

*Stew Hamilton*

*Transport mechanisms responsible for  
selective leach anomalies*

## **Transport Mechanisms Responsible for Selective Leach Anomalies**

S.M. Hamilton

Ontario Geological Survey

### **Introduction**

For a number of years, the OGS has been working on an electrochemical dispersion model to account for selective leach soil anomalies in areas of high water table and thick Quaternary glacial cover. However, this investigation actually began by addressing the possibility of element transport by groundwater advection and this was followed by a brief theoretical investigation into diffusion and gaseous transport as potential mechanisms. Electrochemical transport was considered as a possible mechanism only after it was determined that the other three mechanisms could not account for the presence of selective leach and shallow groundwater geochemical anomalies at the sites investigated. Initially, the appeal of electrochemical transport was speed. At the sites investigated anomalies spatially related to mineralization, occurred over 30m of fine grained glacial materials that are less than 10Ka in age. It was apparent that only electrochemical transport was fast enough to have accounted for such young anomalies.

The purpose of this discussion is to describe the advantages and disadvantages of invoking each these four dispersal mechanisms to account for selective leach anomalies above mineralization. For reasons discussed below, electrochemical processes are increasingly likely to dominate as the primary transport mechanism in thicker and younger, more exotic overburden environments. They are likely to operate in other environments but their dominance, as a transport mechanism, is less certain. The arguments and evidence presented are necessarily weighted toward glacial environments because of the OGS' research and interest in these areas.

### **Selective Leach Anomalies**

Selective leach anomalies spatially related to mineralization and other buried geological features have been reported worldwide in diverse climates, terrain types and overburden conditions. Soil moisture conditions can range from dry and arid with thick unsaturated zones to fully saturated peat terrain where the water table is at ground surface. The age of host deposits can range from very young (<10Ka) to very old (100s of Ma). Numerous selective leach extraction methods have identified these anomalies, which generally take the form of either rabbit-ear (twin peak) anomalies straddling the buried feature or apical (single peak) anomalies almost directly over it. Coincident anomalies in multiple elements are typical but elemental assemblages often do not closely reflect those of the source feature, which makes interpretation of the source of blind anomalies difficult.

Any transport mechanism or model proposed to explain the formation of selective leach anomalies must account for:

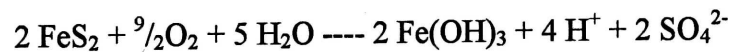
1. the rabbit-ear morphology and close spatial association of anomalies with underlying mineralisation or other buried features

2. the apparent young age (<10Ka) of some anomalies and that can form above thick (>30m) overburden
3. the development of surface anomalies in overburden environments ranging from fully saturated to arid unsaturated
4. development of anomalies over non-oxidisable and/or non-conductive geological features, such as barren faults.

### Groundwater Transport

Many authors have included groundwater transport as a possible mechanism for dispersal of elements from mineralisation and abundant evidence exists that this takes place. Webber (1975) pointed to the much higher potential speed of migration of groundwater in comparison to that of either diffusion or electrochemical transport and concluded that advective groundwater transport is likely to be the more important dispersal mechanism. Groundwater flow rates in coarse-grained media can be very fast – sometimes exceeding many metres per day. Therefore, in terms of mass transport, the capacity of groundwater to move solutes probably exceeds that of other subsurface transport mechanism.

However, there are several problems with applying this mechanism to explain selective leach anomalies over mineralization. These can be demonstrated by considering groundwater from a “plug-flow” perspective. When groundwater first enters the phreatic zone, its maximum concentration of dissolved oxygen is about 11 ppm which is the solubility of oxygen in air-saturated water (@ 15°C and 1 atm. pressure). From this point, the concentration of oxygen can only decrease since no geological sources of oxygen exist. If a “plug” of groundwater containing dissolved oxygen moves through the subsurface and encounters sulphide mineralization, oxidation of pyrite (for instance) will occur according to the equation:



The dissolved products of this reaction, including metals, are not free to diffuse or otherwise disperse upward but will necessarily be transported in the direction of groundwater movement. In stratified geological environments groundwater tends to move laterally and therefore so do solutes being transported by groundwater. This is particularly true with respect to layered glacial overburden and glaciolacustrine varved clays for which horizontal hydraulic conductivities are typically orders of magnitude higher than those that occur in the vertical direction. This results in horizontal groundwater flow being favored over vertical by a similar factor.

If groundwater transport were a significant contributor to mobility of the elements involved in selective leach anomalies over mineralization, one would expect the anomalies to occur down a long dispersal plume in the down-gradient direction of groundwater flow. This has not been reported in surface soils where, as mentioned, anomalies typically occur in either the rabbit-ear or apical morphologies directly over mineralization. Furthermore, selective leach anomalies are often noted in surface soils far above the water table. Since groundwater obviously could not play a direct role in the

formation of many of these anomalies, it is reasonable to conclude that it plays a relatively minor role in the formation of selective leach anomalies as a whole.

### **Chemical Diffusion**

Diffusion along concentration gradients has been named as a possible cause for observed soil anomalies over mineralisation (Govett and Chork, 1977; Smee, 1979, 1983). Chemical diffusion is the slowest of all the potential transport mechanisms that might contribute to the development of surface anomalies over mineralization. Figure 1 shows the result of a 1-D numerical simulation of diffusion of a hypothetical major ion through 30m of clay using the Ogata-Banks equation. The input parameters were reasonable estimates of the conditions that would apply in glacio-lacustrine clay. The results show that, even after 30Ka, there is a relatively minor increase in surface concentration of the hypothetical ion. Smee (1979) carried out similar calculations for a variety of elements and concluded that diffusion was too slow to account for soil anomalies in Quaternary glacial units thicker than 5m. As mentioned, anomalies spatially related to mineralisation have been noted overlying up to 45m of young glacial sediments.

Another complication must be addressed if diffusion is being proposed as a transport mechanism below the water table.  $H^+$ , metals and other ions are likely to be the product of oxidation of mineralisation, which requires the presence of oxygen. A diffusion-based model to account for selective leach anomalies must also include a mechanism by which oxygen or other oxidizing agents can be brought in contact with mineralization. This is a fundamental problem that has often been ignored. If diffusion is proposed as the oxygen transport mechanism this would further limit the rate of reaction, thereby limiting the formation of ions at the bedrock surface, limiting the development of a concentration gradient between bedrock and ground surface, and at least doubling the time (Figure 1) necessary to establish the surface anomalies. Diffusion becomes a more likely transport mechanism with increasing age and/or decreasing thickness of the overlying material.

### **Gaseous Transport**

The measurement of soil gases has been used to identify the presence of mineralisation by a number of workers (e.g. Lovell et al., 1983; McCarthy et al., 1986). Gaseous transport of metals and/or other species has been suggested as a possible mechanism in the development of soil geochemical anomalies (Clark, 1997; Smee, 1998). Case studies in support of gaseous transport are largely cited from arid or semi-arid areas where the water table exists 10s to 100s of metres below ground surface. Large scale and rapid gas transport in these environments is plausible because of the very thick vadose zone (unsaturated zone). Gases in the phreatic zone (i.e. below the water table) in the zone of meteoric groundwater typically exist in dissolved form and therefore their transport occurs largely by diffusion or groundwater advection.

Some authors have suggested a gaseous transport mechanism below the water table in which gaseous carriers move metals in a separate gas phase. This is extremely unlikely. Gases can exist in the vadose zone in gaseous phase at partial pressures that are

considerably below atmospheric pressure. This is not the case below the water table where the sum of partial pressures of all dissolved gases must exceed the fluid pressure for a separate gas phase to exist. By definition the "water table" (Freeze and Cherry, 1979) in a saturated geological medium is the point at which the fluid pressure is exactly equal to atmospheric pressure. Below the water table, the fluid pressure exceeds the vapour pressure and above it, the vapour pressure exceeds the fluid pressure. In the zone of meteoric groundwater, gases typically only exist as a vapour phase below the water table in the following circumstances:

1. In extremely sluggish groundwater flow environments e.g., as methane pockets in shale where the gas is in pressure-equilibrium with surrounding groundwater and where the only dispersal mechanism is diffusion.
2. In environments where the fluid pressure is decreasing i.e., where groundwater is moving up, such as occurs at discharge zones.
3. In environments where the vapour pressure is increasing or at least being maintained by ongoing processes at a continuously high level, i.e. where gas is being actively generated or being supplied from below.

Scenarios 1 and 2 can be ruled out because, as mentioned, neither diffusion nor groundwater discharge can account for the majority of selective leach anomalies.

If scenario 3 were applicable as a transport mechanism for metals and gases below the water table, a large source of gas would be necessary. If it were applicable as a cause of rabbit-ear anomalies in all environments, a large source of gas would be necessary at every mineral deposit that produces such anomalies. It follows, therefore, that the source of gas must be genetically associated with the weathering of the mineral deposit. Finally, if a separate gas phase were present, it would require that gas be generated at mineralisation in high enough concentrations to partition into a vapour phase. If it did not, it would disperse elements from mineralization at a similar rate to that of most other dissolved species, which is far too slow to account for many of the anomalies noted in thick, young glacial terrain.

Elevated  $\text{CO}_2$  has been shown to be coincident with rabbit-ear metal anomalies over mineralization in arid terrain and will be used as an example. For any gas in equilibrium with water, the concentration of that gas in solution is proportional to total pressure. At a depth of 30m below the water table and assuming  $\text{CO}_2$  is the dominant dissolved gas phase, the partial pressure required to exsolve  $\text{CO}_2$  would be about 4 atmospheres, which is an extremely high concentration (it exceeds the  $\text{pCO}_2$  of soft drinks). Concentrations exceeding 1 atmosphere are very rare in natural meteoric groundwater and usually only occur in thermal springs and spring discharges along seismically active faults (Barnes et al., 1978). Concentrations this high in areas of abundant carbonate would dissolve vast quantities of carbonate, which would re-precipitate as tufa or travertine when the  $\text{CO}_2$  degasses from near-surface groundwater. The general lack of such deposits in association with rabbit-ear anomalies over conductors suggests that transport of elements by  $\text{CO}_2$  or  $\text{CO}_2$ -saturated groundwater cannot be responsible for many of the reported selective leach anomalies.

Smee (1998) proposed a model to account for CO<sub>2</sub> and rabbit-ear anomalies in surface soils in Nevada. Briefly, he proposed that active oxidation of a sulphide body would mainly occur on the flanks of the body due to the presence of a weathered cap over the top. Oxidation would produce acid (see above equation), which would react with carbonate in wall rocks to generate CO<sub>2</sub>. The CO<sub>2</sub> and dissolved carbonate would disperse upward from the flanks of the deposit as vapour and as a dissolved component in soil moisture and produce rabbit ear anomalies in Ca and Sr by deposition of calcite near surface where soil moisture evaporates. Related processes are proposed as possibly being responsible for anomalies in other metals.

This mechanism may operate in areas where an unweathered portion of a sulphide body occurs above the water table and therefore might at least partially account for reported CO<sub>2</sub> anomalies and O<sub>2</sub> depletions that occur over some deposits in arid terrain. However, it is unlikely that a mechanism such as this could account for CO<sub>2</sub> or metal anomalies occurring over mineralization that is entirely within the phreatic zone. In addition to the slow downward diffusion of oxygen limiting the rate of such a process, the oxidation of sulphides below the water table is incapable of producing enough acid to result in a CO<sub>2</sub> gas phase below the water table. As mentioned, the maximum concentration of O<sub>2</sub> in groundwater (at 15°C) is about 11 ppm. Assuming 100% of the O<sub>2</sub> is available for pyrite oxidation, the resulting pH would be around 3.5. H<sup>+</sup><sub>(aq)</sub> dissolves carbonate according to the equation:



Therefore for each mole of CO<sub>2</sub> produced, 2 moles of H<sup>+</sup> are required. Since the starting concentration of H<sup>+</sup> is, at most, 10<sup>-3.5</sup> M, the maximum CO<sub>2</sub> concentration produced is in the order of  $2 \times 10^{-3.5} = 0.00063 \text{ M CO}_{2(\text{aq})}$ . This is about one 70<sup>th</sup> of the solubility of CO<sub>2</sub> at 15° C.

It is difficult to conceive of any naturally occurring gas other than CO<sub>2</sub> that could be called upon to transport metals or other species from sulphide mineralization as a widespread process. Notwithstanding, other gases would also require high concentrations to exsolve as depth and hydrostatic pressure increases and are therefore unlikely to be responsible for transport of metals below the water table. Furthermore, in stratified geological environments, gases do not typically move straight up but are trapped by zones of fine-grained sediments. As such, gases below the water table are likely to be dispersed by groundwater and are not expected to form tight, well centred, anomalies immediately over mineralisation. This is particularly true for rabbit-ear anomalies, which often show a depletion over mineralization.

### **Electrochemical Transport**

The concept of electrochemical transport is based on the fact that charged species in a field of electrical potential will move toward the area where they are capable of passing on electrical charge. If the system includes electrodes, negative charge-carrying ions

(usually anions) will move toward the positive electrode or “anode”. Positive charge carrying ions (usually cations) will move toward the negative electrode or “cathode”. In such systems, electrons move from the anode to the cathode via a wire and charged species must be in an aqueous medium. In general, current in the wire will be spontaneous if the reactants at the electrodes have different redox potentials. In nature, systems that have electrodes are rare – the majority of electrical current-producing cells in nature have no electrodes and no conduction by electrons but rather involve purely electrolytic conduction. Such cells include: the nervous systems and muscles of organisms; spontaneous-potential currents above oxidizing ore-bodies; and other redox “cells” within the Earth’s crust as discussed below.

The Earth’s crust is composed of materials with variable redox properties and between which redox gradients exist. One end of these redox scales is fixed by the near-surface influence of oxygen, the most oxidizing of natural terrestrial substances. The other end is fixed by the ubiquitous presence of water in the shallow crust. Water can act as an oxidizing agent for very reducing materials (eg.  $\text{Fe}_{(s)}$ ,  $\text{Zn}_{(s)}$ ). Substances that are more reducing than water are exceedingly rare in the shallow crustal environment because, had they existed, they would have been oxidized by water eons ago. The resulting range of natural Eh (and pH) is shown on Figure 2. Redox gradients can exist between many geological substances but the maximum voltages generated cannot usually exceed the maximum range of Eh shown on Figure 2. This is consistent with the fact that the vast majority of self potential voltages reported are below 1.5 V.

In addition to local redox gradients between geological materials of differing redox properties, an upward increasing redox stratification exists in the Earth’s crust (Bass Becking et al, 1960; Bolviken and Logn, 1975). This redox field results from the process of oxygen re-supply by the atmosphere continually providing oxidizing agents that are counterbalanced by the presence of mineralogical reducing agents in the Earth’s crust.

Although electrolytic “current” must exist wherever a redox gradient exists, the associated movement of charged species should produce no local “anomaly” if the gradient is entirely uniform. In areas where increased current exists, an anomalous accumulation of charge-carrying species might also be found to exist. Such an area could result from the presence of an SP cell. For the purpose of the following discussion an SP “cell” is defined here as *a natural geological system that induces the spontaneous, long-term flow of electrical current in a focused and clearly definable area in the earth*, i.e. the current flux has to be clearly anomalous with respect to background current flow.

The development of earth cells of this type is entirely predictable by Ohm’s law. Ohm’s law governs current density at low voltages in an electrical medium:

$$E = r \cdot j;$$

where E is electrical field strength, or voltage gradient, and is expressed in V/m; r is resistivity, or electrical resistance per unit length of medium, and is expressed in  $\text{ohm}\cdot\text{m}$ ; and j is current density, or electrical current per unit cross-sectional surface area, and is expressed in  $\text{Amps}/\text{m}^2$ . This simple equation states that in an electrical field, current

density will increase if either the voltage gradient or the electrical conductivity (i.e. the inverse of resistivity) increases within the medium.

According to Ohm's Law, if an area of increased electrical conductivity occurs across an otherwise uniform voltage gradient, an increase in current density in that zone must also occur. As discussed below, a vertically oriented geological conductor crossing the usually horizontal redox equipotential lines in the earth is one example of such a system. Likewise if an area of increased voltage gradient occurs in a medium of uniform electrical conductivity, an increase in current density must also occur. Examples of this type of cell are also discussed below.

### **SP Cells Due to Increased Electrical Conductivity in the Earth**

Sato and Mooney (1960) proposed a model for the development of SP cells over conductive mineralisation that, in effect, put to rest several decades of debate on the origins of negative SP centres in these environments. The greater oxidation potential in the near-surface groundwater-bedrock environment relative to the deep environment was postulated to result in upward movement of electrons through conductive mineralisation. At the surface of the conductor, oxidation of reducing agents in deeper areas provides electrons to the conductor that allows the simultaneous reduction of oxidizing agents in shallower areas where electrons are received from the conductor. For a single-phase conductor, oxidation or reduction of the electronic conductor itself does not contribute directly to the process that results in self-potential currents, i.e. does not contribute to the remote transfer of electrons from one area of the conductor to another. To do so, the conductor would have to be oxidized at depth where there are fewer oxidizing agents and/or reduced in shallow areas where there are few reducing agents. Rather, if the conductor were the reducing agent it would oxidize in its upper part, negative current would not move along its length from depth and there would be no resulting self-potential phenomena associated with the conductor. Oxidation of the conductor takes place as a local "detached" redox phenomenon that does not contribute directly to self-potentials.

The movement of electrical current along the conductor necessitates the mass transport of ions in groundwater to, or away from, the "electrodes" to deposit charge and/or to prevent local charge imbalances caused by the production or deposition of charged species. In general, there will be a migration from surrounding areas of positive charge toward (i.e. negative charge away from) the upper part of the conductor and negative charge toward (i.e. positive charge away from) the lower part of the conductor.

Thus, the conductor functions as both electrode and "wire" in a natural voltaic cell connecting the cathodic part of the conductor near surface with the anodic part in the deeper environment (Figure 3). The reactants are solid-phase and dissolved constituents in the low-Eh and high-Eh environments that respectively surround the anode and cathode. The difference in oxidation potential of the reactants arises from the ubiquitous redox gradient that exists in the Earth's crust. The conductor provides a less resistive route to upward movement of negative current from depth and concentrates this background current thereby "short-circuiting" the redox field.



Electrochemical cells after the model of Sato and Mooney (1960) develop due to zones of anomalously high electrical conductivity in earth materials in what would otherwise be a roughly uniform vertical redox gradient. The issue of the conductor being electronically conductive is, perhaps, a red herring. A zone of fault gouge made up of water-saturated rock flour and phyllosilicates could conceivably have a very high electrolytic electrical conductivity, especially relative to surrounding unfractured rock. This should also develop a significant electrical current within it, provided an upward-increasing redox gradient also exists.

### **SP Cells Due to Increased Voltage Gradient in the Earth**

In model of Sato and Mooney (1960) described above, the impetus for electronic current flow in mineralisation comes from the redox differential between the oxidized groundwater environment surrounding the upper part of the conductor and reducing agents in contact with its lower part. The upward movement of electrons consumes oxidising agents in basal overburden and results in the development of a negative redox anisotropy in groundwater-saturated basal overburden over mineralisation relative to the surrounding overburden over country rock. As electronic current continues, there must be continual outward dissipation of negative charge into surrounding overburden or the build-up of reducing conditions around the top of the conductor would eliminate the voltage differential and current would cease. Once solid-phase oxidising agents are consumed, this dissipation of negative charge must take place by the outward migration of reduced ionic species away from, or the inward migration of oxidised ionic species toward the cathode. This process is necessarily coupled with oxidation-reduction reactions occurring between the top surface of the conductor and the water table that involve both reduced and oxidised species. The dissipation of negative charge away from the conductor is accomplished as the oxidation states of reduced species change during this process, resulting in dissolved, gaseous or precipitated products that have a higher redox potential than the reduced reactants.

Figure 4 provides a hypothetical example of the potential outcome of this process in young, exotic sediments. Figure 4a depicts a fine-grained, glacial material, shortly after deposition in which a background redox differential of 150 mV exists between groundwater at the water table and in basal overburden units. An electronically conductive, steeply dipping mineral deposit occurs in bedrock. More reducing conditions immediately above the conductor result in a redox differential of 300 mV between the top of mineralisation and the water table. Self-potential contrasts exceeding 150 mV between conductive mineralisation and adjacent rock have often been reported.

At the time of overburden deposition, a very strong vertical redox gradient would exist just above the bedrock conductor along which ions would have a tendency to move. The outward movement of reduced ions such as  $\text{Fe}^{2+}$  or  $\text{S}_2\text{O}_3^{2-}$  would result in the migration of a reduced "front" away from mineralisation (Figure 4b). At the front, reduced ions would come in contact with oxidising agents and redox reactions would take place thereby dissipating negative charge away from the conductor. Once the front reaches the

water table, a reduced "column" will have developed in the groundwater-saturated overburden above mineralisation (Figure 4c). In the fully developed column, electrical current must become focused at the flanks of the column because the SP gradient is stronger in that direction than it would be in the vertical direction.

For every electron passed upward along the conductor, one electron's-worth of reduced species must move away from, or oxidised species move toward, the conductor. This continual migration of redox-active species must be coupled with redox reactions in order to transfer charge. If redox equipotential lines are totally static, the production of reduced species at the conductor must be accompanied by the simultaneous consumption of reduced species somewhere between bedrock and the water table. This would result in the almost instantaneous transfer of electrical current despite the much longer time required for mass transport of reduced species to the ground surface.

The model just described was proposed by Hamilton (1998) to account for selective leach geochemical anomalies over conductive mineralisation in high-water table Pleistocene glaciated terrain. It should, however, be applicable in most overburden environments that meet the main criterion for the development of such a cell – i.e. that overly a redox anisotropy on the bedrock surface. The presence of any geological unit that is strongly reducing relative to surrounding rock and/or that is being actively oxidized should result in an overburden cell.

### **Geochemical Anomalies Related to SP Cells**

The two types of redox-cells just described should have similar surface geochemical phenomena associated with them because they would all have similar ionic flow patterns in the uppermost portion of the cell. They are both based on a reduced feature as a source of negative charge and the oxygenated surface as the ultimate source of positive charge and they must involve transfer of ionic current between the two sources. The result will be a general outward movement of ions that are capable of transporting negative charge such as  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{HS}^-$  and  $\text{S}_2\text{O}_3^{2-}$ ; and an inward movement of ions that are capable of transporting positive charge such as  $\text{UO}_2^{2+}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{VO}_4^{3-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and dissolved oxygen radicals. The final transfer of negative charge at the top of the cells involves redox reactions that would, in many cases, attenuate the transported reduced species into the solid phase thereby forming geochemical anomalies.

One outcome of the migration of ions from one redox region into another should be the zonation of elements in relation to the reduced column (Figure 5). Element zonation is a reported feature of selective leach anomalies. Zonation could potentially occur due to a variety of processes the most important of which would be progressive deposition of redox active species as they migrate into or out of the reduced column. The migration paths of reduced versus oxidised ions are predictable provided the current flow patterns can be inferred and therefore, if the redox behaviour of a particular ion is also known, the shape of anomalies can also be inferred.

Two of the factors that should control where mobile elements are deposited in relation to the reduced column are: (1) the Eh at which a redox active species will convert to a species of a different oxidation state; and (2) the mobility of the new species. For example, inward migrating species that are highly oxidising and show low mobility in reducing environments, such as  $\text{UO}_2^{2+}$  are expected to become reduced early and form anomalies at the outer-most edges of the reduced column (Figure 5A). At the other extreme, inward migrating, weakly oxidising species that can show high mobility in reducing environments, such as  $\text{SO}_4^{2-}$ , would not become reduced until they reached the inner part of the column and even then might not form anomalies in soils because of their high mobility. Similar but opposite processes occur with reduced species in the outward direction.

One of the more important reduced species capable of forming anomalies in soils is  $\text{Fe}^{2+}$ . Both the abundance and the secondary processes associated with iron reactions suggest that it will have a major impact on the geochemistry of surface soils.  $\text{Fe}^{2+}$  is moderately strongly reducing and has very low mobility in oxidised,  $\text{Fe}^{3+}$ , form. It is therefore expected to form anomalies at the redox front near the inner edge of the reduced column. When most reduced metals and, in particular,  $\text{Fe}^{2+}$  oxidise, they hydrolyse water to form insoluble metal hydroxides. In the process, large amounts of acid are generated (Figure 13B).  $\text{H}^+$  anomalies are commonly reported in association with rabbit-ear anomalies over mineralisation. In the phreatic zone  $\text{H}^+$  is most likely to be generated, not by the downward diffusion of oxygen and the oxidation of the sulphide itself, as in the past had always been assumed to occur, but by the upward transport of reduced iron along an electrochemical gradient to oxidising agents at the redox front (i.e. the reducing agents are brought to the oxidising agents rather than the other way around).

A secondary process related to iron oxidation may be  $\text{CO}_2$  production in areas where carbonate is present (Figure 5B). Acid produced at the edge of the reduced column by  $\text{Fe}^{2+}$  oxidation should produce dissolved  $\text{CO}_2$  ( $\text{H}_2\text{CO}_3$ , Figure 5B) by dissolution of carbonate in rock or overburden material. In adjacent areas near or above the water table, dissolved  $\text{CO}_2$  can degas causing carbonate supersaturation and deposition. From here,  $\text{CO}_2$  and carbonate-charged soil moisture could also disperse upward through the unsaturated zone by capillary action. As moisture evaporates, near-surface  $\text{CO}_2$  would degas and carbonate would precipitate, forming both soil carbonate and  $\text{CO}_2$  gas anomalies (Smee, 1998). Smee (1998) attributed rabbit-ear anomalies in Ca, Mg, Sr, and possibly also Au and As to their transport in bicarbonate complexes and their precipitation in shallow soils due to processes such as these occurring in the unsaturated zone.

The thousands of potential redox reactions that facilitate charge transfer away from the reduced source could result in a net loss of cations or anions from solution in the vicinity of some reactions. As such, the movement of redox-inert species is likely to be continuously occurring from one part of the overburden electrolyte to another to prevent local charge imbalances. However, it is difficult to predict the transport paths of these ions because their movement depends on the specific nature of the reactions occurring at a given site. Empirical observation is probably the most viable method for determining

the behaviour of a redox-inert species. Clark (1996) reports an empirically observed "oxidation suite" of elements that often occur as rabbit-ear anomalies flanking ore deposits and include Cl, Br, I, As, Sb, Mo, W, Re, Se, Te, V, U and Th. Most of the elements in this suite are far more mobile in oxidized than reduced form and, as such probably migrate inward to form reduction anomalies (notwithstanding the name applied to the suite). However, several elements are likely mobile as redox-inert species (e.g. Cl, Br, I) or perhaps as ligands in metallic complexes and therefore their movement may be a secondary result of other species migrating and subsequent reactions occurring inside and outside the column.

## **Conclusions**

Although groundwater transport, chemical diffusion and gaseous transport are viable mechanisms for the transport of elements in some environments, they cannot explain the specific characteristics of mineralization-related selective-leach anomalies in all environments. Electrochemical transport of elements due to the presence of an SP cell over, or related to, mineralization or other bedrock features appears to account for most of the characteristics observed.

The primary criterion for development of a cell is the existence of a buried reduced feature. Potential economically exploitable features might include the following:

- Conductive sulphide mineralization.
- Non-conductive but oxidisable sulphide mineralization (eg. sphalerite)
- Ultramafic dikes, diatremes and flows. This could include komatiites, kimberlites and lamprophyres.
- Geological contacts between two units with strong redox contrast such as carbonatite and granite
- Shear-zones containing fault gouge
- Graphitic-hosted gold mineralization.
- Bitumen, coal or natural gas seeps.

Potentially non-economic sources of reducing agents that might result in a cell include:

- Barren sulphide mineralization
- Groundwater upwellings
- Geological contacts between two units with strong redox contrast such as diabase and granite
- Barren graphite horizons
- Methane pockets in shale or overburden.
- Gas hydrates

The study of electrochemical cell processes that result in surface geochemical anomalies is still in its infancy. Many apparently unrelated geochemical processes and phenomena over mineralization and other chemically reduced features may turn out to be directly or indirectly related to electrochemical processes. Although electro-geochemical techniques have enormous potential, a great deal of additional work must be done if geochemical sampling over deeply buried features is to be a reliable and easily interpretable technique.

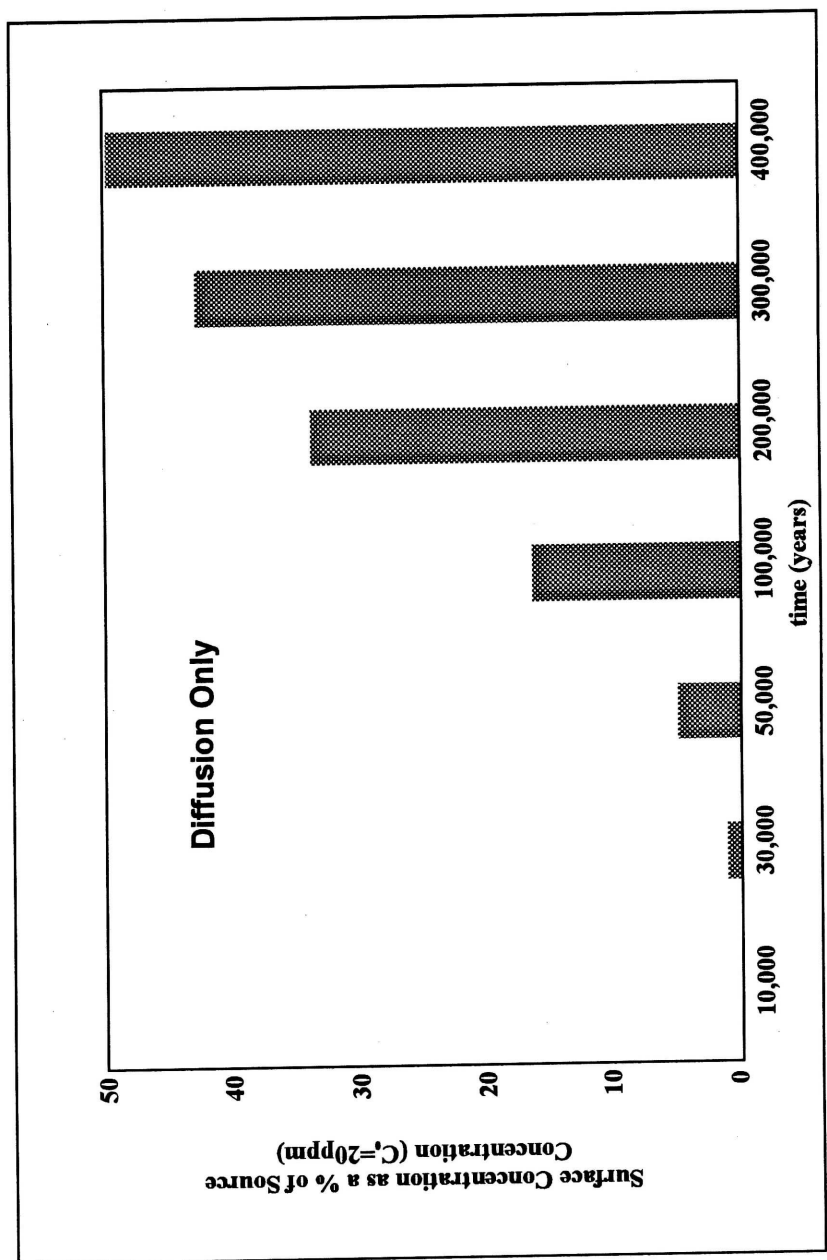
One of the most pressing issues is to determine mass transport rates from bedrock and whether a signature due to bedrock is possible within the age period of young deposits or whether attenuation and perhaps replacement of charge carriers between bedrock and ground surface will result in spurious overburden-related anomalies. Another important issue is the understanding of the specifics of charge and mass transfer from the reduced source to the groundwater environment.

## References

- Barnes, I., O'Neil, J.R., and Trescases, J.J., 1978. Present day serpentinization in New Caledonia, Oman and Yugoslavia. *Geochim. Cosmochim. Acta*, 42: 144-145.
- Bass Becking, L.G.M., Kaplan, J.R. and Moore, D., 1960. Limits of the natural environment in terms of pH and oxidation – reduction potentials. *J. Geol.*, 68: 243 – 284.
- Bolviken, B. and Logn, O. 1975. An electrochemical model for element distribution around sulphide bodies. In: I. Elliot and K. Fletcher (Eds), *Geochemical Exploration 1974*, Elsevier, Amsterdam: 631-648.
- Clark, J.R., 1996. Unique significant enzyme leach anomaly patterns in areas of tropical/subtropical weathering. *Queen's University Conference Proceedings*: 241-256.
- Clark, J.R., 1997. Concepts and models for interpretation of enzyme leach data for mineral and petroleum exploration. Unpublished company manuscript, Enzyme – Actlabs, LLC, 62p.
- Freeze, R.A. and Cherry, J.A., 1979. *Groundwater*. Prentice-Hall, Englewood Cliffs, NJ, 604 p.
- Hamilton, S.M., 1998. Electrochemical mass-transport in overburden: a new model to account for the formation of selective leach geochemical anomalies in glacial terrain. *J. Geochem. Explor.* 63: 155-172.
- Govett, G.J.S. and Chork, C.Y. 1977. Detection of deeply buried sulphide deposits by measurement of organic carbon, hydrogen ion and conductance in surface soils. *Prospecting in Areas of Glaciated Terrain*, Inst. Min. Metall., London: 49-55.
- Lovell, M., Hale, M. and Webb, J.S., 1983. Soil air carbon dioxide and oxygen measurements as a guide to concealed mineralization in semi-arid and arid regions. *J. Geochem. Explor.*, 19: 305-317.
- McCarthy, J.H. Jr., Lambe, R.N., Dietrich, J.A., 1986. A case study of soil gases as an exploration guide in glaciated terrain – Crandon massive sulphide deposit, Wisconsin. *Econ. Geol.* 81, 408-440.

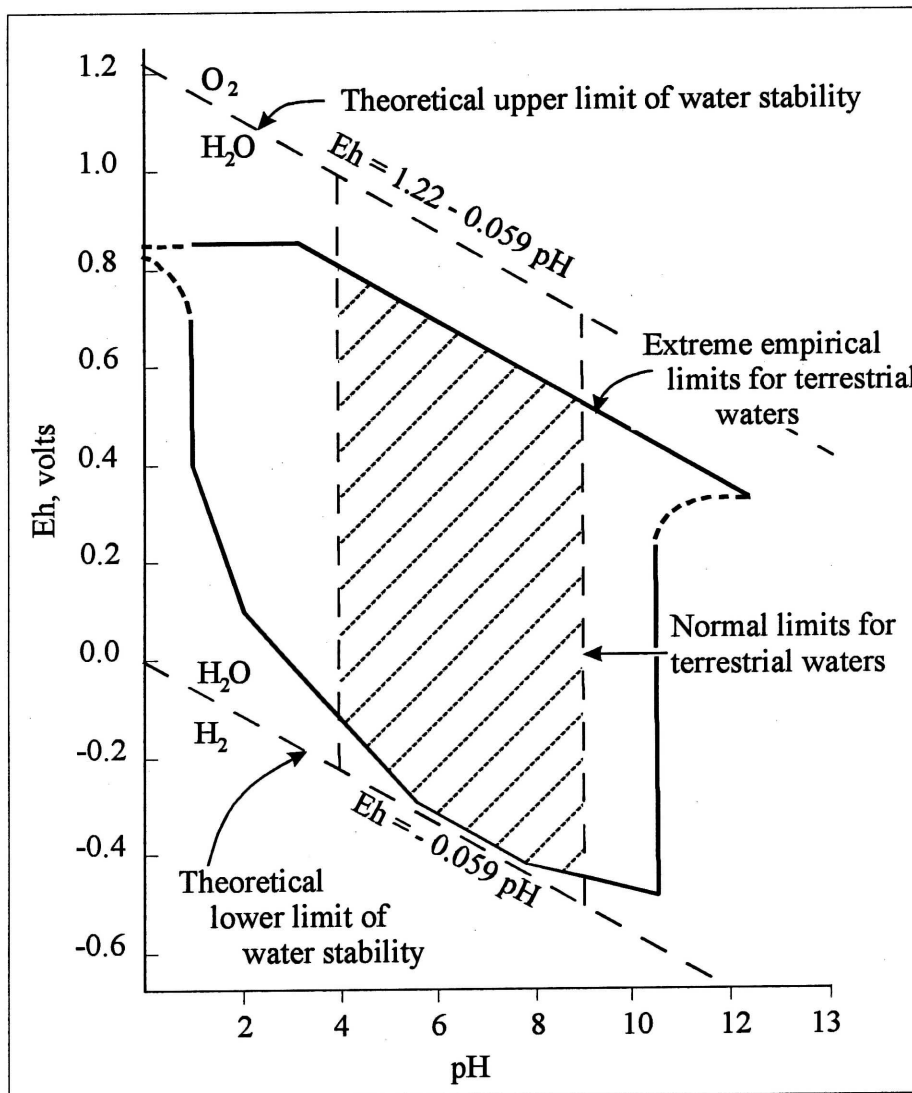
- Sato, M. and Mooney, H.M., 1960. The electrochemical mechanism of sulphide self-potentials. *Geophysics*, 25: 226-249.
- Smee, B.W., 1979. A theoretical estimation of ion mobilities through glaciolacustrine sediments: Diffusion down a concentration gradient. *Curr. Res., Part A, Geol. Surv. Can., Pap. 79-1A*: 367-374.
- Smee, B.W., 1983. Laboratory and field evidence in support of the electrochemically enhanced migration of ions through glaciolacustrine sediment. *J. Geochem. Explor.*, 19: 277-304.
- Smee, B.W., 1998. A new theory to explain the formation of soil geochemical responses over deeply covered gold mineralization in arid environments. *J. Geochem. Explor.*, 61: 149-172.
- Webber, G.R., 1975. Efficacy of electrochemical mechanisms for ion transport in the formation of geochemical anomalies. *J. Geochem. Explor.*, 4: 231-233.



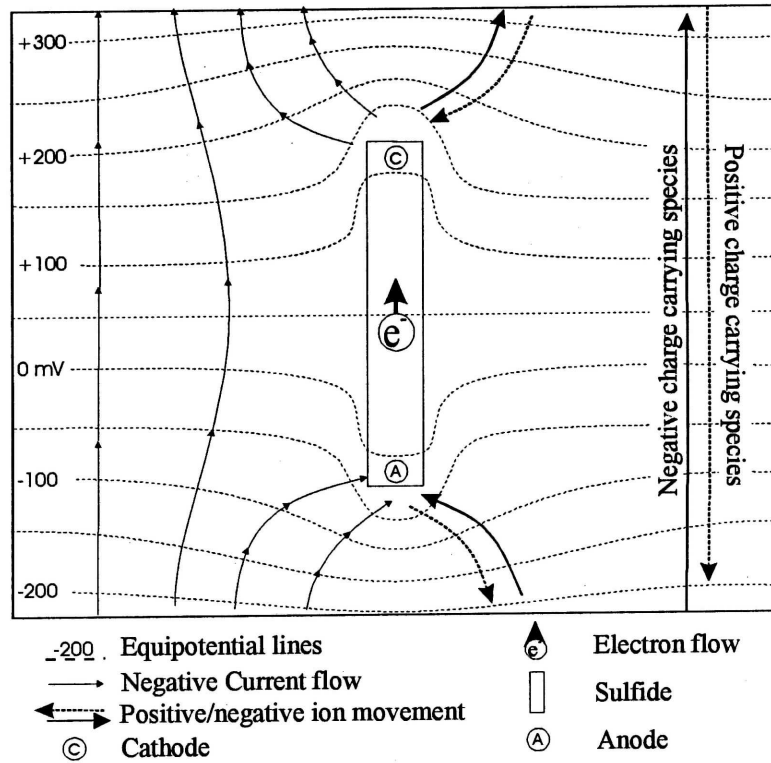


**Figure 1 - Surface concentration vs time during diffusion of a hypothetical major ion (diffusion coefficient = 0.0024 m<sup>2</sup>/year) through 30m of overburden.**

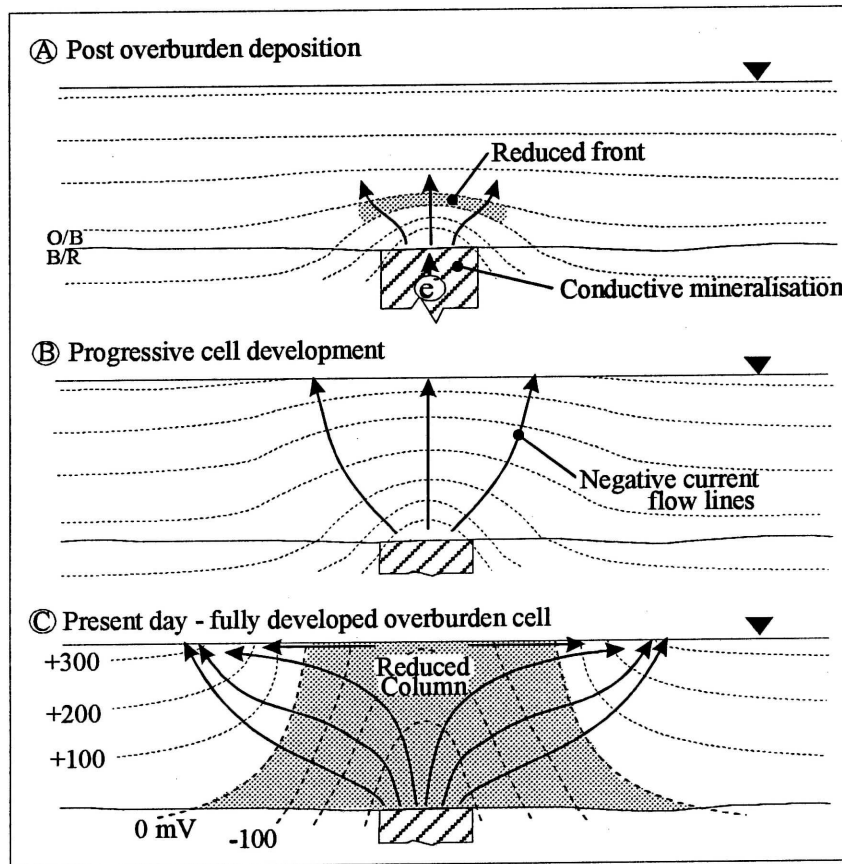




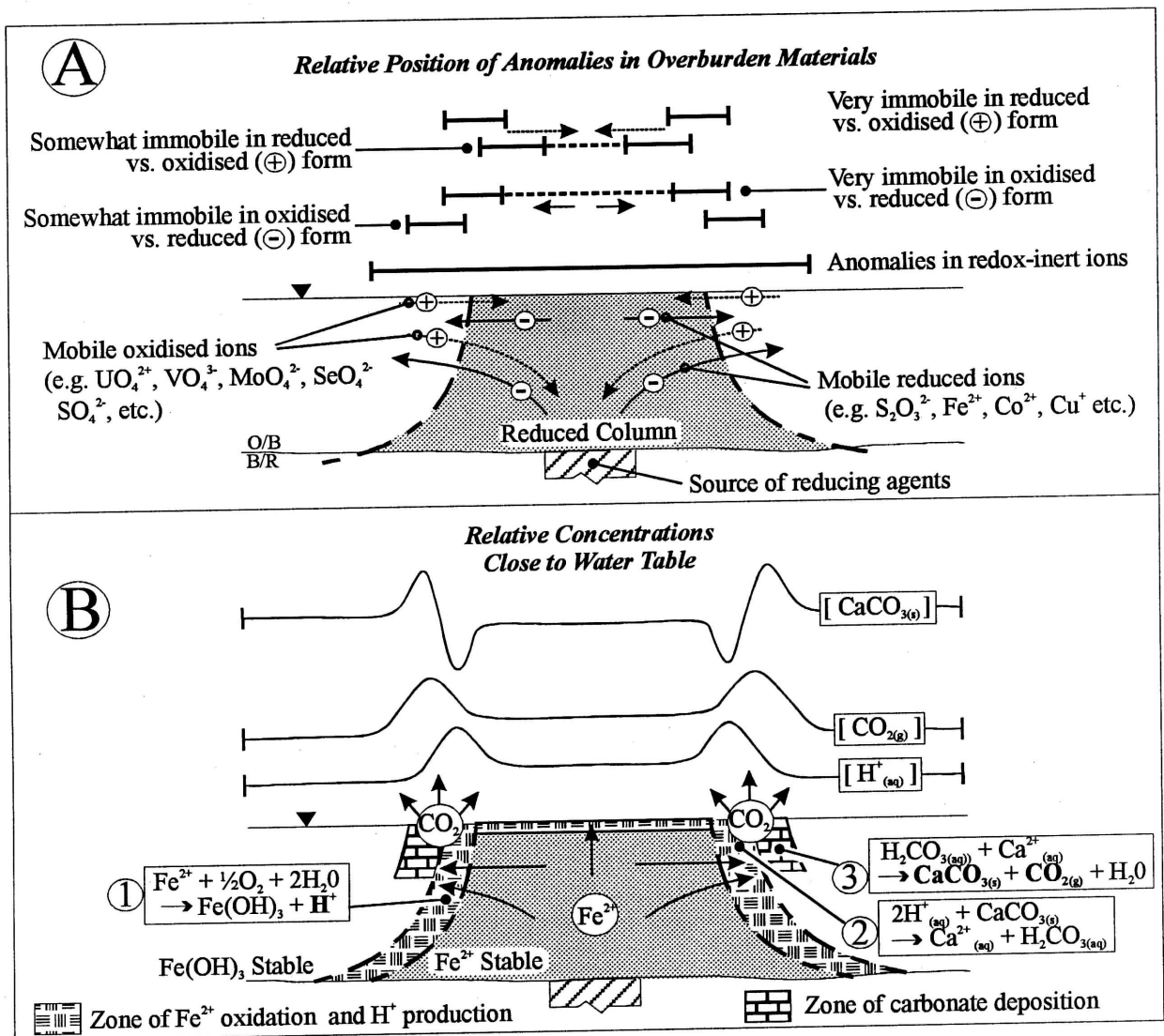
**Figure 2.** The theoretical and empirical stability fields for shallow terrestrial systems (after Bass Becking et al.).



**Figure 3.** Interpretation of the equipotential and ionic current flow lines around a single-phase sulphide ore body in a uniform redox field after the model of Sato and Mooney (1960). Equipotential lines are labelled to depict an upward increasing gradient and are not intended to be an actual representation of the earth field (from Hamilton, 1998).



**Figure 4.** The progressive modification of redox-equipotential lines in saturated overburden overlying an electronic conductor in bedrock (modified after Hamilton, 1998). The purpose of the labelled equipotential lines is as per Figure 3.



**Figure 5.** The development of anomalies that are (A) directly related to electrochemical processes and (B) related to secondary processes occurring as a result of mobility and oxidation of ferrous iron.