



## Review

# A review of metal transfer mechanisms through transported cover with emphasis on the vadose zone within the Australian regolith



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## ABSTRACT

There is a growing trend to try to make surface geochemistry effective for exploring areas of transported cover using sensitive techniques such as partial extractions of soil and gas analysis. However, these techniques have had mixed success in delineating buried ore bodies, because the particular mechanisms and their effectiveness in transferring ore-related metals upwards through transported cover are poorly understood. This precludes discriminating null results (a potentially ineffective technique) from negative results (no mineralization). A review of mechanisms capable of transferring metals through barren transported cover to the surface identified those well documented and others not well studied but nonetheless promising. The mechanisms are classified according to two main processes: phreatic process involving groundwater flow, convection, dilatancy, bubbles, diffusion and electromigration; and vadose processes involving capillary migration, gaseous transport and biological transfer. Microbial metabolism affects the kinetics of many hydrochemical processes, especially sulfide oxidation and other redox transfers, and also impacts, negatively and positively, on the generation of gases throughout the entire cover sequence. Phreatic mechanisms require groundwater to transfer solutes and are most effective. These have the most predictive capability where there are shallow water tables. In the Australian landscape, groundwater occurs commonly more than 5 m below surface except in lower, discharge landform sites, and therefore other mechanisms (biological, capillary, gaseous), are necessary to transfer metals up from the water table. Thus, much of the emphasis in this paper is on vadose processes. An integrated approach is necessary, combining different mechanisms with the nature and evolution of the transported cover and climatic settings. Regions and landforms of highly weathered transported cover with current or past water tables residing within the cover and long-standing vegetation will favor combined mechanisms such as electrochemical, plant uptake, capillarity, and bioturbation. Fresh, relatively unweathered and thick (> 30 m) transported cover may prove the most unlikely to develop surface geochemical anomalies. Gas (e.g. CO<sub>2</sub>, H<sub>2</sub>S) mechanisms may work, provided that sufficient gases are generated from the oxidation of ore to produce a surface signature.

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## Contents

1. Introduction . . . . .	395
2. The mechanisms . . . . .	395
3. Phreatic zone mechanisms . . . . .	396
3.1. Introduction . . . . .	396
3.2. Dilatancy pumping . . . . .	397
3.3. Glacial tectonic pressure . . . . .	397
3.4. Electrochemical processes . . . . .	397
4. Vadose zone mechanisms . . . . .	399
4.1. Vegetation . . . . .	399
4.1.1. Phreatophytes and groundwater uptake . . . . .	401
4.1.2. Hydraulic lift . . . . .	402
4.1.3. Metal uptake and transformation . . . . .	402

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4.2.	Bioturbation	403
4.3.	Capillarity	404
4.4.	Gaseous dispersion	406
4.5.	Microbes	408
4.5.1.	Immobilization and biomineralization of metals	408
4.5.2.	Mineral dissolution	410
4.5.3.	Biomethylation and demethylation	410
4.5.4.	Metal acquisition by plants	410
5.	Influence of nature and evolution of transported cover on mechanisms	410
5.1.	Paleowater tables within transported cover	410
5.2.	Transported cover profile stacking	411
5.3.	Variation in stratigraphy and depth of cover	412
5.4.	Time	412
5.5.	Geology	412
6.	Summary and conclusions	412
	Conflict of interest	413
	Acknowledgments	413
	References	413

## 1. Introduction

As discoveries of world-class mineral deposits continue to decline, increased attention is being focused on geochemical exploration methods specifically designed for terrains with significant transported cover (Kelley et al., 2004). Transported cover here refers to material of exotic or redistributed origin such as alluvium, colluvium, glacial, lacustrine, marine and aeolian material that blankets fresh or weathered bedrock. Exploration is difficult and expensive in these areas. Surface soil sampling has tremendous advantages for mineral exploration, and where effective, low-cost programs can be conducted in areas of transported cover, covering large areas and quickly eliminating barren ground. More expensive techniques, such as drilling, can then be concentrated in areas with higher probabilities of success. Aside from the expensive option of pattern drilling through transported cover, a number of geochemical techniques may be used, the main gas or vapor, biogeochemical and groundwater sampling, being partial extractions, and electrochemical techniques (Goldberg et al., 1997; Wang et al., 1997; Gray et al., 1999; Hale, 2000; Putikov and Wen, 2000; Gray, 2001; Cameron et al., 2004; Mann et al., 2005; Kelley et al., 2006; Anand et al., 2007; Klusman, 2009; Cohen et al., 2010; Cao et al., 2010; Lintern et al., 2013; Noble et al., 2013; Morris, 2013; Anand et al., 2014). Over the last two decades, one of the most common geochemical approaches has been to use partial extraction geochemistry to assist detection of weak geochemical dispersion haloes by chemically targeting the regolith components that are thought to host these haloes (Cameron et al., 2004). Partial extraction techniques rely on the premise that ore-associated elements are being actively transported upwards through the transported cover and occur in a labile, readily extractable form (Mann et al., 2005). However, what such mechanisms may be, and whether they occur (or have occurred) to any significant extent is unclear. Furthermore, active soil-forming processes may also involve labile elements, unrelated to mineralization, that will also be dissolved by these extractants, resulting in mixed data, potentially producing false anomalies. Poor understanding of the mechanisms of metal transfer precludes discriminating null results (ineffective technique) from negative results (no mineralization). This has limited the use and credibility of these techniques (Cohen et al., 1998; Gray et al., 1999; Butt et al., 2000a; Mokhtari et al., 2009; Anand et al., 2014).

Although false anomalies are common, the critical question is whether a lack of anomalous surface geochemical response can be interpreted as unmineralized bedrock below. An example of the value of understanding of whether metal signatures from mineralization are transferred upwards to the surface is illustrated in Fig. 1. Gold from the underlying mineralization has dispersed into the overlying older

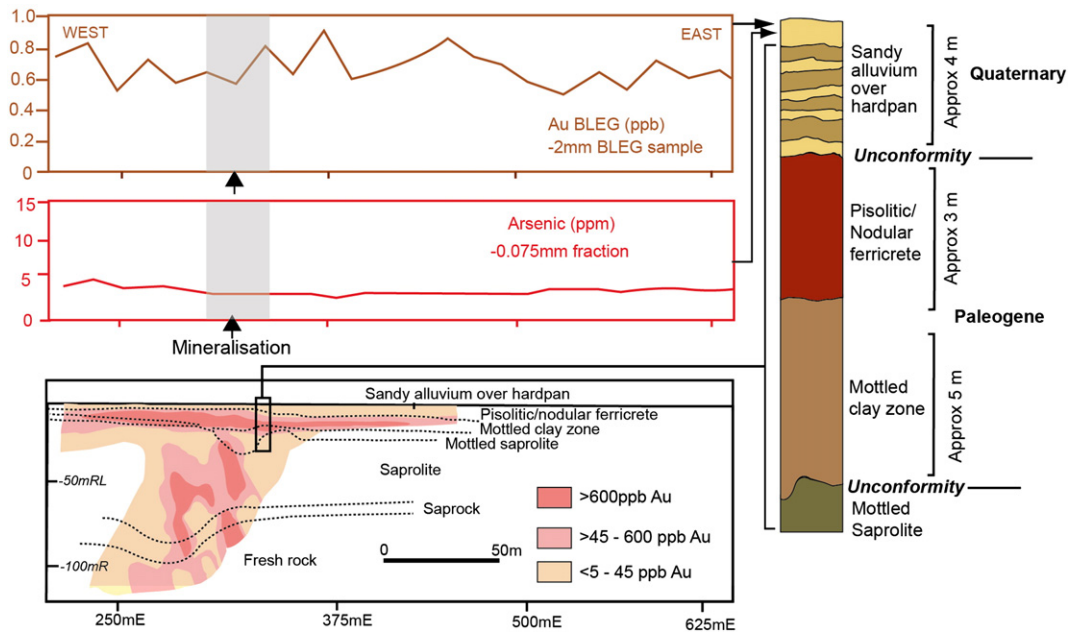
and intensely weathered transported cover, but not within the thinner, but less weathered near surface cover and soils, and subsequently surface geochemical sampling provided a null result (Fig. 1; Radford and Burton, 1999). The example highlights the lack of predictive capability of the surface geochemical technique because understanding how metals are transferred upwards through different cover and environmental settings is lacking. In comparison, the understanding of geochemical dispersion processes in residual regolith is well established with proven successes in Australian regolith settings (Butt et al., 2000a; Anand, 2000; Smith et al., 2000; Anand and Butt, 2010).

This paper reviews the potential mechanisms by which metals may transfer from the ore body upwards and laterally through unmineralized transported cover, with an emphasis on application to the Australian regolith. Where there appears a linkage between the operation of different mechanisms and the effectiveness of surface geochemical techniques, the paper alludes to the linkage. The diverse mechanisms and their underlying processes, cover a multitude of scientific disciplines.

## 2. The mechanisms

The mechanisms capable of transferring metals upwards can be grouped into two main categories based on whether they are within the saturated groundwater zone (phreatic zone) or above this saturated zone (vadose zone) (Fig. 2). This distinction is important for a dry continent like Australia because the water table across the semi-arid and arid regions is deep and therefore the unsaturated zone mechanisms are ultimately critical to upward transfer of metals to surface. Previous reviews (Cameron et al., 2004; Kelley et al., 2006) of metal transfer mechanisms have concentrated on the phreatic zone. Although most of the mechanisms described below have in the past been postulated to contribute to upward transfer of metals through transported cover, some have, as yet, not been proposed to achieve the same result (Aspandiar et al., 2006). Movement of ions and particles through transported cover is upwards against gravity, and therefore a medium (water, gas, mineral particles) and force (concentration, electrical, temperature or pressure gradients) are necessary to cause the upward transfer by diffusion or advection. The major transfer mechanisms categorized according to the main processes are summarized in Table 1 and Fig. 2.

The above mechanisms, if effective, can cause a direct and/or an indirect anomaly at the surface (Snee, 2003). In a direct anomaly, the target metals (metals associated with mineralization) are transferred to the surface. An indirect anomaly at the surface arises in response to another stimulus associated with the ore body. For example, the excess  $H^+$  and  $Fe^{2+}$  from sulfide weathering may diffuse to the surface and cause a detectable chemical change in the soil that implies buried sulfides.



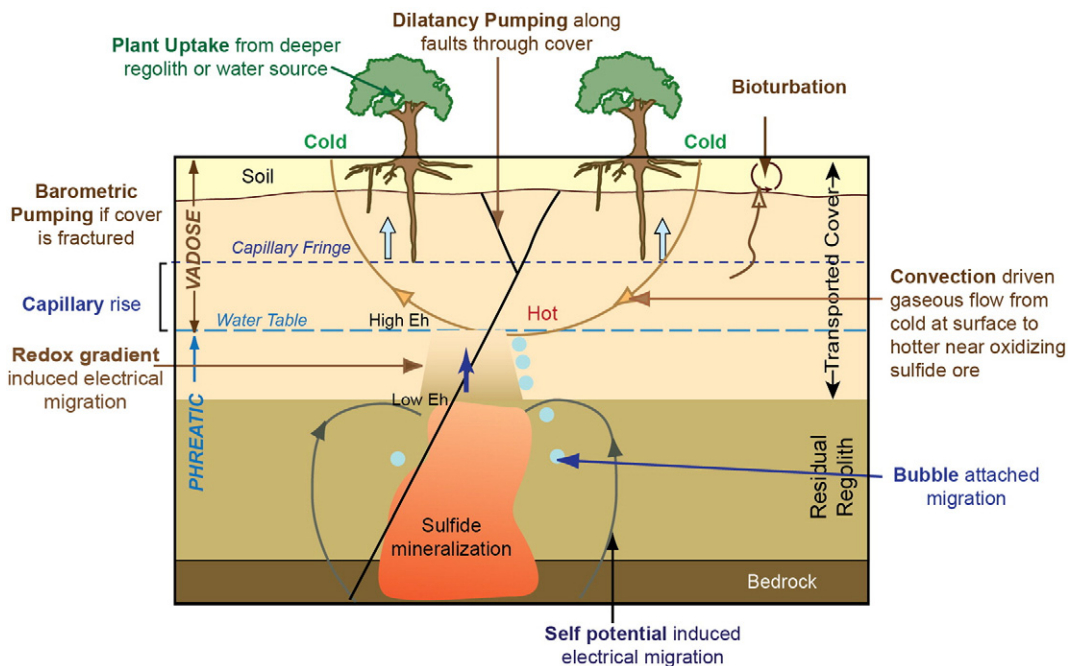
**Fig. 1.** Gold concentration contours over regolith cross section from Big Bell deposit. A magnified view of the regolith profile with interpreted unconformities is shown on the right. Part of the soil geochemistry (Au and As values) over the deposit is shown. The data and profile interpretation indicate dispersion into older deeply weathered transported cover but no detectable transfer into younger, fresh cover as indicated by negative As and Au signal in soil. Modified after Radford and Burton (1999).

**3. Phreatic zone mechanisms**

**3.1. Introduction**

Phreatic processes require groundwater to transfer solutes. Groundwater and infiltrated rainwater are the main agents of chemical weathering that facilitates the dispersion of metals from the ore body. Numerous hydrochemical studies around buried mineralization

indicate high metal contents in groundwater close to ore bodies (Giblin and Mazzucchelli, 1997; Gray, 2001; Cameron et al., 2004; Leybourne et al., 2006; Noble et al., 2010). Sub-surface mineralized water can be transferred to the surface by convection, bubbles, dilatancy, diffusion and electrochemical migration (Fig. 2). Excellent reviews of phreatic processes are provided by Cameron et al. (2004) and Kelley et al. (2006). Of the phreatic processes, two mechanisms, cyclical dilatancy pumping and electrochemical dispersion, have received significant



**Fig. 2.** A schematic view of phreatic and vadose zone dispersion mechanisms. They are classified according to processes occurring in two dominant mediums of phreatic and vadose zones: i) phreatic zone processes involving groundwater flow, convection, dilatancy, bubbles, diffusion, and electrical migration and ii) vadose zone processes involving capillary migration, gaseous transport and biological transfer. Modified after Aspandiar et al. (2006).

**Table 1**  
Major transfer mechanisms according to main classes.

Mechanism	Force	Medium
Phreatic		
• Advective		
▪ Groundwater flow	Potential energy	Water
▪ Dilatancy pumping	Stress	Water
▪ Glacial tectonic pressure	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 potentials	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/regolith
• Bioturbation	Animal metabolism	Regolith
Besides these main transfer mechanisms, two other factors are also described, because they significantly affect most of the mechanisms. These are		
• Microbial induced reactions		
• Time, climate, nature and evolution of the transported cover.		

attention over the last decade. A third mechanism involving active advection of groundwater as a result of remnant glacial tectonic pressure proposed by van Geffen et al. (2012), has received less attention (Fig. 3). These three mechanisms are discussed here briefly.

### 3.2. Dilatancy pumping

Although water and its dissolved constituents typically flow down-gradient, subsurface mineralized water can be transferred to the surface through faults by seismic or dilatancy pumping (Sibson et al., 1975). 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 near-surface anomalies (Cameron et al., 2002; Kelley et al., 2003). This is limited to low-rainfall and neo-tectonic areas that have regular seismic activity. It has been proposed at the Spence porphyry copper deposit in northern Chile that has 50–100 m of transported Miocene gravel (Cameron et al., 2002, 2004). The gravel shows vertical fractures formed by reactivation of basement faults. Soil and fractures are anomalous in Cu above the ore body. Several other workers (e.g., Morris, 2013) have postulated a similar mechanism for forming a Au anomaly in block-faulted sedimentary rocks. Dilatancy pumping is the most promising mechanism that can bypass the limitations of water table heights, but appears restricted to actively tectonic areas. Although the Australian Cratons and Fold Belts are considered tectonically “stable”, there have been recorded recent earthquake activity and associated faulting within the Cratons, but widely developed effusion of groundwater at the surface after an earthquake remains to be proven for this mechanism to be considered widely applicable to Australian Cratons and Fold Belts.

### 3.3. Glacial tectonic pressure

In a related mechanism to dilatancy pumping, changes of surface induced hydrostatic pressure can force fluids at depth upwards, particularly in areas of rocks and sediments with contrasting permeabilities (Boulton and Caban, 1995; Boulton et al., 1995; Boulton et al., 1996; van Geffen et al., 2012; Fig. 3). In a proglacial environment, the rate of

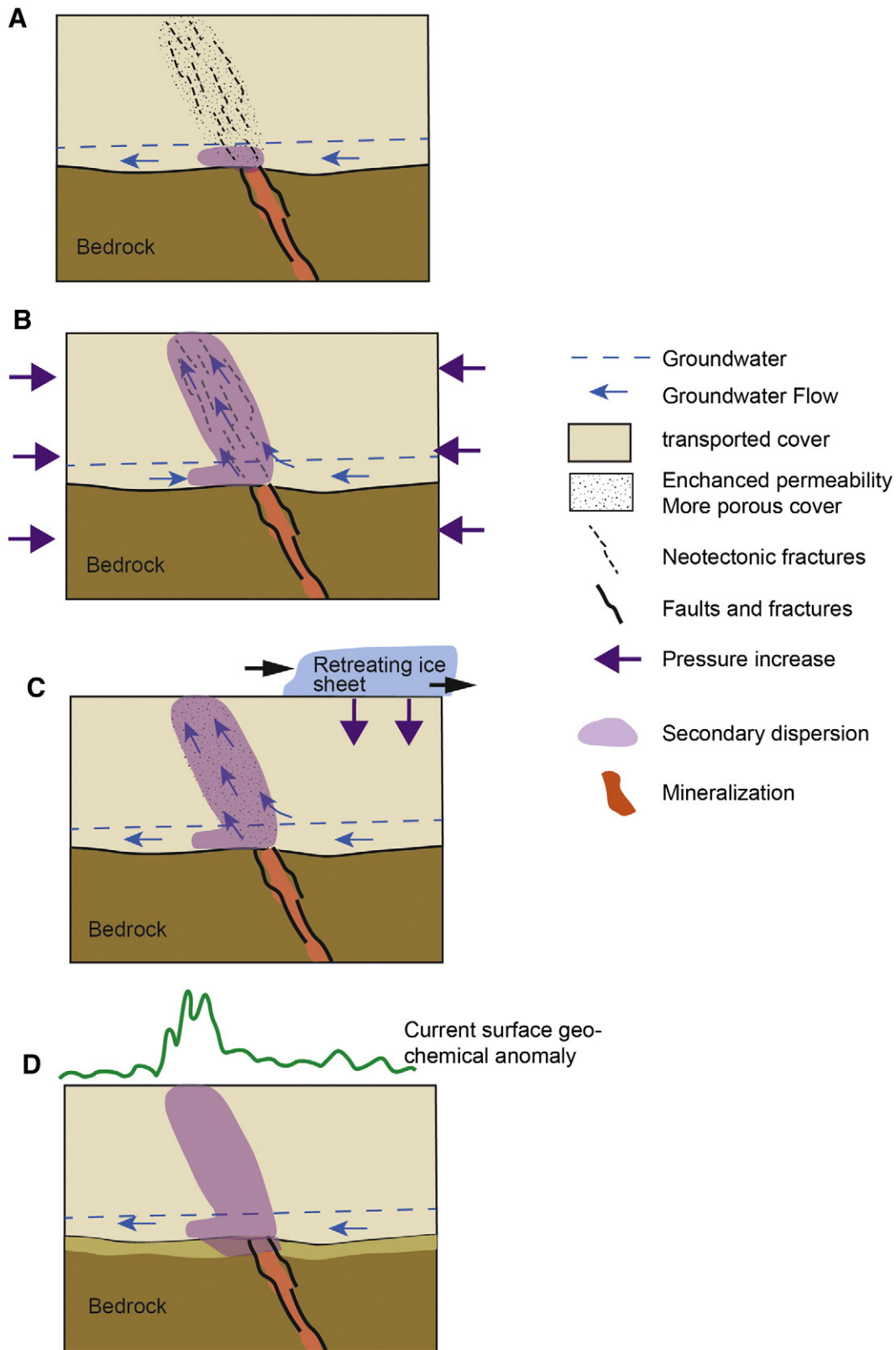
ice retreat may be much greater than the rate of vertical isostatic rebound of the lithosphere (van Geffen et al., 2012) and large seepage pressures are generated adjacent to ice sheet margins. Permafrost and low permeability rocks can maintain the excessive hydrostatic pressure forcing water to move rapidly and against gravity through highly permeable rocks such as karst environments and glacial moraines. Research has observed the upward fluid migration (Boulton and Caban, 1995; Boulton et al., 1996) and, like dilatancy pumping, any soluble elements are mobilized with the fluids to potentially form near surface anomalies.

### 3.4. Electrochemical processes

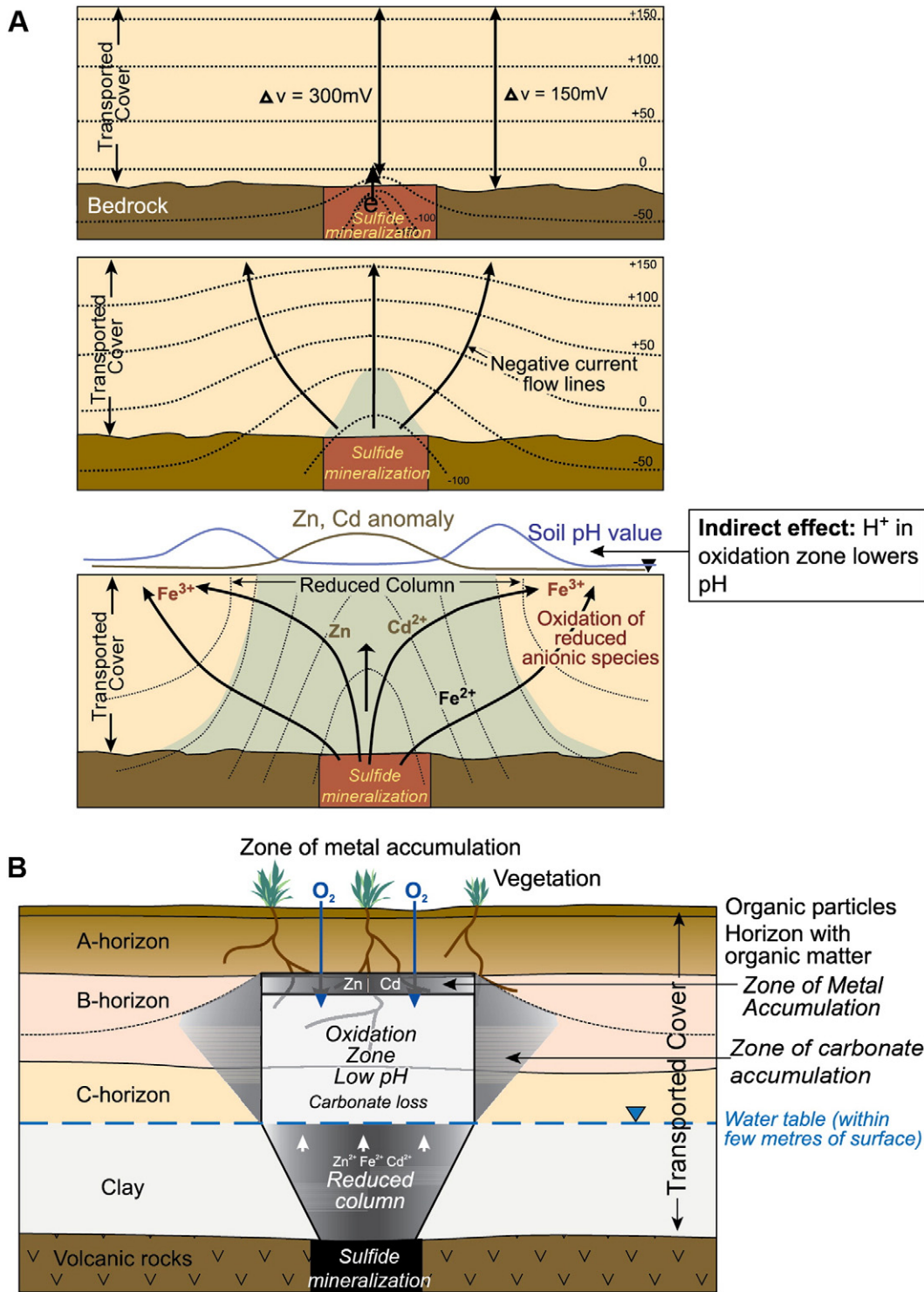
Electrochemical processes involve the movement of charged ions within an electrical field and are considered to be efficient migration mechanisms because they favor rapid upward ionic migration (Fig. 4). Electrochemical forces arise from spontaneous potentials around an ore body (Sato and Mooney, 1960) and result in excess cation concentrations at the upper edges of the sulfide ore with subsequent diffusion of cations along concentration gradients. This accounts for a near surface anomaly through transported cover (Govett et al., 1984). The resultant migration of  $H^+$  to surface can modify soil conditions (reduced pH) that can, in turn, mobilize specific cations within the soil. The proposed dual peak (“rabbit ear”) pattern of surface cation concentrations in regolith is argued for the operation of an electrochemical cell mechanism (Govett, 1976; Govett et al., 1984). Hamilton (1998, 2000) proposed a different electrochemical model to account for rapid upward dispersion of elements through saturated glacial clays. His model is based on the onset, development and continuance of a redox gradient between the buried sulfide body (reducing) and water table (oxidizing) and requires a balance of availability of reduced and oxidized species within the saturated transported cover (Fig. 4). Redox differentials arise and are maintained by reducing conditions at the sulfide 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 (Fig. 4). Surficial geochemical responses through 30 m of transported cover over deeply buried sulfide-hosted gold and VMS deposits in northern Ontario with high water tables (within 1–2 m of surface) have been attributed to electrochemical dispersion (Cameron et al., 2004; Hamilton et al., 2004). Theoretical ion migration rates in electrochemical fields, linked to redox gradients, are much faster than diffusion rates and may permit the formation of geochemical anomalies at surface in young (c. 8000 years), thick, glacial sediments overlying mineral deposits (Hamilton, 1998).

However, the efficiency of electrochemical mechanisms needs to be evaluated in terms of the style of mineralization, saturation conditions, water table levels and mineralogy of the medium. It is not clear whether sulfide-poor ore types will provide the initial self-potential differential necessary to induce a large enough redox gradient or vice versa to produce the “reduced” column or supply the excess  $H^+$ . Alternatively, vertical redox gradients occur in many deeply weathered regolith profiles without an underlying ore body (Anand and Paine, 2002) and the value of the reduced column as a singular product of conductive mineralization or otherwise needs to be tested. Another critical factor affecting the electrochemical mechanisms is the depth of water table and the related diffusion of  $H^+$  ions and cations. In the Australian landscape, groundwater is commonly more than 5 m below surface (except in low, discharge sites) and therefore diffusion of cations must work upwards against gravity, mostly through a dry, even cemented medium of variable mineralogy. Electrokinetic experiments demonstrate that the efficiency of the electrochemical process decreases markedly where medium saturation is <10% (Reddy and Shirani, 1997; Reddy et al., 2001). Thus, other mechanisms are necessary to transfer metals up from the water table. The vadose zone processes are crucial in semi-arid and arid zones, where vadose zones are thick and groundwater deep.





**Fig. 3.** A. Conceptual model of secondary metal dispersion in a deep cover arid zone with blue arrows showing groundwater flow direction and the subsequent dispersion of metals from the primary source. B. Tectonic pressure forms fractures in the cover and causes upwelling of groundwater to the surface carrying the metal rich groundwater. C. Retreating ice changes the hydraulic head pressures and causes a similar upwelling of groundwater in zones of more porous cover. D. The current surface geochemical anomaly is present adjacent to primary mineralisation in cover that has preferential flow paths for metal-rich groundwater. The figure is adapted from Boulton et al. (1996), Cameron et al. (2004), Kelley et al. (2006) and van Geffen et al. (2012).



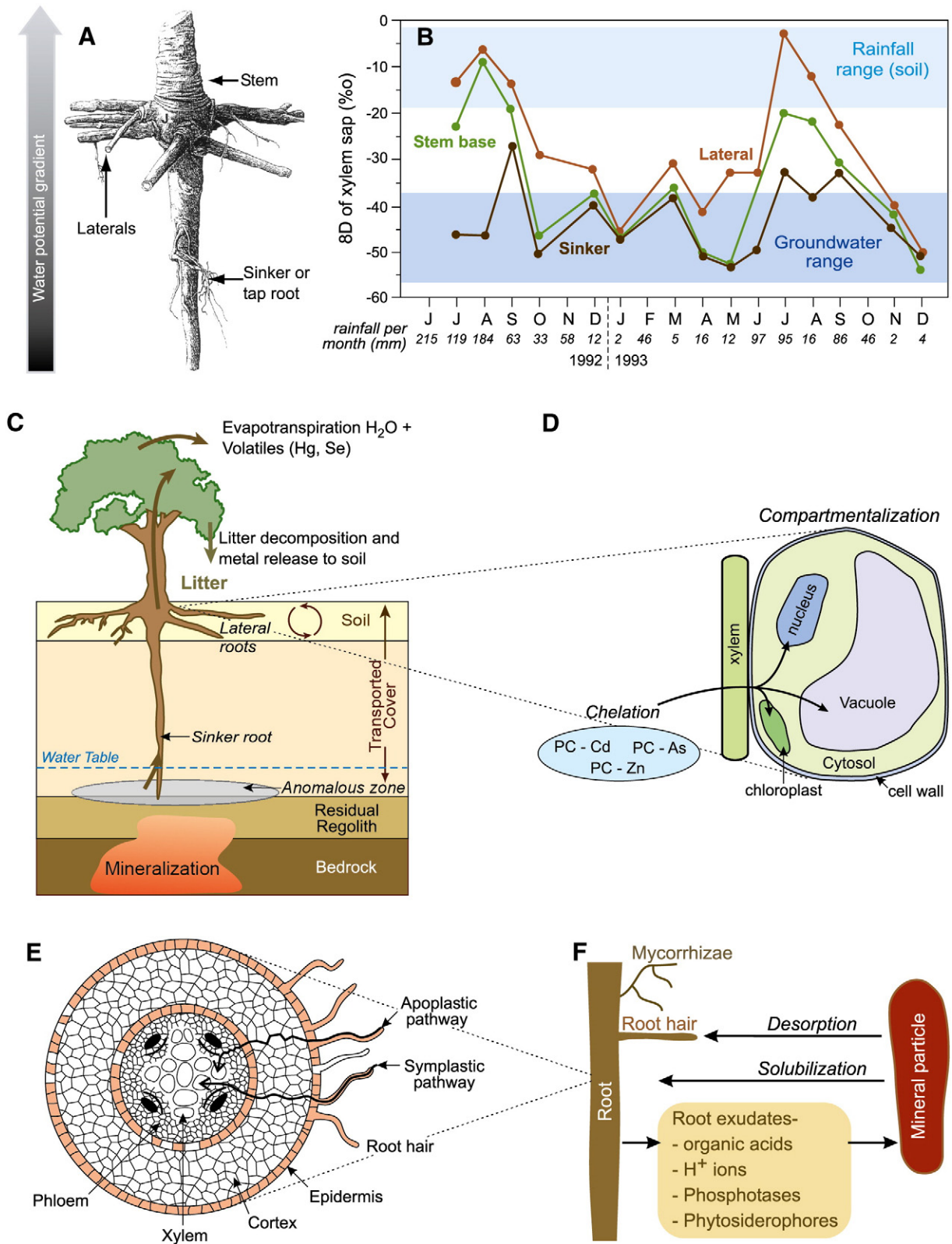
**Fig. 4.** The redox gradient model. A. The stages in the evolution of a “reduced column” and associated metal migration in a saturated cover sequence. The diagrams show the progressive modification of redox equipotential lines (after Hamilton, 2000). B. A model for the development of soil anomalies 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<sup>+</sup> ions that, in turn, dissolve soil carbonate. Modified after Cameron et al. (2004).

**4. Vadose zone mechanisms**

**4.1. Vegetation**

Use of vegetation as a mechanism to transfer metals from deep mineralization to the surface is attractive because water and its contained nutrients are driven upward by the water potential differences between

leaves and roots, and also the trace metal content of vegetation often reflects the composition of its substrate. Vegetation takes up and metabolizes a wide range of elements from groundwater or mineral surfaces and either stores or expels them (Brooks et al., 1995; Dunn, 2007). Biologically-essential elements (such as Ca, K, Mg, Na, S, Cu, Fe, Mo, Se and Zn) and non-essential elements, including those that are potentially toxic (Ag, As, Au, Cr, Pb, Sb, Cd and U), are taken up selectively and may



**Fig. 5.** Plant water and nutrient uptake mechanisms 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 southern hemisphere summer months (after Pate et al., 1998). 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.



reflect more closely the composition of the substrate. Metals acquired from the groundwater can be carried to the surface in plant tissues and subsequently released as litter, released into the atmosphere or possibly released directly into the near surface soil (Figs. 5 and 6). There are numerous examples in the literature of the use of vegetation to characterize metal dispersion around mineral deposits of various types (e.g., Andrade et al., 1991; Hulme and Hill, 2003; Hill et al., 2005; Dunn, 2007; Anand et al., 2007; Reid et al., 2008; Ma and Rate, 2009; Lintern et al., 2013; Anand et al., 2014; Dunn et al., 2015). Vegetation as a sample medium must be distinguished from that of a mechanism for upward metal transfer from the deep regolith. Several studies demonstrate the collocation of soil anomalies with vegetation anomalies. Ease of sampling and/or wide anomalies in vegetation is their perceived benefit (Dunn et al., 1996; McInnes et al., 1997; Cohen et al., 1999) but this does not necessarily prove that vegetation transfers metals from the deep regolith, through transported cover.

Much of the effectiveness of plants in upward metal transfer is linked to three plant characteristics, associated with adaptations the plant uses to cope with water and nutrient stresses. These are:

- Access and uptake of groundwater. Are the anomalous metal concentrations in groundwater most likely to reflect the presence of ore?
- 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 established?
- What nutrient deficiency adaptations do plants show that enable them to access and uptake non-bioavailable metals?

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

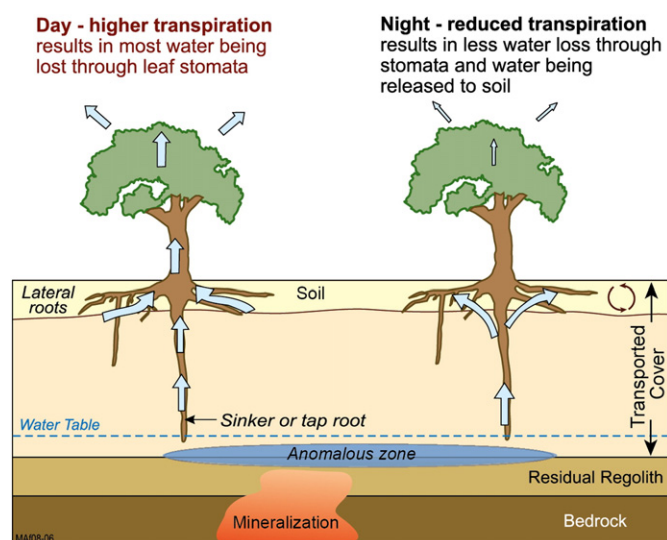
#### 4.1.1. Phreatophytes and groundwater uptake

Transfer of metals in transported cover through shallow roots (top 500 mm) does not appear to be a viable mechanism. However, many plants in arid environments have adapted to cope with different water and nutrient sources available in the landscape. One adaptation, notably in dry environments such as Australia, is that phreatophytes (deep rooted plants) send their roots into the deep groundwater or capillary fringe

to obtain water for transpiration and photosynthesis during the dry summer months (Ehleringer and Dawson, 1992; Canadell and Zedler, 1995). Many phreatophytes have dimorphic root systems with a set of laterals radiating from the main root crown, and a sinker or tap root, growing vertically into the regolith (Fig. 5A; Dawson and Pate, 1996; Pate et al., 1998). Evolving a dimorphic root system appears to be necessary to exploit different water sources during an entire wet–dry cycle or throughout droughts, so a continuous supply of water is maintained. The laterals roots are generally restricted to the top 500 mm of the soil; the tap roots penetrate much deeper, being limited by the water table or hard regolith. A survey of root penetrations indicates that deep roots, especially sinkers, are ubiquitous with > 10 m depths recorded for several species in several climatic settings (Canadell et al., 1996). *Acacia* and *Eucalyptus* woodlands are common in arid Australia. There is very little published information on the maximum penetration of *Acacia* and *Eucalyptus* roots but they commonly reach > 10 m depth and > 15 m in Western Australia (Kimber, 1974; Dell et al., 1983; Pate et al., 1998; Radford and Boddington, 2005; MacFarlane et al., 2009; Lintern et al., 2013; Anand et al., 2014) and elsewhere up to 60 m (Burgess et al., 1998; Le Maitre et al., 1999; Ludwig et al., 2003). Even small plants, such as *Triodia*, have deep root systems that belie their stature (Reid et al., 2008). Anecdotal evidence from open pit mines in the Yilgarn Craton indicates that roots occur deeper than 50 m. The biggest impediment to constructing an objective analysis of rooting depths and their functions is reliance on rudimentary techniques such as trenches and mine and road cuts to study rooting depth, root density, and efficiency of deeper root nutrient uptake (Canadell et al., 1996). New techniques such as root DNA sequencing to determine species of roots show promise (Jackson et al., 1999).

Knowing the source of water used by trees is critical to determine the significance of biogeochemical anomalies in plants. Hydrogen isotope (deuterium,  $\delta^2\text{H}$ ) signatures of soil and groundwater allow some inference of the depth of water accessed by plants. These studies have been conducted in a number of geographical regions. Isotopic studies in Australia have confirmed the dependence of specific plant species (e.g., *Acacia aneura*, *Eucalyptus* sp.) on groundwater or deep regolith water during dry seasons, with root depths of 6–20 m (Fig. 5B; Dodd and Bell, 1993; Dawson and Pate, 1996; Pate et al., 1998; Zencich et al., 2002; MacFarlane et al., 2009; Anand et al., 2014). In the Californian savanna, the *Quercus douglasii* (blue oak) switched from soil water in the wet season to groundwater at a depth of 9 m in the dry season (Gou and Miller, 2014). Studies in South Africa on root penetration and water extraction from a deeply weathered granitic 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). The extent to which a species relies on groundwater as compared to soil water depends on the availability of permanent or ephemeral water sources (Thorburn and Walker, 1994; Mensforth et al., 1994; Zencich et al., 2002). These studies confirm that specific plants tap into deeper sources of water and therefore have the potential to transfer metals from the groundwater to the surface and release metals to the soil as litter (Fig. 5B). However, a larger number of stable isotopic studies of plant and groundwater uptake are required from different environments, especially arid and tropical regions to confirm or define limitations to seasonal metal transfer from subsurface to above ground plant tissues.

The cycling of lithophile elements such as P, Ca, K and Si by plants often leads to an upward transport that causes a surface enrichment of these elements that cannot be explained by abiotic processes (Lucas, 2001; Amundson et al., 2007). Biological uplift of Si has been proposed as the mechanism for the unanticipated kaolinite-rich horizons that overlie oxide-rich horizons in the warm, humid tropics (Lucas, 2001). The release of Si from litterfall is greater than Si released by mineral weathering, thereby maintaining a near-surface, Si-rich mineral assemblage that would otherwise be impossible under abiotic conditions (Lucas, 2001). Vegetative cycling of Au has been suggested to



**Fig. 6.** 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. The inverse of this function also works where soil water is transferred downwards.



have formed a 5 m thick supergene laterite Au deposit over a period of 5 Ma in the rainforest region of Brazil (Andrade et al., 1991). In recent years, a biogeochemistry research program, using a wide variety of native trees and bushes, has been undertaken in a variety of regolith-landform settings and groundwater regimes in arid Australia. In the Yilgarn Craton of Western Australia, studies show that metals are taken up by both lateral and sinker roots but the extent of the presence of metals in deep rooted plants are determined by the metal source, depth of transported cover, nature and depth of groundwater. Analysis of *Acacia*, *Eucalyptus* and *Spinifex* (*Triodia* sp.) foliage and leaf litter provide indicators to the composition of water in the deep regolith and/or bedrock, and correlate with the position of an underlying ore body, where the transported cover is up to 20 m thick and rarely 30 m (Anand et al., 2014). However, if the groundwater occurs within 10–20 m of the surface and is not hypersaline, the depth of transported cover ceases to be a barrier (Reid et al., 2008; Lintern et al., 2013). Where water tables are deep (>20 m) and transported cover is <20 m thick, it seems to be important to have a source of metals in the upper in situ regolith as it is highly unlikely that roots will penetrate sufficiently to reach lower mineralized regolith (Anand et al., 2007; Reid et al., 2009; Lintern et al., 2013; Anand et al., 2014). Vegetation anomalies may not span the entire sub-surface dispersion halo. In other regions such as in the Curnamona Province (South Australia), southwestern Thomson Orogen (New South Wales) and Northern Territory, mulga (*A. aneura*), *Eucalyptus*, White cypress pine (*Callitris glaucophylla*), *Spinifex* (*Triodia* sp.), bluebush (*Mairean sedifolia*) and bladder saltbush (*Atriplex versicaria*) have been successfully used for locating mineralization through shallow (2–20 m) transported cover (Lintern and Sheard, 1998; Hill, 2004; Giblin, 2005; Hulme and Hill, 2005; Hill et al., 2005; Hill et al., 2008; Fabris et al., 2008; Reid et al., 2009). These studies provide strong evidence that vegetation is able to detect a signature through shallow (20 m) transported cover but significant vertical movement from depths of more than 20 m is unlikely.

#### 4.1.2. Hydraulic lift

Hydraulic lift moves water from relatively moist, high water potential to dry, low water potential soil layers, through plant roots (Fig. 6; Richards and Caldwell, 1987; Caldwell et al., 1998). Transfer of water along water potential gradients occurs diurnally; differences in transpiration rates between day and night determine the rate of water use by plants. During the day, water from all depths is taken up and travels through the plant in the transpiration stream to be evaporated from the leaf stomata. When the leaf stomata are closed at night and the water potential difference between deep roots and shallow dry roots is high, water is brought up, but largely released into the drier soil layers, rather than taken up by the plant in the slower transpiration stream (Fig. 6). This released water is then reabsorbed by the shallow roots and transpired during the day. The general direction of hydraulic lift is from the subsurface to 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).

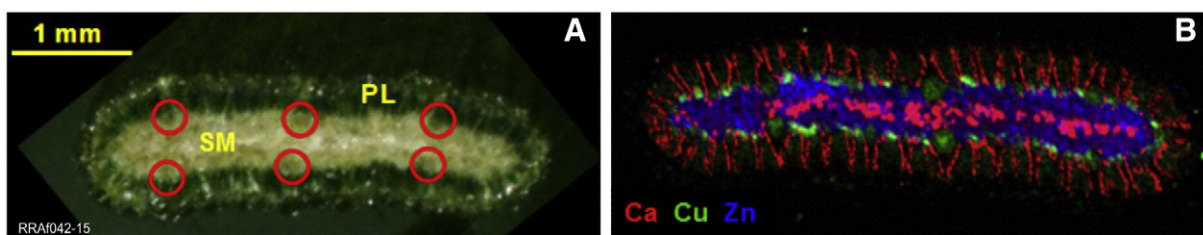
Although, initially, the theory of hydraulic lift was questioned (Caldwell et al., 1998), deuterium isotope studies combined with heat pulse measurements have proved its operation, and over 50 species from Africa, North America, Australia and Brazil have been documented to display hydraulic redistribution. However, the amount of water lifted is unclear; estimates range from very little to over 100 l/day (Moreira et al., 2003). 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.

#### 4.1.3. Metal uptake and transformation

Metallic nutrients are either not available in highly leached regolith environments or where present are tightly “bound” to soil particles (minerals and mineral aggregates) and are poorly 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 (Fig. 5C–F). This enables plants to acquire and uptake a range of ore related metals (Jones, 1998), both essential micronutrients (S, Zn, Cu, Mo, Ni) and metals with unknown biological function (As, Cr, Pb, Co, Ag, Cd, Hg). Roots in general also exude a variety of organic acids that either stimulate bacteria to sequester nutrients or facilitate the complexation and solubilization of non-bioavailable nutrients (Dakora and Philips, 2002) (Fig. 5F). 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 (Fig. 5F). The influence of mycorrhizae in the uptake of micronutrients at depth rather than the top soil is unclear.

The entire process of metal uptake from the root to above ground tissues by plants is complex and only a brief overview is provided. The metal can enter the xylem either through the symplastic or the apoplastic route. Once in the xylem, the flow of the xylem sap in response to transpiration transports the metals to the shoots and leaves. In the leaves, the metal will cross a membrane to be sequestered into the leaf. The metals dissolved through the roots are transferred and stored in diverse plant cell types as different metal species. For example, Cu is not readily mobile in many plants but it is known that nicotianamine (NA), a nitrogen containing protein, participates in the loading of Cu in xylem (Curie et al., 2009). The Cu–NA complex is stable under mild acidic conditions, which suggests that it could be found in an ‘apoplastic’ environment such as the xylem (Curie et al., 2009). Uncoupling of this complex at the end of the transpiration stream in the leaf may result in accumulation of Cu near the vasculature which would account for the higher concentrations observed in this region of the *Acacia* phyllode at Jaguar VMS deposit (Fig. 7; Smith and Hough, 2009). Slightly less concentrations of Cu occur in the palisade layer, which is the main site of photosynthesis. Some of the highest concentrations of Zn in *Acacia* phyllodes are near the vasculature (Fig. 7; Smith and Hough, 2009). A similar distribution occurs in the leaves of the gray mangrove (*Avicennia marina*). Zinc concentration decreases with increasing distance from the vasculature (MacFarlane and Burchett, 1999). It is unclear why Zn does not diffuse equally into the cells of both the palisade layer and spongy mesophyll of the *Acacia*, but predominates in the latter.

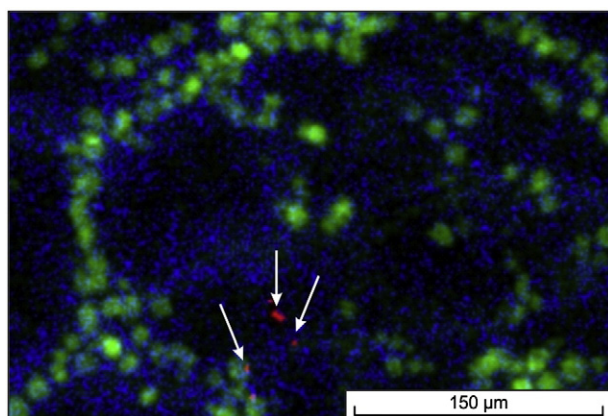
The uptake of toxic metals requires special mechanisms of detoxification and storage, and three general mechanisms employed by hyperaccumulators are chelation, compartmentalization and biotransformation (Salt et al., 1998; Fig. 5C,D). In response to toxic metal stress, plants produce two main metal-binding polypeptides: metallothioneins (MTs) and phytochelatins (PCs). These peptide ligands chelate metals, reduce the concentration of free metal ions in tissue solutions and thereby limit damage to metabolic processes. The toxic metals and metal-chelates are subsequently sequestered into specific sub-cellular compartments, by binding to cell walls, cytosol and vacuole, with most chelated species being stored in the cell vacuole (Fig. 5D). The dissolved metals can also be biotransformed and converted to inorganic (reduced), organic or colloid species within the plant tissue, to reduce metal toxicity (Fig. 5D). Many toxic mineralization-associated elements (As, Cd, Se, Pb, Cr, Au, Hg, Sb) are immobilized by binding to organic complexes (sphytochelatins and thiols). This prevents them occurring as free ions and thus achieves detoxification. For example, As occurs in more than one species in plant tissue which may be chelated with phytochelatins (Meharg and Hartley-Whitaker, 2002). Gold nanoparticles can form within tissues of live plants (Lintern et al., 2013; Fig. 8). Gold enters roots most likely in a soluble form. Inside cells, this soluble Au is reduced to Au<sup>0</sup> and/or transported to the shoots. In the shoots it



**Fig. 7.** A: Optical image of the cross section of an *Acacia* phyllode. PL = palisade layer, dark green in color. SM = spongy mesophyll in the center of the phyllode. Red circles indicate approximate location of major vascular bundles. B: PIXE three element map showing the distribution of Ca, Cu and Zn in the cross section of an *Acacia* phyllode collected at the Jaguar VMS deposit in Western Australia. Modified after Smith and Hough (2009).

may be stored in vacuoles, associated with cell walls or in intracellular spaces.

In northern hemisphere ecosystems with contrasting seasons, metal contents in plants, particularly foliage, are seasonally variable (Stednick et al., 1987). In Australia, much of this variation is related to new growth, which follows significant rainfall events, particularly during the summer. Temporal water uptake studies show less variation in As, Zn, Cu, Ag and Ni and a greater variation in Au (e.g., Hulme and Hill, 2004; Anand et al., 2007; Lintern et al., 2008). The variability may reflect better tolerance for specific metals or a tendency for seasonal uptake of Au suggesting that care should be taken when comparing samples from different sampling programs. The question of the type of species and the particular organ that best accumulates metals to uniquely reflect mineralization has been addressed in a number of studies. Results have shown that foliage provides the most consistent results (Lintern et al., 2008; Lintern et al., 2013; Anand et al., 2014). However, there are differences in metal contents between phyllodes/leaves and twigs. For example at the Moolart Well Gold deposit in Western Australia, essential elements for plant growth (Zn, Mn, B, Mg and Se) and Au are enriched in phyllodes relative to twigs. In contrast, non-essential element contents (Cd and Pb) in twigs are about two and a half times greater than phyllodes (Anand et al., 2007). Particulate Au in *Eucalyptus* (Lintern et al., 2013) and non-uniform distribution of Au in *A. aneura* (Anand et al., 2014) and *Casuarina luehmannii* and *C. glaucophylla* (Roach and Walker, 2005) causes problems with sample homogeneity. Other elements such as Zn, Ni, Cu and U do not show large variations (nugget effect). *A. aneura* has many phyllode types but the type of phyllode does not appear to control the metal distribution (Reid et al., 2010; Anand, unpublished data). Consistency in sampling plant material is necessary to minimize sampling-related variation.

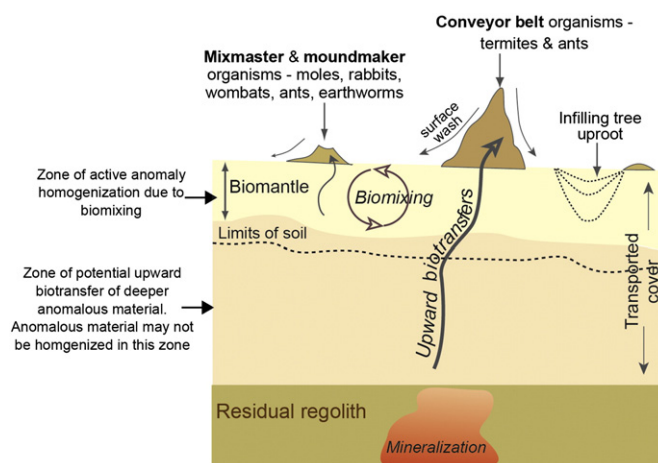


**Fig. 8.** Particulate Au in leaf and roots from natural specimens of *Eucalyptus*. Detailed synchrotron  $\mu$ XRF image showing isolated particulate Au grains (red, arrowed) and two of which are attached to the surface of Ca oxalate crystals (green) from the Freddo Au deposit in Western Australia. Modified after Lintern et al. (2013).

#### 4.2. Bioturbation

Bioturbation by a myriad of regolith meso and macro fauna and macro flora homogenize the biомantle and also homogenize metals brought to the surface by other mechanisms and may transfer anomalous material from depth (Fig. 9). The bioturbators can be classified according to their bioturbation style as proposed by Johnson et al. (2004; there are more than two but only relevant ones are discussed here): (A) 'Conveyor-belt' organisms (termites, ants) that transfer material from the biомantle and deeper, into the near surface biомantle and along the surface; and (B) 'Mixmaster' organisms (moles, pocket gophers, wombats) that mix the soil dominantly within the biомantle. Their processes of metal transfer and anomaly homogenization are illustrated in Fig. 9.

Termites burrow to the subsoil and contribute to soil profile development (Watson, 1970). Consequently, termite nests have long been used as a geochemical and mineralogical sample medium for prospecting beneath weathered cover and shallow sediments (Watson, 1970; d'Orey, 1975; Gleeson and Poulin, 1989). There are several reports documenting great depths of termite galleries, especially in search of water, and some are reported in Table 2. Many reports of deep termite galleries are from environments mostly in Africa, often sand-dominated settings. A statistically robust method to evaluate ant and termite depth was considered by Jensen and Hooten (2000) where the depth to which a percentage of ant and termite species burrow was reported. Jensen and 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



**Fig. 9.** 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).

**Table 2**  
Extreme bioturbation depths recorded in specific countries.

Depth (m)	Region	Reference
70	Kalahari, Africa	Lock (1985)
70	Africa	Yakushev in Lee and Wood (1971)
45	Sahel	Lepage et al. (1974)
25	Iraq	Awadh (2010)
24	Zimbabwe	West in Gleeson and Poulin (1989)
10–15	Africa	Ghilarov in Lee and Wood (1971)
6	Australia	Davison in Lobry de Bruyn and Conacher (1990)
5	Australia	Stewart et al. (2012)
5	Australia	Petts et al. (2009)

Hooten, 2000). However, their analysis was restricted to specific dry North American locations.

Termite nests studied for mineral prospecting in Africa have generally been large. Studies have focused on *Macrotermes* sp. from Africa that attain heights of several meters and are up to 10 m across (Watson, 1970; d'Orey, 1975). However, research to date has indicated that smaller mounds that are common in the Australian interior are equally effective at vertical transport of subsurface material (Petts et al., 2009). The termite species (*Tumulitermes tumuli*) forms mounds up to 600 mm in height (Stewart et al., 2012; Stewart and Anand, 2014). Termites penetrate deeply for water, and this is often used as evidence of their ability to transport subsoils vertically. However, the depth to which termites can forage for water is different from the depth from which termites vertically move subsoil. Awadh (2010) showed termites (species and nest size unknown) could penetrate to 25 m in the Western Desert of Iraq. However, inclusions in their mounds of distinctive sands showed transported materials were from only the top 2–4 m of transported cover. The much referenced paper by d'Orey (1975) described seven nests (*Macrotermes* sp.) in central Mozambique containing anomalous levels of Cu and Ni, where local colluvial cover was 15 m thick. It is not clear if the source of the metals in the termite mounds was actually from the ore body or from a much shallower transported cover. Likewise, an investigation of four termite species (*Macrotermes bellicosus*, *Macrotermes natalensis*, *Odontotermes latericius* and *Rhadinotermes coarctatus*) in the Kalahari Desert of Zimbabwe reported high Zn concentrations in termite mounds over mica schist buried by 10 m of transported cover, but the immediate source of Zn incorporated in termite nests was demonstrated to be from subsoil at a depth of 60–274 cm (Watson, 1970). There is no evidence for a correlation between termite mound size and the depth of soil bioturbation.

Termite studies in Australia and Africa have demonstrated vertical movement of soil from up to four meters depth (Hesse, 1955; Gleeson and Poulin, 1989; Petts et al., 2009; Stewart et al., 2012; Stewart and Anand, 2014). At Moolart Well gold deposit in Western Australia, evidence of incorporation of deep regolith sources within termite nests was discovered in the form of small ferruginous pisoliths that are very rich in Au. These occur within termite nests but not in surrounding soil (Stewart et al., 2012). Within the regolith, pisoliths characterize the supergene zone several meters from the surface. Where the depth of mineralization is greater than 5 m, there is no expression within the nests. This provides strong evidence that *T. tumuli* nests have an effective bioturbation profile of 5 m. It is clear that termite activities influence relative elemental abundances in soils immediately adjacent to mounds. This halo extends at least 1 m for Au (Stewart et al., 2012). This is important specifically in relation to exploration sampling protocols that may otherwise ignore these processes resulting in unnecessary sampling 'noise'.

Analysis by Particle Induced X-ray Emission (PIXE) spectroscopy and synchrotron  $\mu$ XRF spectroscopy has been used to map mandibles of termites and ants (Ohmura et al., 2007; Stewart et al., 2011). The aim of this work was to determine specific distribution of metals in the termite *T. tumuli* (Froggatt) and identify specific organs within the termite that host elevated metals and therefore play an important role in the

regulation and transfer of these back into the environment. Whole body PIXE imaging of termites over a VMS deposit in Western Australia reveal local concentrations of Fe, Zn, Cu, Ca and Mn (Fig. 10; Stewart et al., 2011). Iron is found throughout the termite with local high concentration spots predominantly in the antennae, head and lower abdomen. High Zn concentrations ( $\approx 2\%$ ) appear as lines through the abdomen corresponding to Malpighian tubules. Copper and Mn appear confined to specific anatomical structures, predominantly the Malpighian tubules, however Ca and Fe have a much more scattered distribution. The centralized nature of nest structures results in insects excreting within the nest. These excretory products contain concentrations of key elements (e.g. 1.6% Zn). Through this, concentrations of many elements (e.g. Ca, Na, Mg, S and Zn) occur within nests compared to the surrounding soil. Elements accumulated in the nest are likely to occur in highly soluble forms, allowing rapid leaching and a consequent halo around individual nests (Stewart et al., 2011).

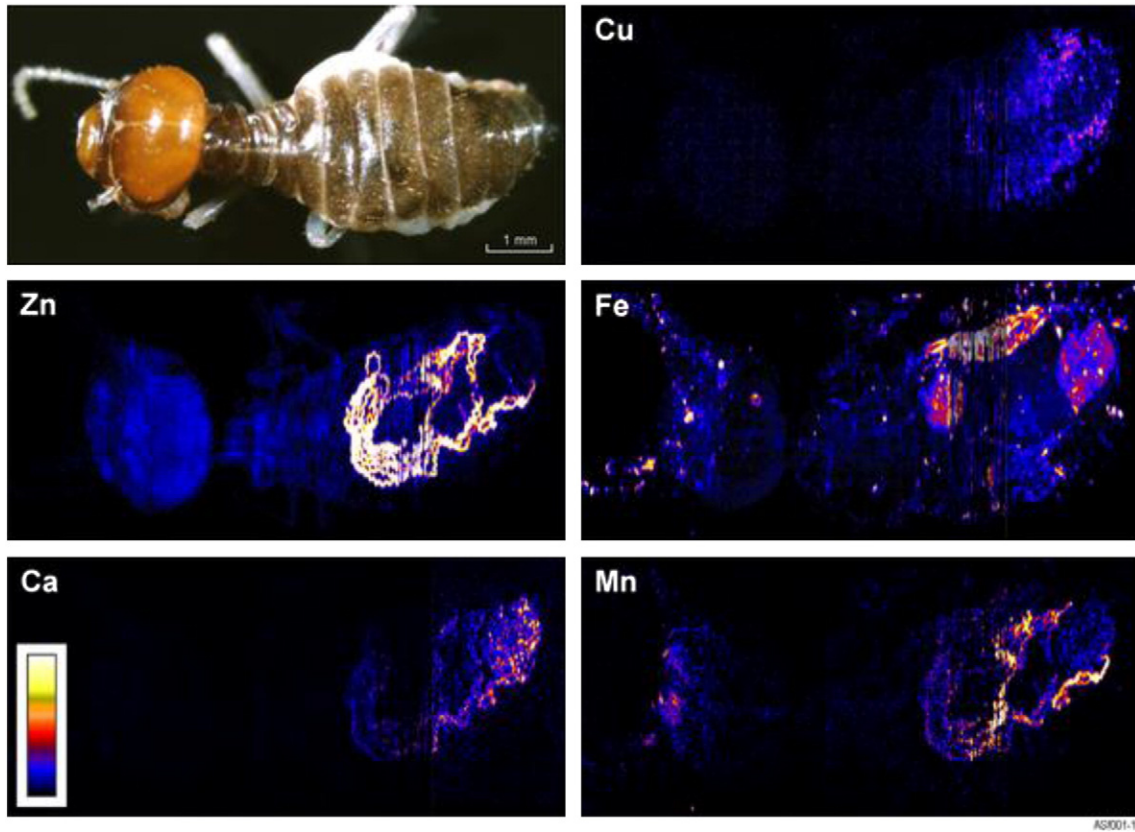
#### 4.3. Capillarity

Capillary rise can bring metal-bearing waters several meters above the water table and therefore is a potential mechanism of upward metal dispersion. Water at the water table is subject to an upward pull due to surface tension of the mineral–water interface. Immediately above the water table (pressure head  $p = 0$  at water table), pores are saturated but the pressure head is less than atmospheric ( $p < 0$ ). The negative pressure head or tension above the water table drives the 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) (Fig. 11). The upper limit of rise of the water due to capillary action from the water table is the capillary fringe (CF) (Berkowitz et al., 2004). Water held between grains is due to capillary forces, while water adsorbed on mineral grains such as hydration envelopes is due to adhesion (Fig. 11).

The distance of capillarity depends on the nature of the soil and the degree of dryness. Clay soils exert greater capillarity than sand or silt, and dry soil more than damp soil. 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 ( $\sim 4 \mu\text{m}$ ) and even up to 37 m in coarse clays ( $2 \mu\text{m}$ ). Kelley et al. (2003) suggested that anomalies could form by capillary rise of groundwater into soil through a thin sedimentary cover. Fontes et al. (1986) described a site in the Sahara desert where capillarity draws water to the surface from a depth of 10 m. Keeling (2004) provided an example where capillary rise may have occurred in clay sediments above mineralized basement, but not where clay sediments were interrupted by sands. This highlights the importance of texturally heterogeneous regolith where capillary-driven water movement across the stratified grain size (clay versus coarse gravel) materials is likely impeded. 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 1 m through stratified textured materials needs to be evaluated. Mann et al. (2005) found that capillary rise of metal-bearing water was up to 1 m high within a short time in laboratory experiments. Recently, pit experiments provide evidence for upward movement of Cu, Zn and Au by capillarity in unsaturated conditions through 2 m of sandy to sandy clay material over a period of seven months in a Mediterranean climate (Anand et al., 2009, 2014). It was suggested that anomaly formation for Cu and Zn in this pit experiment is an episodic and cyclic process largely driven by capillarity where batches of metals in water-soluble form are introduced in soil.

In arid areas, the water table is at greater than 10 m depth and therefore it is unlikely that this mechanism of metal transport would independently be sufficient to develop surficial anomalies. However, capillarity can combine with vegetation to transfer metals to the near

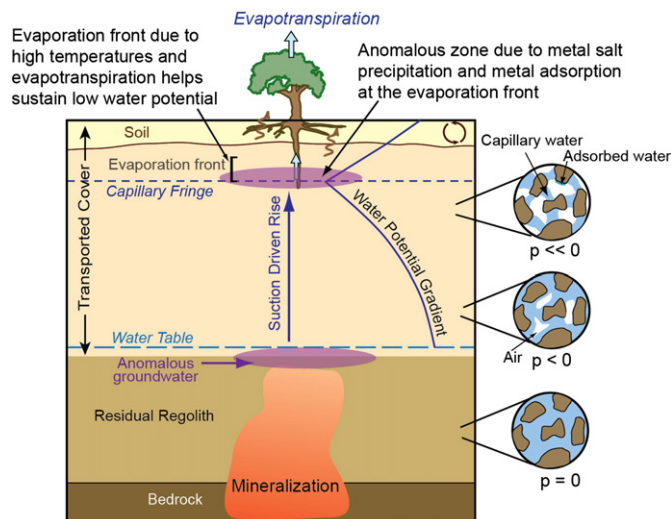




**Fig. 10.** Composite PIXE image of a worker termite (*Tumulitermes tumuli*) showing distribution of Cu, Zn, Fe, Ca and Mn. More intense colors indicate higher concentrations of metals. Iron appears concentrated around the antennae and lower abdomen; Zn and Ca in the Malpighian tubules with a weak accumulation over the entire body of Zn; Mn is concentrated within the Malpighian tubules and mandibles. Modified after Stewart et al. (2011).

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 vapor 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 (Fig. 11). The precise depth at which the evaporation front develops varies with annual precipitation and soil types. The high loss of the water from the root zone and just below due to evaporation and evapo-transpiration creates a drying front which can gradually move downwards. The evapotranspiration 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 (sulfates, 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 together to transfer metals upwards through a greater distance than capillarity alone. An example of an evaporation front causing the precipitation of salts by capillary upflow is documented in salt crystallization in soils with shallow groundwaters and in the experiments conducted by Mann et al. (2005).



**Fig. 11.** Capillary driven rise of mineralized water to the evaporation front. Drying at the evaporation front due to high temperatures and evapotranspiration will induce high suction 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.

**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?



#### 4.4. Gaseous dispersion

Soil gases offer a good potential mechanism for metal migration because of their high mobility through transported cover (Klusman, 1993). Gases are not as limited by the distance of vertical dispersion, as is biogeochemical cycling by tree root depth or water table depth or capillarity limitations for hydromorphic dispersion. Soil gases are produced by chemical, biological and physical processes, all of which depend on the environment. Factors that affect their formation, upward transfer and their ability to manifest a mineralization-related anomaly in the soil are listed in Table 4 and illustrated in Fig. 12. No known gases are uniquely related to ore deposits, and most species can be generated by several mechanisms including biological action unrelated to ore deposits (Kelley et al., 2006). Anomalous CO<sub>2</sub> enrichment and O<sub>2</sub> depletion in soil gas over buried mineral deposits have been documented (Hinkle and Dilbert, 1984; McCarthy et al., 1986; Lovell, 2000; Zhang, 2000; Polito et al., 2002). The origin of these signatures is controversial (Kelley et al., 2006). In one example, McCarthy et al., (1986) showed that a strong O<sub>2</sub> depletion of 4.5% (maximum of 20.9%) and a CO<sub>2</sub> enrichment of 3.8% (minimum of 0.035%) occurred above the Crandon VMS deposit, Wisconsin. This deposit is covered by 65 m of glacial till. Biological metabolism within soil produces CO<sub>2</sub>, COS and CH<sub>4</sub> (Table 4) and has a strong influence on the composition of soil gas (Amundson and Davidson, 1990). For example, Alpers et al. (1990) studied the stable isotopic composition of soil CO<sub>2</sub> over the Crandon deposit and found that anomalous concentrations reported by McCarthy et al., (1986) were derived from root respiration rather than from mineralization. Despite the complex and multiple origins of soil gases, numerous gas species (e.g., CO<sub>2</sub>, O<sub>2</sub>, Hg, Rn, He, sulfur compounds, and light hydrocarbons) appear to be related to buried mineral deposits (Carr et al., 1986; Klusman, 1993; Hale, 2000; Pauwels et al., 1999; Polito et al., 2002; Klusman, 2009; Muntean and Taufen, 2011; Noble et al., 2013). Specific ore bodies have been shown to contain varying amounts of light hydrocarbons having C chains of C<sub>1</sub>–C<sub>9</sub> and include methane, ethane and propane (Disnar, 1990; Hulen and Collister, 1999; Polito et al., 2002).

Dispersion of gases depends on the properties of the gas and the medium through which it travels. In theory, three transport mechanisms affect the migration of gases: diffusion (concentration gradients), advection (pressure gradients) and buoyancy (or bubble migration) (Hale, 2000; Ruan and Fei, 2000). 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 illustrated in Fig. 13. Gaseous diffusion experiments suggest that gases will diffuse rapidly along paths of least resistance such as contacts and structural conduits (Ruan et al., 1985). Most studies on gas measurements, where faults and other structural elements associated with the ore body were established, have noted the higher CO<sub>2</sub> (Etiope, 1999; Highsmith, 2004; Polito et al., 2002), Hg (Carr and Wilmhurst, 2000), CH<sub>4</sub> (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) above faults or shears. This strong correlation between preferential pathways and gas anomalies at the surface suggests the diffusion assisted by atmospheric pumping mechanism transfer gases rapidly via conduits to the surface (within days to years). However, what remains unclear is the nature of gas transport and extent of dispersion through structurally unaffected or non-fractured transported cover, which in many cases manifests strong physical and chemical heterogeneity due to the weathering overprint. Simulations of diffusion of volatiles 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 connections between pores remain critical to 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<sub>2</sub> and CH<sub>4</sub> 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 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.

Support for advective transfer of gases comes from detonation of nuclear devices 400 m below ground in fractured, bedded tuff. The detection at ground level of specific gases and volatiles (I<sub>2</sub>) released by 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 a barometric or atmospheric mechanism coupled with minor gas diffusion

**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 <sub>2</sub> and O <sub>2</sub>	Oxidizing sulfides, deposit related carbonate reaction, consumption of O <sub>2</sub>	Regolith microbial metabolism; introduction into groundwater via recharge; natural degassing	Lovell (2000)
Sulfur: COS, CS <sub>2</sub> , SO <sub>2</sub> , H <sub>2</sub> S, CH <sub>3</sub> SH	Sulfides & oxidizing sulfides, especially pyrite	Regolith microbial metabolism generates similar gases; temporal and oxidative stability very low for some gases	Taylor et al. (1982), Hinkle et al. (1990), Oakes and Hale (1987)
Mercury: Hg	Weathering of sulfide minerals: epithermal base-metals, VHMS	Microbial metabolism transformations to metal; adsorb within overburden matrix	Carr and Wilmhurst (2000)
Radiogenic daughters: Rn, He,	U and Th sources; mineral sands, kimberlites	Natural degassing from rocks; Rn very short-live; atmospheric interferences	Butt et al. (2000b), Dyck and Jonasson (2000)
Light hydrocarbons: C <sub>1</sub> –C <sub>10</sub>	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), Mulshaw (1996), Polito et al. (2002)
Organometallics: CH <sub>3</sub> As, (CH <sub>3</sub> ) <sub>3</sub> Sb, CH <sub>3</sub> I, (CH <sub>3</sub> ) <sub>2</sub> Se, CH <sub>3</sub> Hg	Weathering of sulfides to release metal(loid) and microbial metabolism to produce organometallics	Many require reducing environment and/or appropriate strain and quantity of microorganism	Hirner et al. (1998)
Halocarbons & halogens: CH <sub>3</sub> Cl, CH <sub>3</sub> I, CH <sub>3</sub> Br	Weathering of Pb–Zn sulfides; alkalinization of halides during oxidation of organics; fungi	High temperatures or organic matter and specific microorganisms required for volatilization — higher in soil	Keppeler et al. (2000)
Volatile hydrides: AsH <sub>3</sub> (arsine), SbH <sub>3</sub> (stibnine), NiH <sub>3</sub>	Weathering of sulfides — reducing conditions	Trace quantities produced and hydride stability in natural air limited to days	Klusman (1993), Turpeinen et al. (2002)

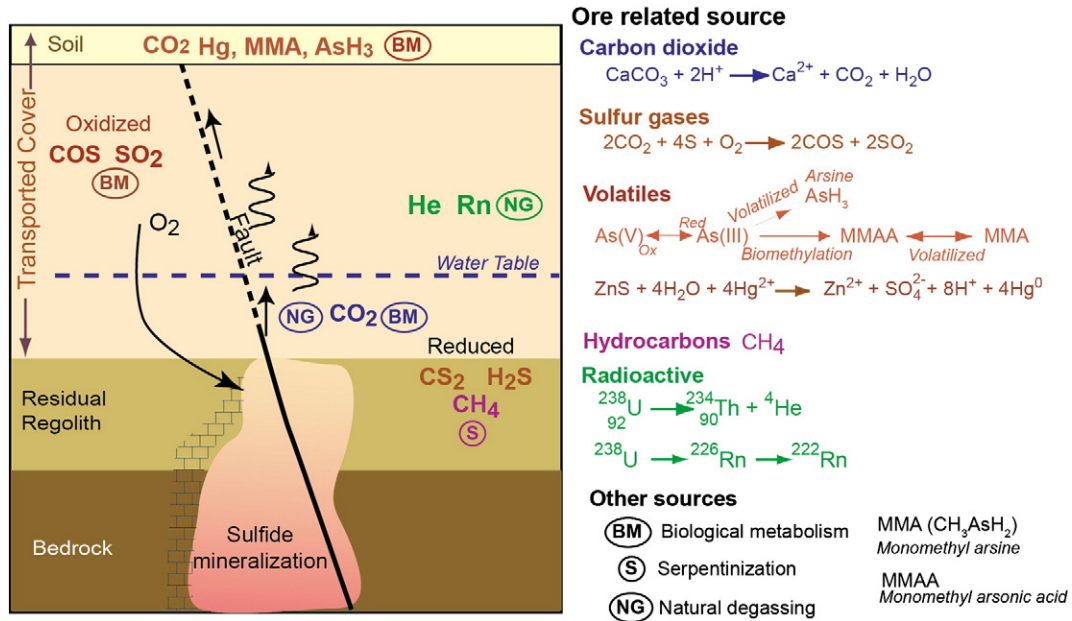


Fig. 12. The source of different gases and volatiles whose concentrations are used as indicators of buried mineralization (Sourced from Table 4).

(Cameron et al., 2004). The advective transfer of gases through stimulated barometric pressure gradients have been employed in remediation of organic contaminants where artificially induced pressure changes force fresh air into the ground and organic vapors are

pumped out. Although the barometric pressure induced advective gas flux is limited to fractured media, it can be active in a heterogeneous, porous sedimentary regolith, especially if long time scales are considered.

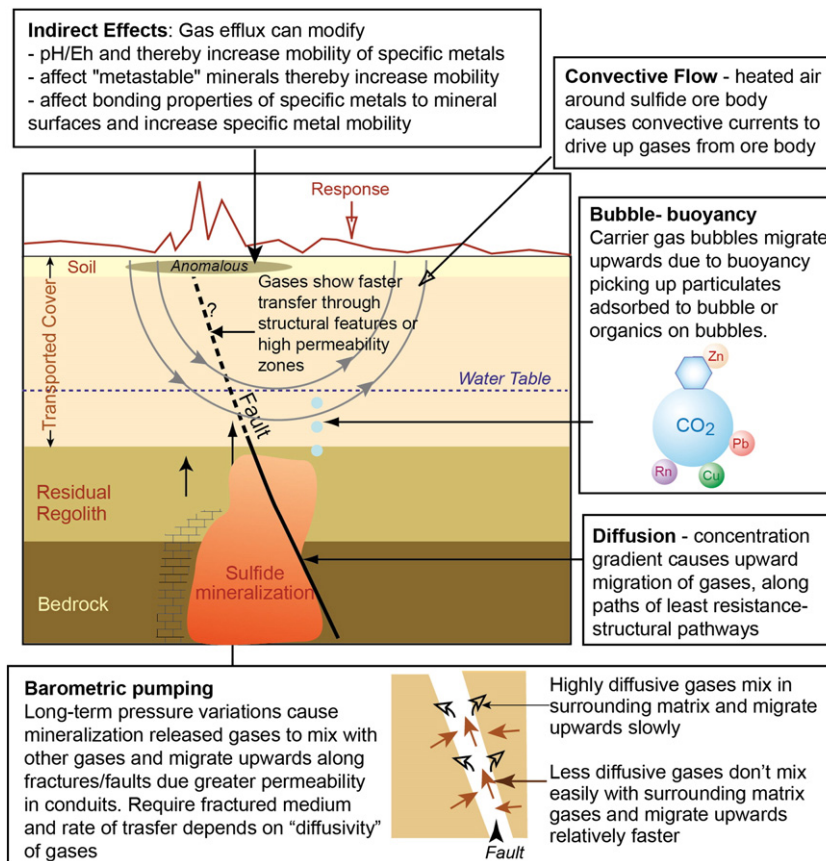


Fig. 13. The gas based mechanisms of metal transfer from buried mineralization to surface. Surface gas surveys show higher concentrations of gases corresponding to subsurface conduits like fractures and faults. This is likely due to faster diffusive and advective flow along paths of least resistance. The indirect pathway of anomaly formation due to gases will also be reflected above subsurface conduits.

Some workers have suggested bubble streaming as a vapor phase migration in the phreatic zone (Kristiansson and Malmqvist, 1982; Etiope and Martinelli, 2002). 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. The gases with sufficient concentration to form bubbles are referred to as carrier gases and are predominantly CO<sub>2</sub> and CH<sub>4</sub> (Etiope and Martinelli, 2002). Specific compounds (Cu, Zn, Pb, Hg, actinides) and ultra-fine particles (clays, oxides, bacteria) can attach to the surfaces of ascending gas bubbles, especially if the gas bubbles have an organic coating acquired from trace organics in groundwater (Malmqvist and Kristiansson, 1984). The bubbles move upwards to the near surface, where the bubbles burst and release attached metals (Malmqvist and Kristiansson, 1984). Several examples of vapor metal migration were shown by Kristiansson and Malmqvist (1987), Pauwels et al. (1999); Noble et al. (2013) and Anand et al. (2014) using collector devices buried in soil. The main reason for difficulty in evaluating bubble associated transfer of metals is the poor knowledge of stability and behavior of bubbles or a bubble “stream” above the water table within the unsaturated zone. Hamilton (2000) and Kelley et al. (2006) have questioned the formation of bubbles below the water table on a physical and chemical basis. For a bubble to form, the sum of partial pressures for all dissolved gases must exceed the hydrostatic pressure, which increases with depth below the water table (Kelley et al., 2006). The stability of bubbles during their transfer from a saturated to an incompletely saturated medium as well as the fate of adsorbed matter on bubbles, when the bubbles burst, remains unclear. More recently, laboratory studies have shown that Au nanoparticles can be transported by gas through alluvial cover (Cao et al., 2010). The study of Cao et al. (2010) complements field observation of metals in gas collector devices like those of Wang et al. (2008) and Gao et al. (2011) among other previously cited references. Klusman (2009) also demonstrated by modeling that sub-micron particulate Au could be transported to the surface by air during barometric pumping. It is important that future studies expand on this by observing the particles retained in the gas collectors and apply it to other metal nanoparticles such as Ni, Cu, Zn, Pb and Ag.

The reasoning behind the formation of indirect anomalies at the surface from gases is based on subtle modification of the geochemical environment by continuous transfer of gases from an ore body to the surface over time or changes in microbial populations at the surface that in turn release specific gases. Gradual flux of methane as microseepages to the surface over gas fields could create a reducing environment in the soil directly above the gas field. This resulting reducing environment reduces 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 (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). The cases documented for indirect effects are largely confined to non-metalliferous mineralization, such as petroleum fields and nuclear blasts. The magnitude of hydrocarbon flow from a gas field would be far larger than would be expected from base metal or Au mineralization or the flux of iodine over an efflux conduit associated with a nuclear explosion (Hall et al., 1997). Nevertheless, it is important to investigate the long-term influence of gases released from mineralization and their formation of indirect surface anomalies.

#### 4.5. Microbes

Microbes (*Bacteria*, *Archaea* and Eukaryotes such as fungi and algae) are ubiquitous in the regolith and are now thought to influence, and in some places directly control, the geochemical cycle of many elements (Ehrlich, 1997; Konhauser, 2007; Gleeson et al., 2007, 2008). This influence may extend to a depth of 2 km of the Earth's crust (Newman and Banfield, 2002). Microbes have, as yet, not been suggested as a sole mechanism of metal transfer without the aid of another medium such

as water, air (bubbles) or plants. Microbes, however, positively and negatively influence the rate and efficiency of metal transfer by their metabolic activities in a range of environments and scales.

The influence of microbes on metal mobility and upward transfer 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 and metal solubilization (e.g. weathering of sulfides and oxidation of Fe and S).
- Biomethylation (and demethylation) of metals and nonmetals, affecting metal speciation, complexation, phase (aqueous, solid and gas) and mobility.

All the above reactions are due to the ability of microbes to accomplish redox reactions by their cellular functions. Positive and negative effects of microbial induced metal transformations on the different transfer mechanisms are highlighted in Table 5 and illustrated in Fig. 14.

##### 4.5.1. Immobilization and biomineralization of metals

Microbes assist in precipitating oxides, hydroxides, sulfates and metals within the regolith (Konhauser, 1998). They can interact with minerals and affect their structure by mechanical and biochemical mechanisms, and affect the speciation and mobility of component metals (Ehrlich, 1997; Gleeson et al., 2007; Gadd, 2008; Uroz et al., 2009). Where metal mobilization, transfer and immobilization are important for spatial distribution of metals, the role of microbes in Au and some pathfinder elements serves as examples. Several workers (e.g., Savvaidis et al., 1998; Reith, 2003; Reith et al., 2007; Southam et al., 2009; Reith et al., 2013) provide good reviews for gold–microbe interactions. In vitro studies on Au microbial interactions have demonstrated the capacity of a common soil bacterium, *Bacillus subtilis*, to take up mobile dissolved Au<sup>3+</sup> 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). Lengke and Southam (2006) focused on the mechanisms of Au<sup>3+</sup> (auric chloride) and Au<sup>+</sup> (aurous thiosulfate) precipitation by other bacteria. They show that

**Table 5**

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

Hydrochemical (general)	<ul style="list-style-type: none"> <li>• Limit mobility of metals by intracellular and extracellular mineral precipitation (biomineralization)</li> <li>• Increase the weathering rate (dissolution, complexation) of minerals facilitated by organic secretions (not quantified)</li> </ul>
Electrochemical	<ul style="list-style-type: none"> <li>• Iron and sulfur oxidizing microbes increase the rate of sulfide weathering</li> <li>• 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<sub>2</sub></li> </ul>
Gas	<p>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</p> <ul style="list-style-type: none"> <li>• CO<sub>2</sub></li> <li>• SO<sub>2</sub></li> <li>• Dimethyl mercury – Hg(CH<sub>3</sub>)<sub>2</sub></li> <li>• MMAA, DMAA, arsine</li> <li>• Dimethyl selenide (DMSe)</li> <li>• Trimethyl antimony (Me<sub>3</sub>)<sub>3</sub> Sb</li> <li>• Methyl iodide (CH<sub>3</sub>I)</li> <li>• Dimethyl telluride (CH<sub>3</sub>)<sub>2</sub>Te</li> </ul>
Vegetation	<p>Facilitate possible uptake of ore related metals through root systems: Mycorrhiza (fungi), excretion of exudates (organic acids) for metal complexation and facilitation of transfer into roots</p>



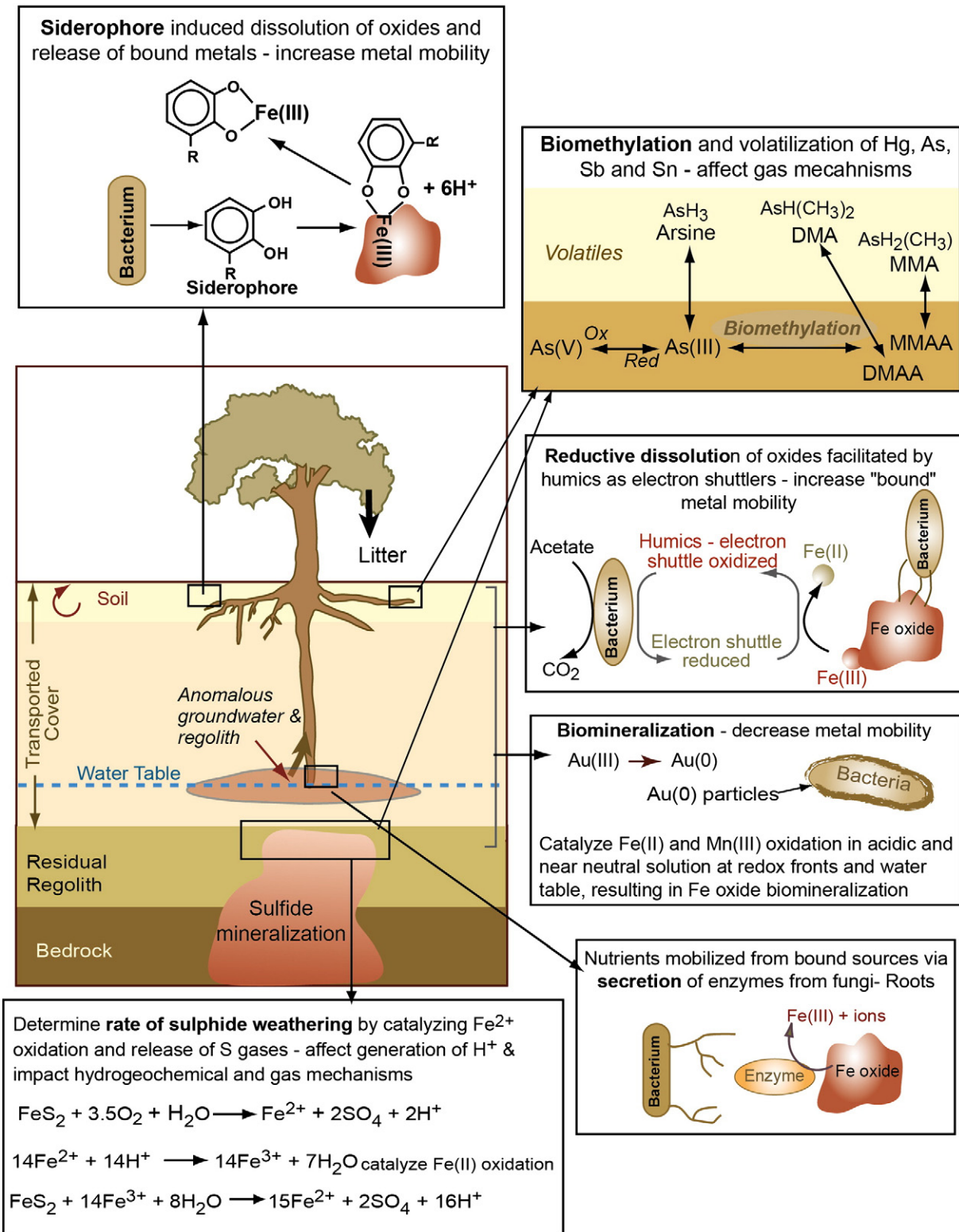


Fig. 14. The various processes by microbes can affect metal mobility and migration efficiency across the entire regolith.

reduction of Au<sup>3+</sup> to elemental Au by the cyanobacterium *Plectonema boryanum* involved the formation of an intermediate Au<sup>+</sup>-species, Au<sup>+</sup>-sulfide-with S originating from cyanobacteria proteins. Other studies have demonstrated the ability of antinomycetes (a filamentous or rod shaped bacterium) to precipitate gold nanocrystals, 5–15 nm in diameter on and within the cell walls without harming the bacterium

(Ahmad et al., 2003). Numerous other studies have shown the ability of algae and fungi to absorb gold (Savvaidis et al., 1998). The precise mechanism of Au uptake, reduction and precipitation remains unclear, but reactions on the plasma membrane are considered important in the ability of the microbe to bind gold. The origin of secondary Au grains in regolith has been the subject of discussion among geologists. Both



biotic (Reith et al., 2007, 2012) and abiotic (Hough et al., 2008; Hough et al., 2011) processes have been advocated for their formation. Biofilms dominated by *Cupriavidus metallidurans* have been observed on Au grains retrieved from soils and sediments from temperate and tropical Australian sites (Reith et al., 2007).

Another way microbes can affect metal mobility is 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 use O<sub>2</sub> as an electron acceptor to reduce a variety of metals from mobile to immobile forms (Lovely and Anderson, 2000; Lloyd, 2003) 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 that the microbial influence on metal mobility may be especially important in the weathered zone and soils (Sparks, 2005; Amundson et al., 2007; Brantley et al., 2007). Conversely, the presence of high concentrations of metals (e.g., Cu, Zn, As and Ni) can influence the microbial community and activity (Giller et al., 1998; Giller et al., 2009) with variable reduction in the size of the microbial community followed by a gradual adaptation to toxic metals (Turpeinen et al., 2004). Recently Wakelin et al (2012) has shown that the biogeochemical anomaly associated with the buried VMS mineralization at Jaguar in Western Australia is also expressed in soil microbial communities with Gemmatimonadaceae, Acidobacteriaceae, Oxalobacteraceae, Bradyrhizobiaceae, Caulobacteraceae, TM7 genera incertae sedis, and unclassified bacteria. These data significantly broaden our knowledge of the bacteria present in metallomorphic ecosystems, establish that mobile elements are key drivers of community structure, and that primary biogeochemical cycling is directly influencing other geochemical interactions in the samples.

#### 4.5.2. Mineral dissolution

Microbes, through their metabolic activities, directly and indirectly, affect the rate of metal complexation and dissolution of minerals. The nature and rate of sulfide weathering within the ore body underpins several phreatic zone and gas based mechanisms. The role of microbes in consuming O<sub>2</sub> by organic matter reduction, and thereby driving the expansion of “reduced columns” has been alluded to in the redox models of Hamilton (2000), but the capacity of different microbes to catalyze the dissolution of sulfides, oxidize the released Fe<sup>2+</sup> and/or oxidize sulfur or even reduce Fe<sup>3+</sup> within saturated environments is less understood.

The rate of oxidation and dissolution of sulfides depends on the availability of oxidants at the weathering front or the sulfide mineral surface. The mechanism of sulfide dissolution by enzyme oxidation on the sulfide surface with direct microbial contact is still debated, but results indicate preferential colonization of sulfides by specific microbes (Baker and Banfield, 2003). The increase in sulfide dissolution stems from the indirect pathway of microbes catalyzing iron and sulfide oxidation rather than dissolving minerals by surface contact. Studies in natural environments indicate the microbial induced rate for Fe (II) released by sulfide weathering accounts for 75% of the total Fe (II) release (Edwards et al., 2000). The number and level of activity of iron oxidizing cells determine the rate at which microorganisms enhance sulfide dissolution (Baker and Banfield, 2003). Recent studies indicate a high degree of biodiversity in the microbial communities that flourish within the extremely acid waters arising from sulfide mineral oxidation (Sánchez-Andrea et al., 2011). However, the studies to date have been on subsurface mine environments. Microbial communities on weathering sulfide ore bodies below transported cover may be different. The contribution of microbes in increasing the rate of sulfide dissolution and altering pH and Eh could also influence sulfur and CO<sub>2</sub> gas generation, formation of metal hydrides, electrochemical or redox gradients.

#### 4.5.3. Biomethylation and demethylation

Methylated metals and metalloids form by biomethylation, a process by which microbes transfer methyl groups to metal and metalloid cations (Craig et al., 2003; Fig. 13). Methylated compounds are known of some ore-related metals (Hg, Co, As, Se, Sb, Te, I, Bi, Sn and Pb) but the amount of metal that is biomethylated varies from being extremely minor (As) to large (Hg, Se). For example, As is biomethylated to produce volatiles such as arsine (AsH<sub>3</sub>), monomethylarsine (MMA), dimethylarsine (DMA) and trimethylarsine (TMA) by both fungi and bacteria (Turpeinen et al., 2002). Much of the work on biomethylation of ore related metals has been on laboratory cultures or estimated in specific environments (sewages and swamps); it remains to assess biomethylation qualitatively and quantitatively at the weathering front and within soil.

#### 4.5.4. Metal acquisition by plants

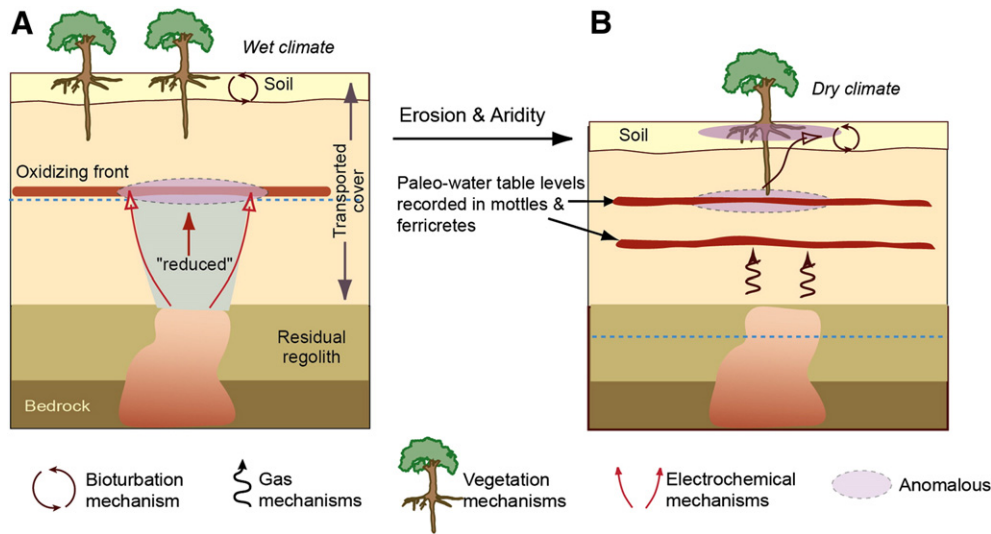
As in the regolith, microbes inhabit many parts of plants – from roots to leaves. Their role in the pumping cycle of metal transfer is confined to facilitating metal uptake by roots. The role of microbes in symbiotic association with roots of most plants is critical to the amount and efficiency of metal 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 decompose organic matter to produce enzymes that mobilize nutrients, especially P, although Cu, Zn and Au may also be mobilized. The fungi take up the nutrients and transfer them to the plant and, in exchange, 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.

### 5. Influence of nature and evolution of transported cover on mechanisms

Several types and ages of transported cover may overlie an in situ weathered profile. The nature and evolution of transported cover can strongly influence the effectiveness of metal transfer. Mechanisms that are relevant in a particular regolith and climatic setting with high water tables may not be relevant in another cover sequence under dry conditions. Thus it is important to integrate the evolution and character of the cover with different transfer mechanisms to rank their effectiveness.

#### 5.1. Paleowater tables within transported cover

Although much of Australia is now semi-arid to arid, old transported cover may have a long history of weathering under very different climates. Transported cover across Australia can date back to the Permian (Veevers, 2000). Depending upon past climatic and landscape positions, the water table could have been near the surface with connected saturation reaching from buried ore to the top of the water table (Fig. 15A). The development of a water table within transported cover sets up a redox gradient with oxidizing conditions prevailing at and above the water table and reducing conditions below. The water table-associated Eh difference causes reduced ions (Fe<sup>2+</sup>, Mn<sup>2+</sup>) released from the weathering front to migrate upwards and oxidize at or near the water table (oxidation front), resulting in ferrollysis with the generation of acidic conditions at the oxidation front (Mann, 1983). Thus, high water tables in wet climates are likely to drive electrochemically transferred metals into the cover across an Eh gradient (Fig. 15A). Anomalous zones are likely to be in water table-associated redox zones such as ferricretes. A shift to a drier climate coupled with erosion, would lower the water table generally to below the transported cover, but the old anomalous redox zone would be within reach of biota



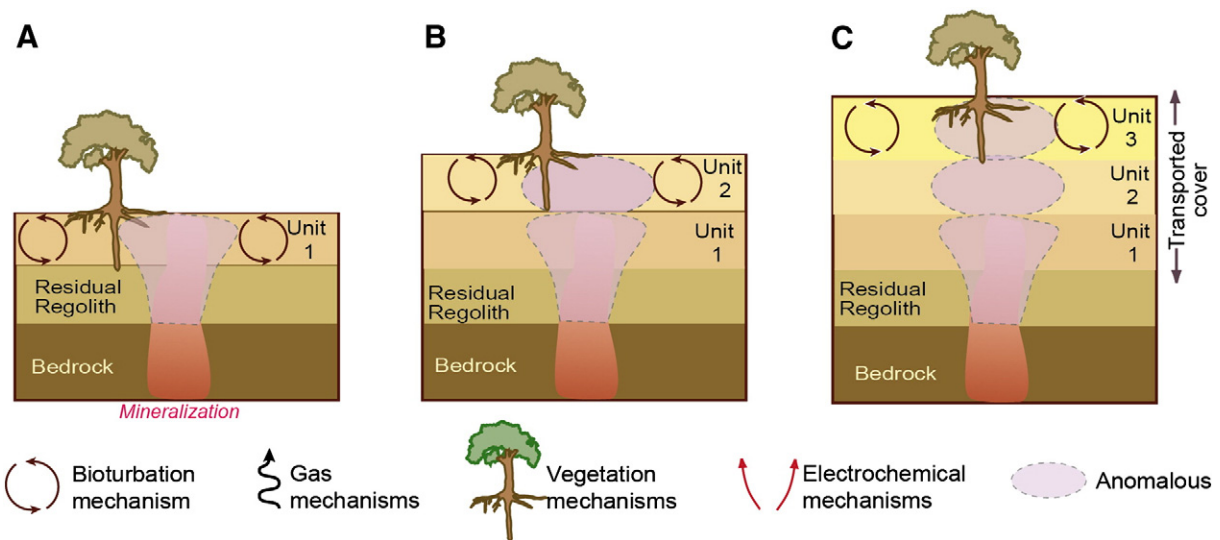
**Fig. 15.** Metal transfer processes in weathered regolith situations highlighting the effect of climate on mechanisms. (A) A high water table within the transported cover, during a previous wet climate would favor electrochemical metal transfer to and adsorption onto redox materials (mottles/ferricretes). (B) Subsequent onset of aridity lowers the water table but the original anomalous zone is still within the rooting depth of plants. Bioturbation transfers metals to the surface. Other mechanisms such as gas may continue from the ore body.

(vegetation, bioturbation) that would then transfer metals to the surface (Fig. 15B). These situations are common in Australia (Anand and Paine, 2002). An example of such a case is described by Lawrance (1999) where paleoredox fronts, thought to be still stands of past water tables, occur within Mesozoic sediments. These paleoredox fronts in transported cover host high metal contents due to adsorption on Fe–Mn oxides and hydroxides (Lawrance, 1999; Anand, 2001).

5.2. Transported cover profile stacking

The components of in situ regolith will occur in the overlying transported cover by constant redistribution during step-wise deposition (Fig. 16). Terrestrial sedimentation is not continuous, but episodic, across the evolving landscapes, depending on climate, uplift, and sea-level change. However, although weathering appears to be continuous, its intensity is governed by climate, tectonics, biota, and lithology. The interplay between sedimentation and weathering can lead to the

evolution of multiple profiles, as demonstrated in the literature on paleosols (Kraus, 1999). The formation of stacked paleosols (or weathering profiles) in distinct sedimentary units favor the transfer of metals across each paleosol and eventually reach the present surface by bioturbation and water–vegetation interactions (Fig. 16 Anand et al., 2014). This is the case at the Lancefield Au deposit, where stacked weathered profiles in each sedimentary unit (Permian, Cenozoic and Quaternary) allowed transfer of Au, As, Cu, and Zn across the weathered profiles (paleosols) as they evolved. Although regolith anomalies are weak, especially in the Tertiary and Quaternary cover, due to post-depositional weathering over a long time, they still remain (Anand and Robertson, 2012). This metal transfer only occurs in stacked weathering profiles without intervening fresh sediments. Kelley et al. (2003) suggested the possible upward transfer of metals where different Tertiary landsurfaces interacted due to shallow cover. This landscape evolution-controlled mechanism combines the mechanisms of vegetation transfer, bioturbation, and capillary action.



**Fig. 16.** (A–C) Metal dispersion in a depositional landscape where several shallow sedimentation events are followed by weathering, resulting in interaction between profiles and transfer of metals upwards, largely by bioturbation but also by plant uptake and capillarity. (A) Residual weathering resulting in a wide secondary dispersion halo in Unit 1. (B) Deposition of sediment Unit (2) followed by weathering and physical and chemical interaction between buried Unit 1 and new Unit 2. (C) Deposition of another unit (Unit 3) and its subsequent weathering resulting in transfer of metals to surface via Unit 2.

### 5.3. Variation in stratigraphy and depth of cover

The variation in the stratigraphy of transported cover and the nature of the buried residual profile can also influence specific mechanisms. For example, at Moonta (Cu–Au) in South Australia, where Tertiary clay directly overlies weathered basement, metals are transferred through the clay but anomalies are not expressed at the surface where the clay is underlain by 2 m of Cambrian sandstone. Keeling (2004) suggested that capillarity action operates within the clay in cases where it overlies the weathered basement, but the mechanism was less effective where coarse-grained sandstone was present between clay and weathered basement.

Another variation in regolith stratigraphy that needs to be considered for the Australian landscape is the occurrence of buried lateritic profiles. The concept behind electrochemical mechanisms is that transported cover resides on unweathered, exposed sulfide mineralization (Hamilton, 1998; Cameron et al., 2004), whereas in Australia transported cover commonly overlies oxidized lateritic residuum, ferricrete or saprolite (Anand and Paine, 2002). In regolith settings where oxidized profiles overlie mineralization, self-potential may not be sufficient to generate the voltages for electrical migration and the source of  $H^+$  generation from buried mineralization may be limited. Whether the buried residual profile has a lateritic residuum and/or saprolite may affect the size and strength of its supergene halo which is the source of metals for plants or gas transfer. Lateritic residuum generally has a much wider dispersion halo than the primary mineralization (Anand, 2001). The dispersion in saprolite may be restricted and may be strong or weak which, in turn, may determine the response (or lack of it) in plants.

Greater cover depths (>30 m), especially those with variable stratigraphy and/or unweathered cover, are where many of the upward metal transfer mechanisms are least effective. The mechanisms that could potentially work through thick cover are (a) gaseous transfer, (b) diffusion along fractures, (c) convection where sulfide ore occurs and is oxidizing, (d) barometric pumping where cover is fractured, and (e) dilatancy pumping where the region is neo-tectonically active. Micro-seepage from deep petroleum basins along fault zones has been documented in several studies (e.g., Klusman, 1993). Barometric pumping can transfer gases along fractures from depths of around 400 m (Carrigan et al., 1996). Other studies have suggested transfer of trace gases and metals along conduits over large distances as bubbles (Etiope and Martinelli, 2002).

### 5.4. Time

Although time influences the evolution of the cover, affecting all metal transfer mechanisms, it is rarely considered. It takes time (i) to establish a groundwater table within the cover, so that groundwater-based mechanisms can function, (ii) for gas to be generated by an oxidizing orebody, (iii) to colonize the sediment with vegetation to commence physiological metal uptake and near surface transfer, and (iv) for bioturbation to homogenize the near-surface to produce a biomantle. However, the minimal durations for operation of different mechanisms vary; some become operative within years (e.g. gases) and some over hundreds or even thousands of years. Smee (1983) notes that, on a theoretical and inorganic basis, only the  $H^+$  ion can diffuse through 20 m of saturated clay in 10,000 years, but most other ore related metals cannot do so or require more time. Pit experimental work by Anand et al. (2014) showed that anomalies can form quickly (over 7 months) through 2 m of cover by capillarity.

### 5.5. Geology

The role of geology on metal transfer mechanisms is twofold: i) syn- and post-depositional structural evolution (faults, shears and fractures) of the area, and (ii) the mineralization type or style of the deposits being

sought (mainly dependant on sulfide content). The gas-based mechanisms and dilatancy pumping are closely linked to conduits traversing the main ore zone and the overlying transported cover. A high sulfide content, which is typical of exhalative–diagenetic VHMS and SEDEX deposits, favors electrochemical and gas-based diffusive and convective transfer. Sulfide-poor types, such as orogenic gold deposits and some porphyry-associated deposits will be less favorable for these mechanisms.

Mechanisms are either limited or enhanced by the nature of the cover or its postdepositional modification. The cover settings will vary from region to region, or within a region, and accordingly the one or two mechanisms that work in one setting are not necessarily operating in another. If a surface extraction technique is optimized for a particular mechanism (for example weak digests to detect gaseous transfer) then that particular digest may not be applicable in different climatic and cover settings where the gas flux is weak.

## 6. Summary and conclusions

A review of mechanisms capable of transferring metals through barren transported cover to the surface 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 6). The different mechanisms are grouped according to their effectiveness in the phreatic (saturated) zone or the vadose (unsaturated) zone of the regolith.

Phreatic-based mechanisms are most effective and therefore are the most potentially predictive in environments with shallow water tables. Electrochemical models, where metals migrate upwards under the influence of an electrical gradient related to the ore body are the most studied. The redox gradient model is the best suited to transfer metals from the ore body upwards through saturated cover. The effects of heat generated by an oxidizing ore body on the 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 present or past depth of the water table. Dilatancy pumping – effusion of mineralized groundwater at the surface following earthquakes – is the most promising mechanism that can bypass the limitation of water table depths, but appears restricted to neo-tectonically active areas.

Vadose zone mechanisms – vegetation uptake and bioturbation, gaseous diffusion along concentration gradients, gas advection via barometric pumping and convective currents, particulate matter transfer via carrier gas bubbles and capillary upflow from the water table are all valid mechanisms that can operate routinely and rapidly throughout the entire unsaturated transported cover. Most of the mechanisms (plants, termites, ants and capillary) require that the regolith or groundwater in the immediate vicinity of the ore is anomalous. The plant uptake of metals from the subsurface to the surface has long been regarded as a predictive metal transfer mechanism. Despite arid climate and nutrient-poor soil, it is significant that *Acacia* and *Eucalyptus* trees are able to thrive in many parts of Australia, largely because of their deep, extensive root system. Sinker roots penetrate to more than 10 m and source their water and nutrients from deep groundwater and the surrounding regolith. Metals are taken up by both lateral and sinker roots but the extent of anomalies in deep rooted plants are determined by the metal source, depth of cover, and climate. Upward element transfer by vegetation (*A. aneura* and *Eucalyptus* spp.) occurs in areas of transported cover up to 20 m thick and rarely 30 m, but not in environments that lack supergene enrichment and have hypersaline acid groundwater. The role played by the different species still need to be established to make this a predictive technique in situations with shallow cover.

Termites burrow into the ground and bring material to the surface when making their nests. In general, the depth of bioturbation needs to be established in different regolith and climatic settings to make its application predictive. Termite activities have a limited influence on

**Table 6**

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	<ul style="list-style-type: none"> <li>• Sulfide-rich oxidizing deposit needed</li> <li>• Effectiveness over deposit not fully proved or explored</li> </ul>
	Dilatancy pumping	Groundwater pumped upwards due to compressional stress along faults/fractures. Arid climates favor rapid evaporation and restriction of metals	<ul style="list-style-type: none"> <li>• Limited to water table</li> <li>• Requires neotectonic active areas – faults through transported cover</li> </ul>
	Glacial tectonic pressure	Groundwater pumped upwards in more porous zones due to change in hydraulic gradient as ice shifts	<ul style="list-style-type: none"> <li>• Confirmation of visible groundwater effusion after earthquakes</li> <li>• Requires retreating glacial ice</li> </ul>
	SP (electrochemical)	Electrical currents set around from sulfide ore with concentration of cations at edges	<ul style="list-style-type: none"> <li>• Requires preferential flow paths through the cover via more permeable cover of faults and fractures</li> </ul>
	Redox gradient (electrochemical)	Redox differences between oxidizing near surface and reducing base of cover. Faster migration in voltaic gradient	<ul style="list-style-type: none"> <li>• Process is limited to shallow cover</li> <li>• Relies on diffusion process to pass through thick cover</li> </ul>
	Diffusion (indirect effects)	Diffusion along concentration gradient from base of cover to surface	<ul style="list-style-type: none"> <li>• Needs saturation conditions and associated redox gradient for effective transfer</li> </ul>
	Capillary	Surface tension related rise of groundwater above water table. Evaporation at surface drives suction upwards	<ul style="list-style-type: none"> <li>• Very slow process with only H<sup>+</sup> migrating fast enough through saturated cover</li> <li>• Upward extent unclear and operation in heterogeneous textural materials unproven</li> </ul>
Vadose	Gaseous diffusion	Oxidizing ore body produced gases (CO <sub>2</sub> , COS, SO <sub>2</sub> , CH <sub>4</sub> ) and volatiles (Hg, AsH <sub>3</sub> ) diffusion through porous media	<ul style="list-style-type: none"> <li>• Groundwater generally &gt; 10 m in arid areas</li> <li>• Migration along preferential pathways (structural conduits).</li> <li>• Gas signal complicated by biological released gases</li> <li>• Temporal stability of many gaseous species limited</li> <li>• Limited to fractured media</li> </ul>
	Barometric pumping	Rapid advective transport of gases in fractured media via barometric pumping	
	Bubble	Metal ions and nanoparticles attach to upward streaming carrier gas bubbles (CO <sub>2</sub> )	<ul style="list-style-type: none"> <li>• Fate of bubbles and attached particles unclear above water table</li> </ul>
	Gas convection	Air temperature differences drive hotter gases from ore body upwards	<ul style="list-style-type: none"> <li>• Limited to hilly regions or for low relief regions, permeable covers, high sulfide contents and oxidizing conditions</li> </ul>
	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	<ul style="list-style-type: none"> <li>• Limited root penetration depths (maximum 30 m)</li> <li>• Anomalous water or regolith required for plants to give response</li> <li>• Species related uptake unclear</li> </ul>
	Plant uptake and release to soil – hydraulic lift	Water absorption from depth (water table) and release near surface (upper soil horizon)	<ul style="list-style-type: none"> <li>• Metal transfer with water not confirmed</li> <li>• Depth from which water lifted poorly constrained</li> <li>• Limited understanding of the process</li> </ul>
	Bioturbation and gravity (mechanical)	Vertical and lateral movement of material from depth to surface by burrowing activities of conveyor belt organisms (termites and ants) – bioturbation	<ul style="list-style-type: none"> <li>• In many areas limited by depth of bioturbation (&lt;5 m)</li> <li>• Further information on burrowing depths of ants and termites in dry settings</li> </ul>

relative elemental abundances in soils immediately adjacent to mounds. This is important specifically in relation to exploration sampling protocols that may otherwise ignore these processes, resulting in unnecessary sampling ‘noise’.

The gas-based mechanisms are all strongly affected by preferential pathways in the ore body and overlying cover. Most studies demonstrate the migration of gas and volatiles along conduits and suggest “leakage” along the structures. A number of studies have detected transfer of metals but the form of the metals mobilized by gases is unknown. Laboratory studies have shown Au nanoparticles can be transported by gas and it is important that future studies expand on these results and observe the particles retained in gas collectors. For the gas-based mechanisms to gain sufficient predictive capability, excess contribution of gases by biological metabolism, temporal stability of gases and bubbles with attached metals and natural degassing towards efflux of gases needs to be evaluated.

Capillary rise of water from the water table can reach significant heights (~20 m) in fine-grained sediments and dry conditions. The fine-grained sediments allow a higher rise of water and the dry conditions at the surface generate and maintain a negative water potential and a resulting upward gradient. However, variation in the cover sediment texture may preclude high capillary rises. In arid areas, the water table is at > 10 m depth and therefore it is unlikely that this mechanism of metal transport would independently be sufficient to develop surficial anomalies.

Lastly, an integrated approach, combining different mechanisms with the nature of the transported cover and climatic setting needs to be considered to provide 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 favor the operation of a combination of mechanisms such as electrochemical, capillary, plant uptake and bioturbation. Dry environments may favor capillary, plant uptake and bioturbation mechanism to specific depths. Fresh, relatively un-weathered and deep transported cover provides the most difficult environment through which any of the mechanisms can be expected to work, except if gases from the ore body are generated in sufficient quantity to manifest a surface signature. The gas mechanisms, also, have significant limitations.

### Conflict of interest

None.

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