MECHANISMS OF METAL TRANSFER THROUGH SEDIMENTARY OVERBURDEN

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As mineral exploration moves into regions dominated by shallow sedimentary cover (5-50 m), bulk surface geochemical techniques are considered less applicable, and partial, selective and sequential leaches and gas analysis are increasingly employed to delineate anomalies. However, the application of these techniques have found mixed success, because the particular mechanism(s) and their effectiveness in transferring metals associated with mineralization upwards through transported overburden is poorly understood, thereby complicating and limiting the interpretation of datasets, and precluding the discrimination of negative and false anomalies. There is a major need to critically study potential mechanism capable of transferring metals from buried mineralization upwards through barren cover to the surface. This review assembles a list of potential mechanisms and their application to surface geochemical techniques.

The main mechanisms potentially capable of transferring metals upwards are groundwater (hydrogeochemical), gases, vegetation and bioturbation; most having variants or sub-mechanisms within them, and each being influenced by positive and negative effects of microbial processes.

Groundwater in association with infiltrated water is the main agent of chemical weathering, and facilitates the dispersion of metals from the ore body. Flow directions, solution properties, aquifer heterogeneity, adsorption, complexation and inherent interactions and feedbacks between these processes influence the extent of *lateral and vertical dispersion* within the unconfined aquifer. Redox processes and formation of a possible stagnant zone at varying depths affect vertical migration of specific elements and can lead to the fractionation of specific elements (rare earths, Fe, Mn, V, As) at or within the fluctuating zone of the water table. *Capillary* forces at and above the water table can induce upward migration of solutes, with the rise being dependant on aquifer grain size and evaporation rates. *Seismic* or *dilatancy pumping* occurs in neo-tectonic active areas where faults and fractures act as conduits for upward transfer of mineralized groundwater. Earth tremors promote compressional stresses along faults and force groundwaters upward, with surface discharge after the earthquake, resulting in a near surface anomaly. This mechanism is limited to low-rainfall and neo-tectonic areas that have regular seismic activity after overburden deposition. *Free convection* or buoyancy driven currents within the groundwater can arise due to density differences induced from point sources or subtle heat sources. These can promote faster solute migration in a particular direction and the possible formation of irregular fronts. The denser fluids arising from salt lakes are known to cause convective mixing of mineralized groundwaters in surrounding regions. The applicability of convective flow mechanism to rapidly transfer solutes upwards up to the water table remains unexplored and has only been investigated via simulations and laboratory tests for point source contaminant transport. The formation of *electrochemical cells* around an oxidizing-reducing sulphide body within groundwater can provide excess cation concentrations at the oxidized upper edges of the sulphide body, and the proposed pattern of ("rabbit ear") surface anomalies in regolith suggests its possible operation. An advanced version of the electrochemical cell model posits the onset of redox anisotropy between the buried sulphide body (reducing) and water table (oxidizing) after the deposition of sediments. Self-potentials arise and are maintained due to reducing conditions at the sulphide body front and oxidizing conditions at the water table, leading to upward and outward migration of reduced species and their subsequent oxidation and formation of a reduced column above the ore body. This voltaic cell model is capable of rapidly transferring metals upwards through thick (30 m) saturated cover. The limitation of all the groundwater supported transfer mechanisms is the upward limit to which groundwater rises or the water table (and capillary fringe), except that of seismic pumping. In the Australian landscape, groundwaters reside are commonly more than 5 m below surface except in lower, discharge landform sites, and other mechanisms are necessary to transfer metals from the water table upwards.

Gases migrate via molecular diffusion, advection and gas streaming, out of which advection and gas streaming appear the main sources of rapid upward migration of ore related gases (CO_2, SO_2, COS) and possibly of metals. *Atmospheric pumping*, the depression front set up by large barometric pressure change, causes rapid upward migration of air present in pores and conduits, and is a primary mechanism causing upward migration of trace gases from nuclear blasts, with the capability to transport volatile and radiogenic elements (Hg, Rn, He, As) and also gas bubbles. The effectiveness of atmospheric pumping is restricted to fractured media and possibly operates in a connected, heterogeneous sedimentary overburden. Other mechanisms that may cause advective gaseous migration are thermal convection on hillsides (only along inclined slopes) and rapid fluctuations of the groundwater, the latter being valid only in shallow water tables and high permeability zones. *Gas streaming* or bubble migration is the upward transfer of gases in the form of microscopic bubbles that form within the groundwater due to overpressure and are released from the water table. Specific metals (Cu, Zn, Pb, Hg, actinides) and ultra-fine particles (clays, oxides, bacteria) can attach to the surfaces of ascending gas bubbles (dominantly composed of CO_2) and be transported upwards to the near surface environments, where pressure changes induce bubble instability and cause release of metals. Gas streaming, in combination with atmospheric pressure changes, is a potential mechanism of transferring metals upwards, although the capacity to absorb and carry metals, and their fate during transfer through a clay bearing overburden requires further testing. In any case, most, if not all, studies of gas anomalies at the surface indicate rapid migration along conduits such as faults, fractures and shears, above which the anomalies are present.

Vegetation or plant physiological uptake of elements from subsurface and their release to the surface via litter over time is a potential mechanism of rapid metal transfer. In drier climates, many pheratophyte plants have dimorphic roots systems with laterals and sinker or tap roots (vertical), the latter roots acquiring water from deeper groundwater source, especially during summer (as demonstrated by deuterium isotopic studies). However, the uptake of specific metals, besides the macronutrients, from the groundwater remains untested. Furthermore, the operation of hydraulic lift – redistribution of deeper water acquired by sinker roots to near surface soil horizons to be used by laterals, is a process capable of rapid transfer of water and nutrients within the overburden. The depth of rooting of vegetation is critical to the ability of vegetation in transferring water and possibly ore metals, and a global rooting depth survey suggests that deep roots, especially sinkers, are ubiquitous with 10 m plus depths regularly reached and confirmed in several climatic settings. Vegetation is known to uptake specific mineralization associated elements (Au, Ni, Cu, Pb, Zn, As) with specific flora being adapted to substrates of high concentration of these elements, and use of plants in phytoremediation stands as a testimony. The vegetation uptake can also affect the species of the element. For example, gold absorbed as dissolved form can be converted into colloidal form. The effectiveness of phreatophytes and other vegetation in acquiring mineralization associated metals from the groundwater and releasing them to surface via litter and within the soil via hydraulic lift, has not been intensively tested, but holds promise.

The operation of **bioturbation** process within the biomantle underlying the surface is capable of moving huge amounts of soil material, and thereby bringing up anomalous material from depth to the surface. Ants, termites and earthworms are the main bioturbators, and combined with rainwash are the primary cause of soil (and anomaly!) homogenization and lateral dispersion of surface anomalies over time. However, unlike the other biological pathway of vegetation, the effectiveness of bioturbation decreases rapidly downwards, with activity mostly ceasing at a depth of 2 m. The role of **microbes** in transferring metals upwards is restricted, but they affect most of the processes responsible for metal transfer. Microbial metabolism affects the kinetics of many hydrochemical processes, especially redox and sulphide oxidation. Microbial metabolism can negatively impact on gaseous migration of elements by generating methanogenic, CO_2 and sulphur gases. They can influence the efficiency of metal uptake by roots via redox reactions, symbiotic associations and organic secretions. And they can participate in intracellular and extracellular formation of minerals (and gold particles) within the saturated zone and soil, irrespective thermodynamic solubility products of those minerals, and can affect efficiency of partial and selective leaches.

While all the mechanisms described above have potential to create surface anomalies, it is likely no one mechanism may be singly responsible, and a combination of mechanisms may be pertinent in the Australian environment. The critical, but often neglected aspect of evaluating the operation of the diverse mechanisms responsible for upward metal migration is the **nature** of the transported overburden (pre and post weathering) and its **depth**. Related to the nature of the overburden is the **time** and **landscape** factor that are equated to the age and type of weathering. Weathering of the overburden with development of a weathering profile (sometimes multiple weathering profiles are superimposed) and concomitant water table increases the possibility to transfer metals upwards via a combination of mechanisms such as vertical hydrogeochemical gradient and electrochemical effects, vegetation uptake and bioturbation, to form "incremental" anomalies over time. Alternatively, younger, fresh to slightly weathered sediments, even of shallow depth, will afford a much lesser opportunity for diverse mechanisms to operate, except gas advection and possibly vegetation uptake. However, specific partial leaches, gas measurements and electrochemical techniques, work on the principle of a rapid migration mechanism even in recent, fresh cover, and therein lies the need to understand the rate, extent and overall effectiveness of the mechanism(s) to mobilize ore metals upwards under different transported cover settings, so surface geochemical techniques can be efficiently and predictively applied, or discarded.