very minor part (< 0.5%) of the water soluble As in the soil. The factors considered to affect the production of biomethylated volatiles are likely to be the solubility and bioavailability of As in the regolith (Turpeinen *et al.* 2002). There are some bacteria, fungi and algae that can biomethylate inorganic **antimony** under aerobic and aneorobic conditions to produce volatile methylated antimony compounds especially trimethylantimony. Anitmony present in the substrate in both Sb^{5+} and Sb^{3+} states, was biomethylated aerobically by a fungus *S. brevicaulis* to form volatile trimethylantimony, although the Sb^{3+} state experienced easier volatilization (Jenkins *et al.* 1998). There are numerous bacteria, fungi and algae documented as biomethylaters of inorganic **selenium**, with the main volatile biomethylated compounds produced being dimethyl selenide (DMSe) and dimethyldiselenide (DMDSe) (Chasteen and Bentley 2003). The former (DMSe), due to its high solubility in water, favours the aqueous phase and therefore its production and retention is shown to be higher in wetter soils than in drier soils (Zhang and Frankenberger 1999). Other studies have found that besides organic matter and saturation state of the regolith, regolith properties such as mineralogy and grain size and type of microbes may affect the amount of volatile selenium compounds produced and released to the atmosphere (Guo *et al.* 1999). A wide range of terrestrial bacteria can methylate **iodine** to its volatile form methyl iodide (CH_3I), and the process is likely to occur at oxic-anoxic interfaces, having been documented for rice paddies and swamps (Amachi *et al.* 2001). Recently, **tellurium** was demonstrated to be biomethylated by a facultative anaerobe to volatile dimethyl telluride ($(CH_3)_2Te$) (Basnayake *et al.* 2001).

Biomethylated volatile compounds can also experience demethylation. In demethylation, the volatile compounds are converted back to the inorganic forms. For example, methylmercury is known to undergo demethylation when specific microorganisms can reduce Hg(II) to Hg(0) via mercuric reductase, thereby making elemental mercury less toxic. The extent of demethylation is not well studied.

In summary, biomethylation of several ore related metals such as As, Hg, Se, Sb and I do occur in natural environments in both aerobic and anaerobic conditions, but the amount of metal biomethylated varies from being extremely minor (As) to large (Hg, Se). The volatile biomethylated compounds can rapidly be transferred back to their solid inorganic state. The production and retention of volatile compounds from soil matrix is dependant on the microbial species, bioavailability of the metal in the soil, temperature and water content or moisture of the soils and deeper subsurface. Much of the work on biomethylation of ore related metals has been conducted on lab cultures or estimated in specific environments (sewages, swamps) and there remains a need to assess biomethylation qualitatively and quantitatively at the weathering front and within the soil.

Table 7. Summary of the role of microbes in influencing the effectiveness of particular mechanism.

Hydrochemical (general)
• Limit mobility of metals by intracellular and extracellular mineral precipitation (biomineralization) • Increase the weathering rate (dissolution, complexation) of minerals facilitated by organic secretions (not quantified)
Electrochemical
• Iron and sulphur oxidizing microbes increase the rate of sulphide weathering • Redox (electron transfer). Iron reducing bacteria couple reduction of Fe-Mn oxides to oxidation of redox sensitive metals. Iron oxidizing bacteria increase rate of Fe oxidation and drive the depletion of O_2
Gas
Microbial metabolic respiration generates gases, and biomethylation generates metal volatile species in the soil, and possibly at the ore body weathering front. The gases/volatiles generated by metabolic activities • CO_2 • SO_2 • Dimethyl mercury - $Hg(CH_3)_2$ • MMAA, DMMA, arsine • Dimethyl selenide (DMSe) • Trimethyl antimony $(Me_3)_3$ Sb • Methyl Iodide (CH_3I) • Dimethly telluride $(CH_3)_2Te$
Vegetation
Facilitate possible uptake of ore related metals through roots systems: Mycorrhizea (fungi), excretion of exudates (organic acids) for metal complexation and facilitation of transfer into roots

5.4 Metal Acquisition for Plants

Similar to the regolith, microbes inhabit many parts of the plant, from the roots to the leaves. Their role in the vegetation pumping cycle for metal transfer is confined to facilitating metal uptake by roots. The role of microbes as symbiotic association with roots of most plants is critical to the amount and efficiency of metal uptake by vegetation from the near surface and deeper regolith. Specific fungi have nutritional symbiotic associations with roots known as mycorrhizae, where the hyphae extend from the fungus into the roots. The fungi exploit decomposing organic matter to produce enzymes that enable the mobilization of nutrients, especially P, although Cu and Zn may also be mobilized. The fungi take up the nutrients and transfer them to the plant host and in the bargain receive organic carbon from the plant. The surface area of the root system is improved by mycorrhizae because these fungi penetrate and extend into the soil and thereby significantly increase the surface area for nutrient acquisition. They are particularly suited to the acquisition of relatively immobile elements such P, but also some heavy metals such as Zn and Cu.

6 Other factors - Time, Climate, Nature and Evolution of Transported Cover and Geology

In view of the number of mechanisms, both direct and indirect, that have the potential to transfer metals from buried mineralization through transported cover to the surface, it would appear that metal anomalies at the surface should be a norm even through 30 m of cover. Based on empirical relationships between the detectable responses of ore metals at the surface through 30 m of cover, many exploration geochemists would agree that metal transfer routinely occurs through thick transported cover. Applying the same reasoning, many cases of surface geochemical surveys document no expression of buried ore at the surface, even through thin (~4 m) of cover, especially in Australia. There may be a greater proportion of null results that have not been published or publicized for the very reason – they represent a null result. If metals do migrate to the surface in response to electrical currents generated by ore bodies or as gases or attached to carrier bubbles or via vegetation, then why do we still get null responses? Irrespective of the choice of mechanism(s), there are a number of null and negative case studies, sometimes exceeding positive results, where metals have not made it through transported cover in sufficient quantity to enable unambiguous detection of buried ore via a myriad of surface geochemical methods. It would behoove exploration geochemists to understand the cause of this discrepancy, so surficial geochemical techniques can be effectively applied and limitations of all mechanisms and techniques properly defined.

Figure 1 is one case in the Australian environment that documents both the positive and negatives of transfer mechanisms. Metal anomalies have transferred into highly weathered overlying sediments (cannot be classified as "overburden" because Au content approaches economic grades), but also ore body geochemical signatures are not necessarily expressed through younger ~ 4 m of transported cover to the present surface. This example highlights the very likely culprit – the nature of the transported regolith and its evolution (climate and time) or the regolith-landscape environment. In the profile represented in figure 1, the upper 4 m marked as Quaternary sediments, have subhorizontal laminations and silcrete layers or hardpans, and the uppermost unit is unweathered colluvium deposited as sheet wash. The formation of these cemented materials and unweathered nature of the colluvium are likely factors negating the operation of any mechanism. Therefore, the nature and post-depositional evolution of the transported materials may be crucial to the effectiveness of mechanisms.

The effect of nature of cover and weathering profile have been explained and explored by Butt (2005) in the form of geochemical dispersion models in deeply weathered regions. The model relevant to this discussion are those having an overburden and with a preserved or truncated profile. The presence, nature and post-depositional alteration of the overburden are discussed with respect to dispersion mechanisms.

6.1 Time

It would be difficult to justify classifying time, climate and nature of transported regolith as a mechanism, but they are factors, similar to microorganisms, that strongly influence the effectiveness of most mechanisms. Amongst other weathering agents, **time** influences the evolution of the sedimentary overburden, a process that impacts on all the metal transfer mechanisms, but is rarely considered in evaluating the effectiveness of individual mechanisms. There is a minimal time present between the deposition of the transported regolith and the commencement of operation of most of the documented mechanisms, except possibly rapid diffusive gas transfer. There is a time limit before a groundwater table becomes established within the deposited sediments so groundwater based mechanisms become functional and indirectly affects gas generation from an oxidizing ore body. There is a minimal time before vegetation can colonize the sediment to commence physiological metal uptake and near surface transfer and bioturbation homogenizes the upper surface producing a biomantle. However, the minimal time frames for operation of different mechanisms vary, with some becoming operative within years (gases) and some over hundreds or even thousands of years. Further, the landscape evolution will itself impact on the spatial evolution of cover, as is the case over much of the Australian continent. For example, Smee (1983, 2001) notes that on a theoretical and inorganic basis, only H^+ ion can diffuse through 20 m of saturated clay in 10,000 years, but most other ore related metals cannot or require a longer time frame. Another aspect related to weathering of a transported cover, which has until now received minimal reference in this article, is that weathering commences at top and proceeds downwards with the evolution of biomantle and therefore transfer of matter in the form of infiltrating water is generally downwards. Therefore, metals from various sources, including the cover and airborne particulate deposited contaminants, can flow downwards and can negate upward transfer of metals.

6.2 Climate

Climate influences the effectiveness of different mechanisms on the basis of precipitation and its effect on depth of water tables and therefore influences the thickness of vadose zones. The mechanisms were classified according to the vadose and phreatic zones and the depth of vadose zones will be influenced by the climate of a region. Humid, wet climates are likely to have higher water tables (depending on aquifer and landscape), while the semiarid and arid climates will have thick vadose zones with deeper water tables. Accordingly, the vadose zone mechanisms will have greater influence in the drier climates as opposed to phreatic zone mechanisms which will be more effective in wetter climates.

Similar to current climatic influences on the operation of different mechanisms, is the importance of paleoclimate. Although much of Australia currently experiences semiarid and arid conditions, during the Cenozoic, different parts of Australia experienced humid to perhumid climates with strong rainfall (Macphail 2007). Transported cover across Australia can date back to the Cretaceous and much of it could be older than Quaternary (Anand and Paine 2002). Therefore, the effects of wetter paleoclimates would be manifested in the depositional as well as the post depositional weathering modification to the transported cover.

An example of the influences of paleoclimates on mechanisms can be found in the presence of mottled or redox zones which when present in the transported cover are inferred to be a product of paelo water table position. These regolith materials or zones that have redox reactions associated with fluctuating water tables as their main causative processes, when found removed from current water tables are interpreted as a relict of past higher water tables. Accordingly, paleoclimates could have influenced the effectiveness of dispersion mechanisms as in the past wetter climates, vadose zones would have been thinner and electrochemical mechanisms would have been significant and had a much greater vertical scope. Butt (1998) has postulated that the formation of saprolite supergene Au deposits in Australia are likely to have proceeded through successive humid and arid climatic conditions with the humid climates supplying the conditions for mobilization of Au.

6.3 Nature and postdepositonal evolution of transported cover

It is important to integrate the evolution of transported overburden with the operation of different mechanisms as it permits the ranking of effectiveness of a particular mechanism in different cover and environmental settings. It does not, however, demonstrate that a single or a combination of mechanism having the best potential to transfer metals does work. The efficacy of individual or combination of mechanism and their limitations needs to be addressed at particular sites and regions. Mechanisms that play a dominant role in one particular regolith and climatic setting where high water tables are a norm, may not be transferable to another setting characterized by different regolith and dry conditions. The nature and evolution of the transported sediments can have both positive and negative effects on the operation of the various documented transfer mechanisms. The effects of spatial and temporal evolution of transported regolith on the operation of different mechanism is considered under several categories as are known to exist in Australia, and are summarized in Table 7 and Figure 14.

6.3.1 Fresh sediments versus deeply weathered

Quaternary age cover of greater than 3 m depth may preclude the operation of many mechanisms, except possibly gas transfer (if ore body is sulphidic and being actively oxidized), capillary and bioturbation, especially in the sandy to mud rich and dry sediments. If the ore body commences oxidizing after burial which is possible considering mine waste rock piles do so within years, sulphur and possibly hydrocarbon gases may be generated that will migrate upwards and manifest an ore body signal in the surface cover. If the sediments are sandy and the environment dry, bioturbation is likely to commence operation quickly, penetrate to underlying anomalous residual regolith and mechanically transfer the anomalous material to or near surface, as is shown in several sandy, arid settings. If the sediments are mud rich, capillary suction can rapidly transfer metals upwards, but its effectiveness would depend on grain size of sediments and depth of water table. Besides gas, bioturbation and capillary, the other mechanisms lack the rapid operational criteria to make them viable as rapid metal transfer mechanisms to surface, especially electrochemical mechanisms in semi-arid and arid settings.

Alternatively, older, highly weathered transported cover of variable depth would afford a greater potential for several of the documented metal transfer mechanisms to operate singly or in tandem. Chemical and physical weathering of the overburden generally results in formation of water table (unconfined, perched) at variable depths, which would promote functioning of various phreatic mechanisms, possibly generate trace and carrier gases and provide sufficient time for biota based mechanisms to operate. Hydrochemical mechanisms will transfer metals into the saturated cover as has been found for some supergene gold deposits (Butt 1998). Sufficient time would permit colonization of biota and penetration of vegetation to depths for nutrient and water access resulting in upward metal transfer. The role of time averaged vegetation pull in fostering calcretes hosted Au anomalies through weathered transported cover has been advanced for semi-arid settings where vegetation has been shown to trap deep groundwater (Lintern and Butt 1997). The intensity and extent of the anomaly resulting from metal transfer can also be partly governed by the weathering degree of the cover. Pauwels *et al.* (1999) noticed the larger lateral anomaly of gas associated metals in a deeply weathered overburden, as compared to a narrow haloe in a young, less weathered soil.

However, type and nature of weathering is important because formation of cemented layers within the transported regolith such as silcretes and “hardpans” that can hinder the flow of water and limit biological penetration to subsurface anomalous zones. Such a scenario can be interpreted from Figure 1 where the upper 4 m are composed of Quaternary sediments made up of subhorizontal laminations and silcrete layers or hardpans. The weathering product of these sediments rather than their depth precludes the efficiency of operation of most mechanisms and subsequently no detectable ore related signature is transferred to the surface.

6.3.2 Transported cover profile stacking

The scenario(s) considered above assume weathering of the transported overburden as a single event after the deposition of the entire sedimentary unit. This simple explanation to account for evolution of weathering profiles may not hold true for many regions across Australia, which have escaped the erosive force of Quaternary glaciation and been free of a major orogeny since the Paleozoic.

Terrestrial sedimentation (fluvial, aeolian and lacustrine) is not continuous across the evolving landscapes, but is episodic depending on a number of extrinsic factors such as climate, uplift, sea-level change and intrinsic sedimentation processes (such as avulsion, overbank flooding, hillslope angles, regolith material resistance to erosion, terracing etc). Weathering however, appears to be a continuous process, but with variable intensity governed by several factors such as climate, tectonics, biota and lithology. The interplay between spatially variable sedimentation and operation of weathering can lead to the development and evolution of multiple profiles, as demonstrated in voluminous literature on paleosols (Kraus 1999). The process of formation of stacked paleosols (or weathering profiles) in distinct sedimentary units will be favourable to the transfer of metals across each paleosol and eventually to the present surface because of biomechanical (bioturbation) and biochemical (water and vegetation) interactions that would proceed between paleosols or paleo-profiles during their evolution (Figure 14D). The deposition of a sediment body would be followed by weathering and pedogenesis, and depending on the spatial intensity of terrestrial sedimentation, succeeded by deposition of another sediment body of varying spatial dimensions. Weathering of the second sedimentary unit would result in **biomechanical and biochemical interaction between the two profiles** and transfer metal anomalies to the higher soil, albeit with lesser contrast. Such subsequent sedimentation-weathering events across the landform can result in the transfer of metal anomalies from buried mineralization to the surface. This metal transfer method, however, is only valid in stacked weathering profiles without intervening fresh or slightly weathered sediments, and probably with a limit of ~ 5- 25 m of sediment. Kelly et al (2003) suggested the possible operation of such a mechanism where different epigene landsurfaces interacted with one another due to shallow cover and metals were transferred upwards. This landscape evolution controlled theory employs combined mechanisms of vegetation transfer, bioturbation and capillary.

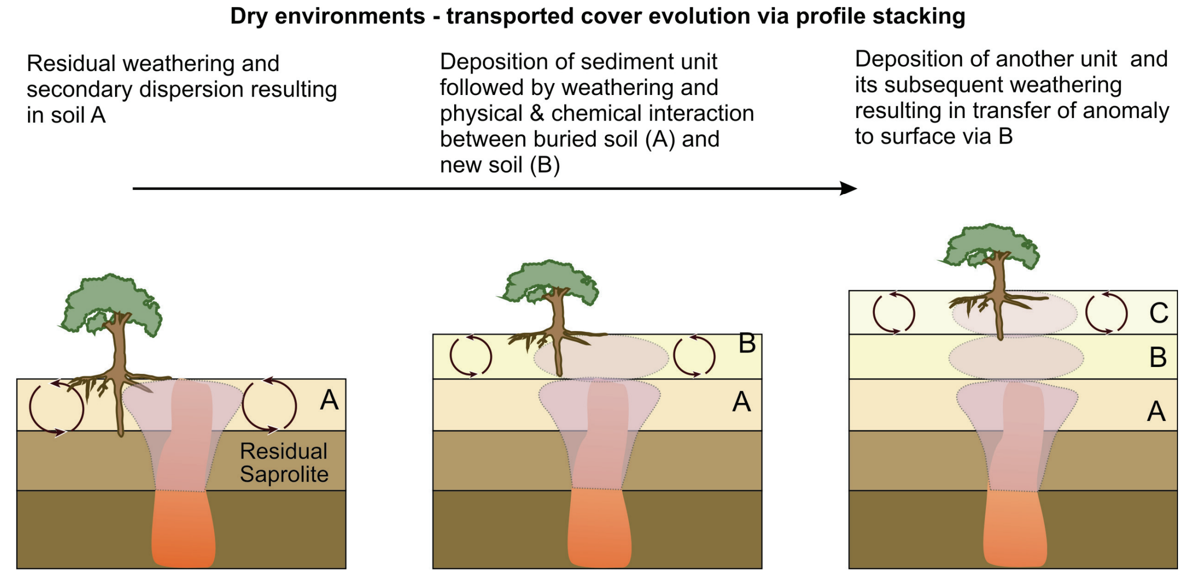


Figure 14 A. Metal dispersion in a depositional landscape where several shallow sediment deposition events are followed by weathering of the shallow sediments resulting in interaction between profiles and transfer of metals upwards, largely due to bioturbation but also due to plant uptake and capillary.

6.3.3 Paleo-water tables within transported cover

Older and thicker transported cover has a longer history of weathering through different climates depending on the region. Depending on past climatic and landscape positions, the water table could have been high with connected saturation existing from buried ore to top of water table. Over time, in response to onset of drier climate or change in landform, the water table has gradually or periodically been lowered to its current lower position, sometimes below the insitu-transported regolith interface. However, the **paleo-water tables** could have been favourable to the operation of multiple mechanisms (electrochemical and capillary) over time and effectively transfer metals to the surface through over 20-30 m of transported cover.

Wetter paleoclimates would favour higher water tables within the transported cover and metals are likely to have transferred into the transported cover via electrochemical processes notable redox facilitated metal transfer across an Eh gradient. The anomlaos zones are likely to be manifested in water table associated redox zones such as mottles and ferricretes. A shift to drier climates with erosion would lead to drop in water tables but the older redox zones manifesting anomalous metals would be within the biota mechanisms reach (Figure 14C). Bioturbation and vegetation uptake could transfer metals from paleo anomalous zones to the surface although the current water table is much lower. An example of such a case is described by Lawrence (1999) where paleo "redox" fronts interpreted as still stands of past water tables are present within Mesozoic sediments overlying buried ore. The paleo redox fronts developed in transported cover host higher metal contents due to their adsorptive capacity of Fe-Mn oxides and hydroxides.

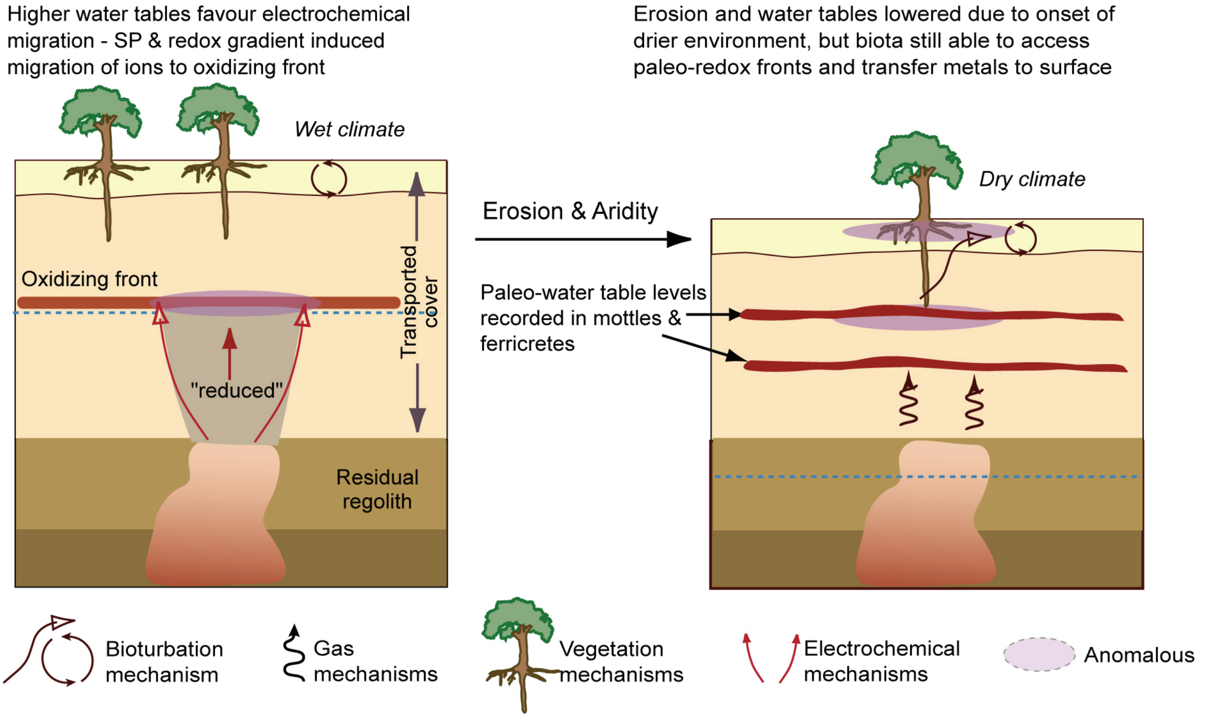


Figure 14B. Deeply weathered regolith situations where during a previous wet climate with higher water talbes present within the transported cover would favour electrochemical mechanisms based metal transfer to and adsorption onto the redox zones materials (mottles/ferricretes). Subsequent onset of aridity lowers the water table but the original anomalous zone is still within reach of plants and bioturbation and metal transfer proceeds to the surface. This highlights the effect of climate on mechanisms.

6.3.4 Variation in stratigraphy and depth of transported cover

The **variation in stratigraphy** of the cover sediments can also impact on the operation of specific mechanisms. For example at Moonta in South Australia, metals are transferred through a weathered Neogene clay unit that overlies weathered basement, but anomalies are not expressed at the surface when the clay unit is underlain by 2 m thick Cambrian sandstone. Keeling (2004) suggested the operation of capillarity mechanism only within the clay unit when directly overlying the mineralized saprolite, but the mechanism was precluded when coarse grained sandstone was present in between. Another variation in regolith stratigraphy situation that needs to be considered for the Australian landscape are the presence of buried residual lateritic profiles. The concept behind electrochemical mechanisms is that cover resides on unweathered, exposed sulphide mineralization, when data across Australia indicates that transported cover unconformably overlies lateritic profiles having an oxidized lateritic residuum or ferricrete (Anand and Paine 2002). In regolith settings where oxidized profiles overlie mineralization, self-potentials may not be sufficient to generate the voltages for electrical migration and the source of H^+ generation from buried mineralization may be limited. Furthermore, metals are found to be strongly “bound” to the iron oxides in the oxidized lateritic residuum and ferricrete, and therefore are not in exchangeable form unless novel strategies of root uptake are involved or microbial assisted reduction of oxides prevails.

Another possibility for variable metal transfer via a combination of mechanisms within the Australian regolith-landscape settings arises due to spatial variation in depth of transported cover. Across vast tracts of depositional landforms, transported cover depth varies considerably over short distances, in part because of local erosional-depositional events superimposed on weathering. Within an open-cut mine, transported cover depths can vary from negligible at one end to around 20 m at a distance of 100 m, and is a result of local uneven erosion of residual regolith and its subsequent burial. Residual regolith, especially the upper parts of lateritic profiles such as ferruginous and mottled zones, have a much wider geochemical dispersion haloe than the primary mineralization zone, sometimes in excess of 100 times the size of the primary dispersion haloe (Butt *et al.* 2000b). Erosional stripping of part of the residual regolith and subsequent burial can result in depth of cover being thicker over the mineralization but shallow adjacent to it with underlying anomalous residual regolith residing within the reach of biological mechanisms (Figure 14C). Biological aided transfer mechanisms- bioturbation and vegetation- can transfer metals from 2-5 m depth. The anomaly though, will not correctly reflect the underlying ore body but be slightly displaced to it. However, the main ore body can still act as a source of metal transfer via gaseous mechanisms.

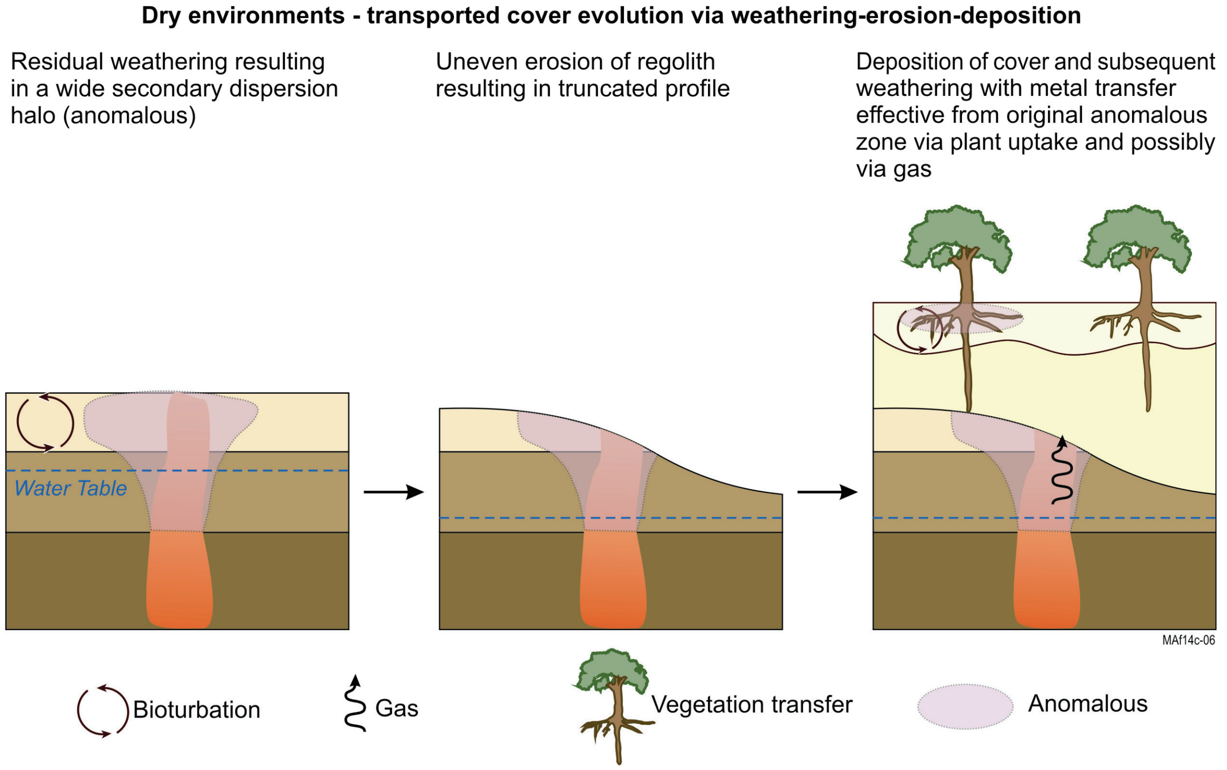


Figure 14C. Metal transfer processes in cover settings where secondary dispersion in residual settings is followed by uneven erosion and subsequent deposition and weathering, resulting in biota transferring metals from buried secondary dispersion haloe. Other mechanisms such as gas and indirect pathways may continue from the ore body. This setting also highlights metal transfer due to uneven thickness of transported cover.

Greater cover depths (> 30m), especially those with variable stratigraphy and/or of an un-weathered character, are the most difficult for many of the upward metal transfer mechanisms to be effective. The mechanisms that could potentially work through thick cover are gaseous transfer; diffusion along fractures, convection where sulphide ore a present and oxidizing, barometric pumping where cover is fratured, and dilatancy pumping where the region is neo-tectonically active. Microseepage arising from deep petroleum basins along fault zones has been documented in several studies (Klusman 1993). As previously described, barometric pumping has the potential to transfer gases along fractures from depths of around 400m (Carrigan *et al.* 1996; Hall *et al.* 1997). Other studies have suggested the bubble associated transfer of trace gases and metals along conduits over large distances (Etiope and Martinelli 2002), however, this mechanism is not substantiated. The long distance transport of trace gases, possibly of metals attached to carrier gases and the operation of dilatancy pumping suggests that the structural character of the ore body and the overlying cover are important parameters in evaluating the application surface geochemistry in deep cover settings.

Another possibility is the operation of several mechanisms in concert if the water table is higher in the cover sequence. If the water table is higher, redox gradient mechanism may operate uptil the water table with capillary above it and plant uptake taking over in the upper 5-20 m of the cover as suggested by Mann et al. (2005). The combined mechanisms could transfer metals through >30 m of cover provided water tables are 20-30m befow surface.

The above mentioned transported cover settings emphasize the operation of mechanisms as being limited or enhanced by the nature and post depositional modification of the cover. The cover settings will vary from region to region if not within a region, and accordingly the operation of one or two mechanism in one setting is not transferrable to another. Furthermore, if a surface technique is optimized to the operation of a particular mechanism, for example weak digests are to gaseous transfer, then that particular digest may not be applicable to different climatic and cover settings.

6.4 Mineralogical scavengers - “traps” in the cover

Some researchers have suggested that the mineralogical composition of the uppermost portion of overburden (topsoil) is also crucial to the overall relevance of application of metal transfer mechanisms in detecting buried ore. The presence of specific minerals that will be able to adsorb metals (or ‘fix’) and thereby act as “traps” at the surface will be conducive to hold on or accumulate the exogenic metals transferred from below rather than the exogenic metals being rapidly dispersed. Therefore, soils rich in organic matter (humic and fulvic material) and Fe/Mn oxides and hydroxides will serve as good “traps” for metals transferred to the surface. The formation of these minerals is tied to the weathering of the transported cover, which over time residually accumulates Fe/Mn oxides and hydroxides and organic matter. Therefore, a highly weathered sedimentary cover at its surface is likely to sustain a better “trap” capacity as compared to a fresh, unweathered cover, although some exceptions are possible. However, a weathered cover sequence will also have minerals favourable to adsorb metals (Fe/Mn oxides, clay layer silicates) along the vertical length of the profile, and a mechanism that transfers metals through the entire transported regolith – water and gas based – will encounter “traps” along the way and not merely at the surface, unless there are preferential pathways such as gas transfer along faults or through vegetation cycling and bioturbation.

6.5 Role of geology

The main role the geology and landform evolution of the area in influencing the effectiveness of the different metal transfer mechanisms is two fold: syn and post depositional structural evolution (faults, shears and fractures) of the area and mineralization type or style of the deposits being sought (mainly dependant on sulphide content).

The gas based mechanisms and dilatancy pumping appear strongly linked to the conduits traversing the main ore zone and the overlying sedimentary or transported overburden. Considering the variation in ages of the sedimentary overburden, but mostly of Cenozoic age, neo-tectonic activity of a region appears critical to the functioning of specific mechanisms. Although groundwater effusion may not be observed after earthquakes in many settings and therefore dilatancy pumping may have restricted scope, gas “leakage” along faults, via barometric pumping or diffusion, is possible and may manifest an anomaly at the surface. Neo-tectonic activity is being increasingly recognized in parts of a “stable” continent like Australia (Sandiford 2002) and there are several stress fields across the Australian region. Clark (2005) using high resolution digital elevation models to interpret fault scarps found over 30 potential Quaternary scarps expressions in the south-western area of Western Australia. Clark’s (2005) analysis of the fault scarps in SWA found minimal linkage between the interpreted fault scarps and current or historic earthquake hotspots, which suggests the migration of earthquake activity over time. Considering much of the SWA has transported Neogene cover across it, fault expressions may serve as conduits for metal migration via several of the gas based mechanisms. The spatial extent of neo-tectonic activity across many aspects of Australia still remains unclear, and buried ore bodies linked to neo-tectonic faults need to be tested.

The sulphide content or style of mineralization being sought is critical to the operation of several mechanisms, namely those mechanisms, such as electrogeochemical and gas based diffusive and convective transfer, that are underpinned by the presence of mineralization with a high sulphide content. Firstly, higher sulphide contents within the mineralization as compared to adjoining lithology will provide a better self potential gradient for either the electrical or redox gradient for the electrogeochemical mechanis(s) to develop and evolve. Secondly, the higher sulphide contents will also result in a higher production of specific gases such as CO_2 (carbonate presence), COS and SO_2. Further, high sulphide content in addition to type of sulphides (and style of mineralization), needs to be considered for volatile generation and migration. For example, Hg concentrations are only high enough in specific sulphides and ore styles. A list of Australian mineralization styles and the potential sulphide contents are listed in Table 8. Mineralization styles having moderate to high sulphide contents such as exhalative-diagenetic ore groups (VHMS, SEDEX) will be conducive to the operation of electrochemical and gas mechanisms, while sulphide poor types such as orogenic gold deposits and some porphyry-associated deposits will be less favourable to the operation of sulphide oxidation mechanisms.

Table 8. Australian deposit types and their approximate sulphur abundances. Placer and supergene deposits (gold, nickel laterites, channel iron deposits, bauxites) are omitted as they have negligible sulphide contents (courtesy Ken McQueen).

Ore Group	**Some Deposit Types and Examples**	**Approximate S abundance**
Magmatic	**Komatiite-associated nickel deposits**	
	Mt Keith, Kambalda, Widgiemooltha, Maggie Hays, Jubilee	Moderate to high
	Layered mafic-ultramafic intrusion deposits	
	PGE sulphide and chromite deposits: Munni Munni, Ora Banda, Yarawindah	Low
	Vanadiferous magnetite: Windimurra	Very Low
Metasomatic	**Skarn deposits**	
	Copper-gold skarns: Browns Creek, Big Cadia, Red Dome	Moderate
	Distal gold skarns: Junction Reefs	Moderate
	Magnetite skarns: Biggenden	Low
	Zinc-lead-copper skarns: Ban Ban	Moderate to high
	Tungsten skarns: King Island	Low
Hydrothermal epigenetic	**Fractionated graitoid-associated deposits**	
	Tin-tungsten deposits: Mt Bischoff, Renison, Ardlethan	Low
	Tungsten-molybdenum deposits: Wolfram Camp	Low to moderate
	Pegmatite and complex veins: Greenbushes, Wodgina	Very low to low
	Porphyry-associated deposits	
	Copper-gold stockworks and veins: Cadia-Ridgeway, Northparkes.	Low
	Copper-molybdenum deposits: Dogwood.	Low
	Breccia pipe deposits: Kidston, Mt Leyshon.	
	Epithermal gold-silver deposits:	Low to moderate
	High sulphidation type: Peak Hill, Gidginbung.	Low to moderate
	Low sulphidation type: Pajingo.	
	Iron oxide copper gold deposits	Low to moderate
	Olympic Dam, Ernest Henry, Tennant Creek	
	Syn-deformational hydrothermal and replacement deposits	
	Metamorphic copper deposits: Mount Isa, Nifty	Moderate to high
	Metasediment-hosted polymetallic deposits: Elura, CSA, Peak	Moderate to high
	Replacement deposits, possibly magmatically related: Osborne	Moderate to high
	Orogenic gold deposits	
	Archean greenstone-hosted deposits: Eastern Goldfields WA	Low
	Sediment-hosted reef deposits: Telfer	Low to moderate
	Slate-hosted quartz-vein deposits: Central Victoria, Hill End.	Very low to low
	Granitoid-associated deposits: Charters Towers, Timbarra	Low
	Carbonate-hosted stratabound lead-zinc deposits	
	Mississipi Valley-type: Lennard Shelf.	Moderate to high
	Unconformity-related uranium deposits	
	Alligator River, Coronation Hill.	Low to moderate
Exhalative-diagenetic	**Volcanic-associated massive sulphide deposits**	
	Abitibi type: Scuddles, Gossan Hill, Teutonic Bore, Sulphur Springs, Mons Cupri, Whim Creek	High in massive lens, moderate in stockwork
	Kuroko type: Mt Lyell, Rosebery, Hellyer, Hercules, Woodlawn, Thalanga, Balcooma, Mt Morgan, Halls Peak	High in massive lens, moderate in stockwork
	Sediment-hosted stratiform base metal deposits	
	HYC, Mount Isa, Century, Broken Hill	High
	Sediment hosted copper deposits	
	Sanstone-hosted: Mt Gunson, Cattle Grid	Moderate to high
Marine - sedimentary	**Banded iron formations**	
	Hamersley Range, Middleback Ranges	Very low
	Sedimentary manganese deposits	
	Groote Eylandt	Very low

6.6 Selective extractions and mechanisms

The mechanisms can also be ranked on the basis of applying selective and weak extractions (SWE). The premise behind SWE's is gradual contribution of exogenic metals that remain "labile" or "loosely" bound to soil matrix as compared to endogenic metals present in the transported overburden. Over sufficient time periods, once the metal anomaly is transferred to the surface, the exogenic metals are likely be incorporated and homogenized into the topsoil matrix or biomantle matrix, at a rate that depends on the bioturbation and soil weathering rate at specific sites. Bioturbation, biochemical and chemical weathering rates can homogenize the biomantle continuously with rates varying from within 100 years to > 10^3 years depending on type and nature of mesofauna, climate and landform. This combined process can result in the migrated metal or "exogenic" metal becoming "incorporated" or "bound" within the soil minerals (Mann *et al.* 1998). Therefore, to account for the "unbound" or "labile" or "exogenic" metal content extracted by selective extractions, a continuous or steady mechanism of metal transfer is required. This process, however, assumes that no other localized inorganic and biological mediated reactions occurring within the soil are capable of contributing to the "mobile" pool of ions by facilitating dissolution of minerals or via desorption. The theory assumes the rate of transfer of ions from subsurface to surface is sufficient or sustained to overrule other local soil reactions that may facilitate endogenic components to become "mobile" and contribute to the exogenic component pool.

There are several mechanisms that can fulfill the sustained metal migration criteria in accordance with the reasoning behind use of SWEs. If the water table is high and close to the surface, phreatic zone related mechanisms, both direct and indirect ones, can account for the continued supply of cations. If the vadose zone is thick, then gas mechanisms (diffusion, pumping and convection) can sustain the flow of ions to the surface. Vegetation based mechanisms may contribute but the processes and rate of assimilation of metal ions present in litter into the soil matrix is probably similar to those contributing to the metal becoming "bound". Capillary suction and soil evaporation has been advanced as a mechanism for the formation of "mobile" metals that adsorb to soil matrix due to evaporation and are therefore responsive to SWE. The indirect mechanisms, where the excess H^+ generated from an oxidizing ore body diffuses upwards or a continuous stream of gases migrates upwards via diffusion or advection mechanisms to induce a geochemical change within the soil, the result of which is manifested in an increase in metal extraction via SWE, are also valid. However, the SWE's can be effectively applied only if limitations of the transfer mechanisms through specific cover and climatic settings are judiciously assessed.

The value of SWE's and their underlying reasoning can be appreciated if SWE unambiguously detect mineralization that traditional soil bulk geochemical methods failed to do, besides from SWE's providing a better contrast. Unfortunately, not many studies compare the SWE data to soil geochemical data sets. Cameron *et al*. (2004) document the applicability of selective extractions in detecting buried sulphide mineralization through 30 m of saturated clay and suggest the electrogeochemical process as the main transfer mechanism. Smee (1998) from surface geochemical response data advanced the formation of surficial Ca and Sr anomalies based on development of an H^+ front at the margins of an ore body and H^+ migration to the surface and reaction with $CaCO_3$ in the soil, subsequently resulting in the redistribution of Ca within the soil and its detection via specific SWE. Whether any of the described mechanisms are able to sustain a metal transfer stream to account for "mobile" ions at the surface in all types of transported cover requires testing in several cover settings.

7 Conclusions

A review of mechanisms capable of transferring metals through barren transported cover to the surface to create anomalies, found several mechanisms, some well documented and others not well studied but nonetheless promising. However, all the mechanisms suffer from some drawbacks and require further study and testing (Table 9). The different mechanisms are grouped according to their effectiveness in phreatic (saturated) zone or vadose (unsatured) zone of the regolith.

The **phreatic** based mechanisms are most effectivnes and therefore the most predictive capability in environment with higher water tables. Electrochemical models, where metals migrate upwards under the influence of an electrical gradient related to the ore body are the most studied. From the electrochemical mechanisms, the redox gradient model where the metals migrate in response to a evolving redox gradient from the top of ore to the water table is the best suited to transfer metals from the ore body upwards through the satuated cover. The effects of heat generated from an oxidizing ore body on water table and solute migration have not been investigated in the semi-arid and arid Australian setting. The limitation of all phreatic mechanisms is the current or past height of the water table. Dilatancy pumping – the effusion of mineralized groundwater at the surface following earthquakes – is the most promising mechanism that can bypass the limitation of water table heights, but appears restricted to neo-tectonic active areas.

Vadose zone mechanisms – gaseous diffusion along concentration gradients, gas advection via barometric pumping and convective currents, particulate matter transfer via carrier gas bubbles, capillary upflow from water table, vegetation uptake and bioturbation are all valid mechanisms that can operate routinely and rapidly across the entire unsaturated transported cover. The gas based mechanisms are all strongly affected by the presence of preferential pathways in the ore body and overlying cover, such as structural conduits. Most studies demonstrate the migration of gas and volatiles along conduits and suggest "leakage" along the structures. For the gas based mechanisms to gain sufficient predictive capability, the following issues need to be addressed and evaluated

- Contribution of soil microbial and plant metabolism and other natural processes such as serpentinization and natural degassing towards efflux of gases.
- The genesis and magnitude of methylated volatiles at the sulphide weathering front and their temporal and spatial stability.
- Comparison of magnitude of gas and volatile transfer along structural features over mineralization and non-mineralized areas to assess the "real" contribution from the ore body rather than extra degassing due to structures.
- The stability of bubbles with attached metals across the air-water interface and its stability upwards in the unsaturated zone.

Capillary suction driven rise of water from the water table can reach significant heights (~20m) in fine grained sediments and dry conditions. The fine grained sediments allow a higher rise of water while the dry conditions at the surface generate and maintain a upward water potential gradient for the suction force. However, variation in the cover sediment texture may preclude higher capillary rises.

The plant uptake of metals from the subsurface to the surface has long been championed as a predictive metal transfer tool. Recent studies using isotopic fingerprinting demonstrate that during dry periods or in water and nutrient stressed environments, plants source their water and nutrient demands during drier periods from deeper groundwater. Also, rooting depths are known to extend to > 10m on a regular basis in water and nutrient stressed environments. However, the role played by the different species on metal uptake and a robust method of confirming whether specific species tap deeper sources of groundwater and nutrients still needs to be established to make this a predictive technique in shallow cover (5-20 m) situations. Further studies are required to

- Predict routine root depth penetration of specific species.
- Efficacy to transfer metals to the surface so an ore metal anomalous status is unambiguously detectable either in some tissue of the plant or in the top soil
- Examine the role of metal mobilization by hydraulic lift to the soil.

Bioturbation by the main conveyor-belt organisms mainly ants and termites, has long been viewed as a viable mechanism to metal transfer, and its effects have been applied through 20-30m of cover in dry settings, where termites are known to burrow to depth. Besides a few locations, the depth of bioturbation and the response from the random burrows to depth on manifesting an ore signature at the surface needs to be established in different regolith and climatic settings to make its application predictive. Although biological mechanisms such as plant and bioturbation transfer, provides novel methods to overcome limitations of inorganic mechanisms, they bring their own complexities which are at times more difficult to estimate and predict, and therefore require extensive testing.

Lastly, an integrated approach combining different mechanisms with the nature of transported regolith and climatic setting needs to be considered to obtain the best prediction of metal transfer. Regions and landforms underlain by highly weathered profiles with current or past water tables residing within the cover and a long presence of vegetation will favour the operation of a combination of mechanisms such as electrochemical, capillary, plant uptake and bioturbation. Dry environments may favour capillary, plant uptake and bioturbation mechanism to specific depths. Fresh, relatively un-weathered and deep transported cover settings provide the most difficult cover types through which any of the mechanisms can work, except if gases from the ore body are generated in sufficient quantity to manifest a surface signature. The gas mechanisms, however, have significant limitations.

Table 9. Summary of different mechanisms having the potential to transfer metals upwards through transported cover.

Mechanism		**Process summary**	**Limiting Factors**
Phreatic	Convection (Heat)	Faster upward migration of ions due to density or subtle heat generated currents	• Sulphide rich oxidizing deposit needed • Effectiveness over deposit not fully proved or explored • Limited to water table
	Dilatancy pumping	Groundwater pumped upwards due to compressional stress along faults/fractures. Arid climates favour rapid evaporation and restriction of metals	• Requires neotectonic active areas - faults through transported cover and • Confirmation of visible groundwater effusion after earthquakes
	Bubble	Metal ions attach to upward streaming carrier gas bubbles (CO_2)	• Fate of bubbles and attached particles on unclear above water table
	SP (electrochemical)	Electrical currents set around from sulphide ore with concentration of cations at edges	• Process is limited to shallow cover • Relies on diffusion process to pass through thick cover
	Redox Gradient (electrochemical)	Redox differences between oxidizing near surface and reducing base of cover. Faster migration in voltaic gradient	• Needs saturation conditions and associated redox gradient for effective transfer
	Diffusion (indirect effects)	Diffusion along concentration gradient from base of cover to surface	• Very slow process with only H^+ migrating fast enough through saturated cover
Vadose	Capillary	Surface tension related rise of groundwater above WT. Evaporation at surface drives suction upwards	• Upward extent unclear and operationin heterogenous textural materials unproven
	Gaseous diffusion	Oxidizing ore body produced gases (CO_2, COS, SO_2, CH_4) and volatiles (Hg, AsH_3) diffusion through porous media	• Migration along preferential pathways (structural conduits). • Gas signal complicated by biological released gases • Temporal stability of many gases limited
	Barometric pumping	Rapid advective transport of gases in fractured media via barometric pumping	• Limited to fractured media
	Gas Convection	Air temperature differences drive hotter gases from ore body upwards	• Limited to hilly regions or for low relief regions, permeable covers, high sulphide contents and oxidizing conditions
	Plant uptake and release to surface via litter	Absorption of metals from water table or anomalous zone, accumulation in organs and release to ground via litter	• Species, landform and climate related • Root penetration depths maybe localized • Species related uptake unclear • Rate of transfer to surface and homogenization requires study
	Plant uptake and release to soil - Hydraulic lift	Water absorption from depth (water table) and release near surface (upper soil horizon)	• Metal transfer with water not confirmed. • Depth from which water lifted poorly constrained. • Limited understanding of the process
	Bioturbation and gravity (mechanical)	Vertical and lateral movement of material from depth to surface by burrowing activities of conveyor belt organisms (termites and ants) - biomantle	• In many areas limited by depth of biomantle (<3 m) • Further information on burrowing depths of ants & termites in dry settings

The choice of the mechanism or combination of mechanisms employed to make surface geochemistry predictive will depend as much on the regolith setting (fresh or weathered cover, depth of cover), climatic conditions (wet or dry which influences the thickness of the vadose zone) and the geology of the region (style of mineralization sought, neo-tectonic activity). The integrated approach highlights the need to critically assess the positives but also the limitations of all mechanisms. There is value in establishing that surface geochemistry, as per our **current understanding of transfer mechanisms** and **detection technology**, does not work under **specific cover settings**, for example, great depth of cover, or has its limits, and that a combination of geology, ore processes, geophysics, regolith, deep groundwater geochemistry, predictive numerical modeling and use of the expensive, but necessary tool – the drill rig – needs to be prudently employed in transported cover settings.

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