Secondary Geochemical Dispersion Through Transported Overburden

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As the discovery rate of world class ore deposits continues to decline, increased attention is being focused on geochemical exploration methods designed for covered terranes. For companies that manage their exploration from a risk-based perspective, the development of reliable methods for the detection of ore deposits covered by transported overburden is critical to their future success. For the exploration methods to be reliable, an understanding of the dispersion processes is required.

Numerous published case studies have documented secondary geochemical anomalies in transported overburden above buried mineral deposits in many different environments using a variety of methods (e.g. Cameron et al. 2004, Kelley et al. 2002, Wang et al. 1999, Smee 1998; Mann et al. 1998). There is much debate regarding the factors that form these anomalies but research conducted in the past 10 years has clarified some of the processes involved. In simplest terms, secondary geochemical mobility trough transported overburden can be related to dispersion of dissolved solids in water, of soil gases, and by living systems, such as plants and microbes.

Dispersion of dissolved solids in water

Groundwater surrounding oxidizing sulfide deposits contains a mixture of dissolved components, colloidal material, and secondary reaction products that form precipitates. The aqueous mobility of metals is controlled by pH, Eh (oxidation potential), the speciation of the metals, e.g., anions or cations, presence of other dissolved species in solution, the composition and reactivity of solid phases in contact with the aqueous solution, and the interaction with microbes. The groundwater provides a media for the dispersion of ore and related pathfinder elements away from the sulfide deposit.

If the sulfide deposit and groundwater table are near the surface, electrochemical processes may dominate, resulting in the redistribution of redox-active elements and carbonate (Hamilton 2000). In arid environments, an external force, such as seismic activity, is required to move metal-rich groundwater vertically through the vadose zone (Cameron et al. 2002). In the case where oxidizing sulfide deposits are buried gradually by successive depositional episodes of alluvium, dissolution of water soluble phases followed by infiltration and evapotranspiration of surface water concentrates metals in the newly deposited alluvium (Kelley et al. 2002).

Electrochemical Dispersion
Self-potential currents associated with oxidizing sulfide deposits (Sato & Mooney 1960) form the basis of electrochemical dispersion models in which the upward movement of electrons in the sulfide body results from electrochemical gradients between the underlying reducing to overlying oxidizing environments (Govett 1973, Bolviken & Logn 1975, Smee 1983). The mass transfer of ionic species facilitates charge balance and creates the geochemical anomalies in the overburden. The model of Hamilton (1998, 2000) takes into account the upward propagation of reduced species to the water table forming a reduced column over the mineralized zone. The oxidation of Fe^{2+} produces H^+, causing dissolution of carbonate, which precipitates at the edge of the reduced column. Theoretical ion migration rates in electrochemical fields are much faster than diffusion rates and are consistent with the formation of geochemical anomalies in young (ca. 8000 years), thick glacial drift (Hall et al. 2004 this volume).

Cyclical Dilatancy Pumping
The mass transfer (advection) of groundwater and its dissolved components following earthquakes accounts for the redistribution of metals around buried deposits in some environments (Cameron et al. 2002). In a process termed 'cyclical dilatancy pumping' (Sibson 2001), groundwater held in fractures is expelled during and after earthquake events. Changes in water well levels, increased stream flow during drought periods, and the expulsion of groundwater along faults causing surface flooding have been used as evidence for cyclical dilatancy pumping (Tchalenko 1973, Tchalenko & Berberian 1974, Nur 1974, Sibson 1981, Muir-Wood, 1994). Secondary dispersion from this process would predictably have 1) characteristic high-

amplitude, narrow structurally-controlled response patterns, and 2) chemical associations in soils similar to the groundwater chemistry.

Results of soils and groundwater analyses from an integrated study at the Spence porphyry copper deposit in northern Chile, buried beneath 50 to 100 m of Miocene gravels, are consistent with the vertical movement of metal-rich groundwaters along fractures during earthquakes in this seismically active area (Cameron et al, 2002, 2004). Copper in groundwater is restricted to the mineralized area due to the tendency of Cu^{2+} released by oxidation of sulphides to adsorb to Fe hydroxide colloidal particles and coatings, whereas elements that dissolve as anions (e.g. As, Mo, Se and Re), are dispersed widely. Field measurement of the conductivity of soil-water slurries showed two zones of salt (NaCl) enrichment, one directly over the deposit and the other 1 km away. Trenching of the soils in these zones revealed vertical fractures in the gravels, whereas trenching in a background area showed no fractures. The fracture zones appear to have formed by reactivation of basement faults. Elements present in the soils above the fracture zones are the same that are enriched in groundwater near the deposit and indicate the pumping of metal-rich groundwater to the surface during earthquakes, followed by evaporation and redistribution of elements by rain. Both fracture zones contain NaCl in addition to anomalous anions, whereas Cu is restricted to the fracture zone above the deposit. Similar anomalies were found in the gravel soils above the boundary faults of the Gaby Sur porphyry copper deposit in the same region.

Supercedency

In arid environments, when oxidized sulfide deposits are buried gradually by alluvium, chemical transference from the underlying source material to the newly deposited alluvium may occur (Kelley et al, 2002). Oxidized sulfide deposits exposed at the surface typically have strongly mineralized residual soil with elements occurring in a variety of forms, including water soluble phases. Deposition of the first layer of alluvium produces a physical mixing of the residual soil with the transported material. Dissolution of the water soluble phases produces metal-rich surface water which infiltrates downward. Evaporation of this water causes metal enrichment within the mixed layer of residual soil and alluvium. Successive wet/dry cycles through time facilitates a gradual chemical equilibrium between the older alluvium and the newly deposited alluvium, allowing the surface signature of an originally exposed deposit to be transferred to successive layers. This process is likely more important in arid environments where the overburden is relatively thin, and soluble saline minerals form from evaporation. The characteristic anomaly pattern is a baseline shift with several samples containing elevated values in sequence.

Dispersion of Soil Gases

Soil gases are of great interest because of their high degree of mobility through transported overburden. The formation, stability and migration of gas species within the near-surface environment govern the usefulness of soil gas as an exploration tool. Soil gases are produced from chemical, biological and physical processes, all of which are strongly dependent on environmental variables. There are no known gases that are uniquely related to mineral deposits, and most species of interest can be generated from a number of other mechanisms not related to mineral deposits. Further complications result from mass flow processes induced by barometric pumping, rainfall and seasonal temperature variations that create high background variations and problems with dilution. Despite the complex and multiple origins of soil gases, numerous soil gas species (e.g. CO_2/O_2, Hg, Rn, He, sulfur compounds and light hydrocarbons) have been measured over mineral deposits and these appear, at least empirically, to be related to buried mineral deposits (Klusman 1993, Hale 2000).

In arid environments within the vadose zone, vertical movement driven by buoyancy is expected if the overburden is permeable and the gas has significant vapor pressure. Migration of gas below the water table requires that the vapor pressure exceed the fluid pressure in order for a bubble to form, otherwise the gas dissolves in water. Degassing of groundwater may occur by groundwater advection along faults or following seismic activity (Hamilton 2000, Jones et al. 2000). The vertical migration of volatile light hydrocarbons over considerable depths (ca. >1700 m) has been documented by the oil and gas industry by the sharp drop-off of measured hydrocarbons beyond the limits of defined reservoirs and carbon isotope signatures from altered sediments overlying reservoirs (Saunders et al. 1999). Dispersion by rapid streaming of colloid-sized microbubbles driven by buoyancy is the favored interpretation.

Dispersion Facilitated by Biological Processes

Much of the Earth's biosphere is concentrated within a narrow horizon occurring at the interface between the lithosphere and atmosphere. In this region, eukaryotic ecosystems are supported by photosynthetic carbon fixation (primarily plant-derived). The chemical composition of plant material is related to soil composition and the factors that control element uptake. Elements are classified as essential or

non-essential for plant growth. In cases where non-essential elements become toxic (e.g. Au, U, Cu, Pb, Zn), the offending element is 'detoxified' by partitioning to a non-sensitive part of the plant (e.g. bark or twigs) or by chemical binding (Berry 1986). Toxic elements are eventually returned to the ground surface during plant growth or decay, causing natural geochemical recycling. In these near surface environments, bacteria colonize mineral surfaces, growing as biofilms (Southam et al. 1995) or as complex-particle associations of cells (Ferris et al. 1987), and encounter surface- and groundwater as it 'flows' past (a sessile growth phase). Bacteria typically respond to soluble, toxic heavy metals by binding and precipitating these metal ions on their surface, producing fine-grained minerals (Southam et al. 1995). This precipitation is due to the physical and chemical nature of the bacterial cell envelope and can be promoted by dissimilatory metabolic activity. When combined with the ubiquitous nature of bacteria and the enrichment of specific bacterial populations due to mineral and aqueous substrates, bacteria likely have a profound affect on the formation of metal anomalies surrounding mineral deposits.

In addition to these surface processes, the biosphere is active in the subsurface (Lovley & Chapelle 1995) where bacteria serve as active geochemical agents. As a group, bacteria are physiologically diverse and can gain energy from oxidizing inorganic constituents via biooxidation and alternatively, reduce these inorganic constituents using organic carbon as the oxidant. In these systems, the oxidation of metal sulfides is kinetically hindered; however, it can be greatly enhanced via bacterial catalysis, even under neutral pH conditions (Mielke et al. 2003) producing acid and, oxidized iron and sulfur constituents as by-products of metabolism. As these geochemical signatures (including base metals) are released from the sulfide deposit, they will encounter bacterial populations in the subsurface and ultimately the concentrated biosphere at the Earth's surface. Since iron oxidizing bacteria are aerobic autotrophs, the O_2 they consume would contribute to the reduced column present above sulfide deposits and may support dissimilatory iron reducing bacteria, which would maintain the iron as a reduced, mobile phase.

Conclusion

Ore deposits are exceptionally rare and their occurrence in the near surface environment disturbs the natural equilibrium established between the shallow oxidized and underlying reduced environments. The dynamic processes of weathering and sulphide oxidation liberates ore and related elements, making them available for the secondary redistribution away from the deposit. A complex interaction between physical, chemical and biological processes respond to this disturbance to re-establish equilibrium conditions.

The processes mentioned here are at least some of the mechanisms that cause geochemical anomalies in transported overburden over buried mineral deposits. The degree of interaction between these processes and their applicability to other environments is largely unknown. Considerable research is needed to understand the interrelations between the physical, chemical and biological process that occur in overburden settings above mineral deposits. The development of reliable remote geochemical exploration methods is critical for the sustainable discovery of blind ore deposits. In order for these methods to be reliable, they must 1) be optimized for the processes that cause geochemical dispersion, 2) provide sufficient contrast in the response by isolating the targeted process, 3) be used with a thorough understanding of background variation, and 4) provide a high level of precision.

References
Berry, W.L., 1986, Plant factors influencing the use of plant analysis as a tool for biogeochemical prospecting, in *Mineral Exploration: Biological Systems and Organic Matter,* Carlisle, D, Berry, W.L., Kaplan, I.R., & Watterson, J.R., eds, Princiton-Hall, Englewood Cliffs, New Jersey, 13-32.

Bolviken, B., & Logn, O., 1975, An electrochemical model for element distribution around sulphide bodies, in *Geochemical Exploration 1974,* Elliott, I. & Fletcher, K., eds, Elsevier, Amsterdam, 631-648.

Cameron E.M., Hamilton, S.M., Leybourne, M.I., Hall, G.E.M., & McClenaghan, M.B., 2004, Finding deeply buried deposits using geochemistry, Geochemistry: Exploration, Environment, Analysis, 4, 7-32.

Cameron, E.M., Leybourne, M.I., & Kelley, D.L., 2002, Exploring for deeply-covered mineral deposits: formation of geochemical anomalies in northern Chile by earthquake-induced surface flooding of mineralized groundwaters, Geology, 30, 11, 1007-1010.

Ferris, F.G., Fyfe, W.S. & Beveridge, T.J., 1987, Bacteria as nucleation sites for authigenic minerals in a metal-contaminated lake sediment. Chem. Geol. 63:225-232.

Govett, G.J.S., 1973, Differential secondary dispersion in transported soils and post-mineralization rocks: an electrochemical interpretation, in *Geochemical Exploration 1972*, Jones, M.J, ed, Instn. Min. Metall., London, 81-91.

Hale, M, 2000, Geochemical remote sensing of the subsurface, Hale, M. & Govett, G.J.S, eds, Handbook of Exploration Geochemistry, Elsevier, Amsterdam, 7.

Hall, G.E.M., Hamilton, S.M., McClenaghan, M.B., & Cameron, E.M., 2004, Secondary geochemical signatures in glaciated terrain, SEG 2004, Perth (this volume).

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, Journal of Geochemical Exploration, 63, 155-172.

Hamilton, S.M., 2000, Spontaneous potentials and electrochemical cells, in *Geochemical remote sensing of the sub-surface*, Hale, M. & Govett, G.J.S, eds, Handbook of Exploration Geochemistry, Elsevier, Amsterdam, 7, 81-119.

Jones, V.T., Matthews, M.D. & Richers, D.M., 2000, Light hydrocarbons for petroleum and gas prospecting, in *Geochemical remote sensing of the sub-surface*, Hale, M. & Govett, G.J.S, eds, Handbook of Exploration Geochemistry, Elsevier, Amsterdam, 7, 133-211.

Kelley D. L., Hall, G.E.M., Closs, L.G., Hamilton, I.C., & McEwen, R.M., 2002, The use of partial extraction geochemistry for copper exploration in northern Chile, Geochemistry: Exploration, Environment, Analysis, 3, 85-104.

Klusman, R.W., 1993, Soil gas and related methods for natural resource exploration, John Wiley & Sons, Chichester, UK, 483 p.

Lovley, D.R. & Chapelle, F.H, 1995, Deep subsurface microbial processes. Rev. Geophys. 33:365-381.

Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B., & Perdrix, J. L., 1998, Application of the mobile metal ion technique to routine geochemical exploration, Journal of Geochemical Exploration, 61, 87-102.

Mielke, R.E., Pace, D.L., Porter, T. & Southam, G., 2003, A critical stage in the formation of acid mine drainage: Colonization of pyrite by *Acidithiobacillus ferrooxidans* under pH neutral conditions. Geobiology 1:81-90.

Muir-Wood, R., 1994, Earthquakes, strain-cycling and the mobilization of fluids, in *Geofluids: origin, migration and evolution of fluids in sedimentary basins*, Parnell, J., ed, Special Publication, Geological Society, London, 78, 85-98.

Nur, A., 1974, Matsushiro, Japan, earthquake swarm: confirmation of dilatancy-fluid diffusion model, Geology, 2, 217-221.

Sato, M., & Mooney, H.M., 1960, The electrochemical mechanism of sulphide self-potentials, Geophysics, 25, 226-249.

Sibson, R.H., 1981, Fluid flow accompanying faulting: Field evidence and models, in *Earthquake prediction: an internal review*, Simpson, D.W. & Richards, P.G., eds, Maurice Ewing Series, American Geophysical Union, 4, 593-603.

Sibson, R.H., 2001, Seismogenic framework for hydrothermal transport and ore deposition, in *Structural controls on ore genesis,* Richards, J.P. & Tosdal, R.M., eds, Reviews in Economic Geology, Society of Economic Geologists, Boulder, 14, 25-50.

Smee, B. W., 1998, A new theory to explain the formation of soil geochemical responses over deeply covered gold mineralization in arid environments, Journal of Geochemical Exploration, 61, 149-172.

Smee, B.W., 1983, Laboratory and field evidence in support of the electrochemically-enhanced migration of ions through glaciolacustrine sediment, Journal of Geochemical Exploration, 19, 277-304.

Saunders, D.F., Burson, K.R., & Thompson, C.K., 1999, Model for hydrocarbon microseepage and related near-surface alterations, AAPG Bulletin, 83,1, 170-185.

Southam, G., Ferris, F.G. & Beveridge, T.J., 1995, Mineralized bacterial biofilms in sulfide tailings and in acid mine drainage systems, in *Microbial Biofilms*, Lappin-Scott, H.M. & Costerton, J.W., eds, Cambridge University Press, Cambridge, Great Britain, pp. 148-170.

Tchalenko, J.S. & Berberian, M., 1974, The Salmas earthquake of May 6th, 1930, Annali di Geofisica, 27, 151-212.

Tchalenko, J.S., 1973, The Kashmir (Turshiz) 1903 and Torbat-e Heidariyeh (South) 1923 earthquakes in Central Khorassan (Iran), Annali di Geofisica, 26, 29-40.

Wang X., Xie, X., Cheng, Z., & Liu, D., 1999, Delineation of regional geochemical anomalies penetrating through thick cover in concealed terrains – a case history from the Olympic Dam deposit, Australia, Journal of Geochemical Exploration, 66, 85-97.