

Abstract

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

Phreatic processes are underpinned by groundwater as the main solute transfer process. Subsurface mineralized water can be transferred to the surface via faults due to *seismic* or **dilatancy pumping**. The onset of compressional stresses along faults arising from earth tremors force the mineralized groundwaters upward, with possible surface discharge of water and their rapid evaporation resulting in a near surface anomaly. This mechanism is limited to low-rainfall and neo-tectonic areas that have regular seismic activity. An oxidizing sulphide ore body could act as a point or diffuse **heat source** resulting in buoyancy driven currents and possibly convective currents. The heat produced from sulphide oxidation can induce faster solute migration in a particular direction, especially upwards, with ions released from the ore body being driven upwards as opposed to along lateral flow. The ability of heat driven flow to rapidly transfer solutes upwards to the water table remains unexplored and has only been investigated via simulations and few laboratory tests for point source contaminant transport. **Electrochemical** processes involve the movement of charged ions within an electrical field and are considered to be efficient migration mechanisms because they favour rapid upward ionic migration. Electrochemical forces arising due to spontaneous potentials (SP) around an ore body are considered to result in excess cation concentrations at the upper edges of the sulphide ore with subsequent diffusion of cation along concentration gradient accounting for a near surface anomaly through cover. The resultant migration of H^+ to surface can modify soil conditions (lower pH) which can in turn mobilize specific cations within the soil. The proposed dual peak (“rabbit ear”) pattern of surface cation concentrations in regolith is advocated as a case for the potential operation of the electrochemical cell mechanism. **Redox gradient** model for electrochemical migration posits the onset of redox anisotropy between the buried sulphide body (reducing) and water table (oxidizing) after the deposition of cover sediments. Redox differentials arise and are maintained due to reducing conditions at the sulphide body front and oxidizing conditions at the water table, leading to upward and outward migration of reduced species and their subsequent oxidation and formation of a reduced column above the ore body. **Gas bubble** migration is the upward transfer of microscopic gas bubbles that form within the groundwater due to overpressure or exsolution, and are then released from the water table. Specific metals (Cu, Zn, Pb, Hg, actinides) and ultra-fine particles (clays, oxides, bacteria) can attach to the surfaces of ascending gas bubbles (dominantly composed of carrier gases - CO_2), especially if the gas bubbles have an organic coating acquired from trace organics in groundwater. The bubbles can then be transported upwards to the near surface environments, where pressure changes are proposed to induce bubble instability and release metals. The stability of bubbles during their transfer from a saturated to an unsaturated medium as well as the fate of adsorbed matter on bubbles when the bubbles destabilize remains unclear. All the phreatic processes are supported by groundwater and are limited by the height of the water table, except that of seismic pumping. In much of the Australian environment, groundwaters are commonly more than 5 m below surface except in lower, discharge landform sites, and other, or additional, mechanisms are necessary to transfer metals from the water table upwards.

The **vadose** zone processes are critical in transferring metals from the groundwater to the surface. **Capillary** or tension forces at and above the water table can induce upward migration of solutes. The rise of solutes is dependant on aquifer grain size and evaporation rates with finer grain sized material and high evaporation rates at the root zone in dry climates causing high suction pressures which would transfer thin

film of water and dissolved metals to the root zone. The effectiveness of capillary pull is limited by the variable regolith grain sizes and poor understanding of height to which interconnected water films rise in different textured materials. Weathering of ore body releases gases (COS, CO₂, SO₂, CH₄, Rn, He – depending on ore body type) and possibly metal volatiles (Hg, I, As, Se) that can migrate upwards from the oxidizing ore body and water table if the ore is submerged. The upward **diffusion** of gases has been experimentally shown to be a viable mechanism of volatile metal transfer but has limitations in form of temporal and geochemical stability of individual gases and tortuosity of the weathered and often cemented regolith medium. **Atmospheric pumping**, the depression front set up by large barometric pressure change, causes rapid upward migration of air present in pores and conduits, and has the capability to transport ore associated gases and volatiles along structural conduits. Atmospheric pumping is restricted to fractured media, and its operation in a heterogenous weathered sedimentary overburden is difficult. Heat produced from oxidizing sulphides can set up **convective gas flow** where oxygen diffuses into the oxidizing ore body and released gases advect upwards. This transfer mechanism is limited by heat production (sulphide amount) and permeability of the ore body and cover. Mechanisms supported by gaseous migration have several limitations such as temporal stability of gases, excess contribution of gases from biological metabolism, temporal and spatial stability of bubbles and the channeling of gases and greater contribution via structural conduits.

The other critical vadose zone processes are biological: vegetation transfer or plant physiological uptake and bioturbation. **Vegetation** uptake of elements from subsurface and their release to the surface via litter is a long publicized potential mechanism of rapid metal transfer. Plants take up most ore associated metals (Zn, Mo, Se, Au, Ni, Cu) and even potentially toxic metals such as As and Pb, and have evolved novel methods to biotransform toxic metals, store and release them to the surface. Spatial and temporal water access by plants (determined via deuterium isotopes) demonstrates the ability of plants to seasonally access deeper groundwater via their sinker or tap roots and confirms the uptake of water and metals from potentially mineralized groundwater as compared to mere soil cycling. Additionally, **hydraulic lift** – redistribution of deeper water acquired by sinker roots to near surface soil horizons to be used by laterals is capable of rapid transfer of water and possibly metals within the overburden. Diurnal uptake and transfer of groundwater via hydraulic lift to surface soil has been confirmed for many species spanning diverse climates, but no data exist on ore metal transfer. The **depth of rooting** is critical to define the depth limits to which vegetation assisted transfer can operate. A global rooting depth survey indicates that deep roots, especially sinkers, are ubiquitous with > 10 m depths regularly reached and confirmed for several species in several climatic settings. Identifying the role of plant species, the rate and amount of metal transfer to the surface via particular plants and the regolith and groundwater environments (perched or permanent, saline or fresh) under which plant transfer is operative requires extensive testing.

Bioturbation by myriad regolith mesofauna accomplish biomantle homogenization (homogenize anomalies brought to the surface via other mechanisms) and potentially transfer anomalous material from great depths beyond the biomantle. Material transfer from great depths (~5-50 m) by the main conveyor-belt organisms – termites and ants – has been documented, but reports of such deep burrowing activity are restricted, especially to parts of Africa. The effectiveness of bioturbation is limited mainly to the biomantle and decreases downwards, and further documentation of depth of bioturbation on a local to regional scale is required to make it a predictive metal transfer method outside the regions where it is documented to penetrate deeper.

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

The vital parameter that impacts on the efficacy of the diverse mechanisms responsible for upward metal migration is the **nature** (depth, weathering degree, cemented, faulted) and **evolution** (multiple deposition periods, structural activity) of the transported overburden, both factors in turn affected by **time** and landscape evolution of the region. Weathering of the transported overburden and formation of concomitant water table within the overburden increases the possibility to transfer metals upwards via a combination of mechanisms such as electrochemical effects, capillarity, vegetation uptake and bioturbation, to form “incremental” anomalies over time. Alternatively, younger, fresh to slightly weathered sediments, even of shallow depth, will afford a much lesser opportunity for diverse mechanisms to function, except mechanisms

capable of rapid metal transfer such as gaseous diffusion and advection and possibly plant uptake, depending on porosity, anisotropy and hardness of the transported material. In specific cover situations, true surface geochemical anomalies don't manifest on the surface, and it is vital to define the limitations of all mechanisms in addition to their potential merits, whereby surface geochemical techniques can be predictively applied or not applied.