



INNOVATIVE ENZYME LEACH PROVIDES COST-EFFECTIVE OVERBURDEN/BEDROCK PENETRATION

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INTRODUCTION

Layers of glacial till and glaciolacustrine sediments cover large areas of the Canadian Shield, and much of the bedrock in the Basin and Range Province of United States and Mexico and much of the Atacama Desert of Chile and Peru have been buried by basin fill and volcanic rocks. The problem, when trying to perform geochemical exploration in terranes that are covered by transported overburden, is that the overburden is usually exotic to the bedrock that it covers. In tropical regions, laterite has formed due to intense weathering, which has stripped the surficial material of the original chemical signature of the parent rock. Conventional chemical analysis would reveal only the composition of the overburden and would not give any indication of the underlying bedrock. Total methods of analysis and stronger-leaching techniques produce results that are dominated by the overburden signature, and random variations in this signature suppress any anomalous chemistry emanating from underlying mineralization. In the past, drilling has been the only means of collecting useful geochemical samples in areas of extensive overburden. An inexpensive means is needed for detecting subtle geochemical dispersion through transported or deeply weathered overburden and providing some indication of the chemistry of the bedrock.

Trace elements released by weathering of mineral deposits in the bedrock will migrate up through overburden by such means as ground water flow, capillary action, or diffusion of volatile compounds. However, the amount of these bedrock-related trace elements is typically a very small component of the total concentration of these elements in the overburden. The goal is to determine the amount of a trace element that has been added to the overburden rather than the total amount in the overburden sample. Upon reaching the near surface environment, many of the trace elements migrating through overburden will be trapped in manganese oxide and iron oxide coatings, which form on mineral grains in the soils. One of the most effective traps for trace elements migrating

toward the surface is amorphous manganese dioxide, which is usually a very small component of the total manganese oxide phases in the soil sample. Not only does amorphous manganese dioxide have a relatively large surface area, but the irregular surface and the random distribution of both positive and negative charges on that surface make it an ideal adsorber for a variety of cations, anions, and polar molecules.

A selective leach has been developed that employs an enzyme reaction to selectively dissolve amorphous manganese oxides in soils and sediments. The enzyme catalyzes a reaction between sugar oxygen and water, generating trace amounts of hydrogen peroxide. The trace of H_2O_2 produced tends to selectively dissolve amorphous MnO_2 present in soils. When all the amorphous manganese dioxide in the sample has been reacted, the enzyme reaction slows, and the leaching action also slows. Because the enzyme leach is self limiting, there is minimal leaching of silicate and iron oxide mineral substrates in the sample. Thus, background concentrations for many elements determined are extremely low and the anomaly/background contrast is dramatically enhanced. The preferred sample material is *B*-horizon soils, where they are available. It is in the upper ten to thirty centimeters of the *B* horizon that has the greatest concentration of active amorphous manganese dioxide. Where soils are poorly developed, *C*-horizon soil or weathered scree, the lower (mineral-rich) *A*-horizon soil, and fine-granular layers above caliche also make good sample media. Dense layers of caliche, calcrete, and gypcrete cannot be used as sample media and are to be avoided. Typically, four types of geochemical anomalies are found with the Enzyme Leach:

1. Mechanical/hydromorphic dispersion anomalies;
2. Oxidation halo anomalies;
3. Apical anomalies;
4. Combination anomalies.

TYPICAL ENZYME LEACH ANOMALY PATTERNS

Mechanical/hydromorphic dispersion

In terranes where the bedrock is buried by glacial overburden, mechanical/hydromorphic anomalies are the most common type found (although all four types of anomalies are observed in soils developed on tills). Mechanical dispersion trains were formed in the basal till as mineralized bedrock material was smeared down ice during glaciation. Gradual weathering of this mineralized material releases trace elements into the ground water flowing through the till. Vegetation with roots tapping into either the mineralized till or anomalous ground water picks up trace elements which are eventually shed to the forest floor in plant litter. Anomalous trace elements are often relatively quickly leached from the A-soil horizon and trapped in oxide coatings in the B horizon. In essence, the B-soil horizon often acts as a long-term integrator of vegetation anomalies (Clark, 1993). The Enzyme Leach has been used to detect very subtle mechanical/hydromorphic anomalies related to mineralized bedrock in a number of glacial overburden situations, including areas where the glacial till is blanketed with glaciolacustrine sediments. Subtle hydromorphic dispersion anomalies in stream sediments have also been detected with the Enzyme Leach. Trace element suites comprising mechanical/hydromorphic-related soil anomalies commonly reflect at

least part of the chemical signature of the bedrock source. Anomaly contrast in soils developed on glacial till often range from 2–10 times the background concentrations for the elements forming the anomaly. In some cases, Enzyme Leach anomaly patterns produced by mechanical and hydromorphic dispersion processes are quite similar morphologically to those that are detected with conventional chemical analyses.

Table 1: Boiling points of elemental halogens and some halide compounds.

Compound	Boiling point °C	Compound	Boiling point °C
Cl ₂	-35	AsCl ₃	130
Br ₂	59	AsBr ₃	221
I ₂	184	AsI ₃	403
VCl ₆	152	MoCl ₅	264
VClO ₃	127	ReCl ₅	330
WCl ₅	288	ZrCl ₄	331
WClO ₄	220	SeCl ₄	subl @ 196

Oxidation anomalies and halos

Oxidation anomalies are produced by the gradual oxidation of buried reduced bodies. Any reduced body (an ore deposit, a barren body of disseminated pyrite, a buried geothermal system, a petroleum reservoir, etc.) can produce one of these anomalies. Once these anomalies are found, it is up to the geologist to make a geological interpretation based on all the information at hand, including Enzyme Leach data, as to what the source of the anomaly might be. These anomalies are characterized by very high contrast values for a suite of elements, the “oxidation suite,” which can include Cl, Br, I, As, Sb, Mo, W, Re, Se, Te, V, U, and Th. Often, rare-earth elements and base metals will be anomalous in the same soil samples, but with lower contrast. Evidence indicates that the oxidation suite migrates to the surface as halogen gases and volatile halide compounds (Table 1). These elemental gases and volatile compounds are stable only under highly oxidizing conditions. Thus, they would tend to form under the acid/oxidizing conditions of the anode of an electrochemical cell. Low contrast base-metal anomalies, often found coinciding with oxidation-suite anomalies, may result from the gradual migration of cations away from these anodes along electrochemical or thermodynamic gradients. This juxtaposition of anomalies of the oxidation suite elements, which normally are mobile as anions, with anomalies of base metals, which would be mobile as cations, is at variance with the classical model for electrochemical cells associated with buried sulphide mineral deposits. Less commonly, enzyme-soluble Au and enzyme-soluble Hg will be found in the area of these anomalies. Metallic Au and Hg are not soluble in the enzyme leach. These low-level Au and Hg anomalies often appear to form as a result of the oxidation of these elements in the soil by the subtle flux of oxidizing gases passing through the soil.

Oxidation anomalies typically form an asymmetrical halo or partial halo around the buried reduced body, and that body underlies part of the central low within that halo (Figure 1). The trace element suite in oxidation anomalies, although often enriched in many types of metal deposits, is not typically representative of the composition of the buried

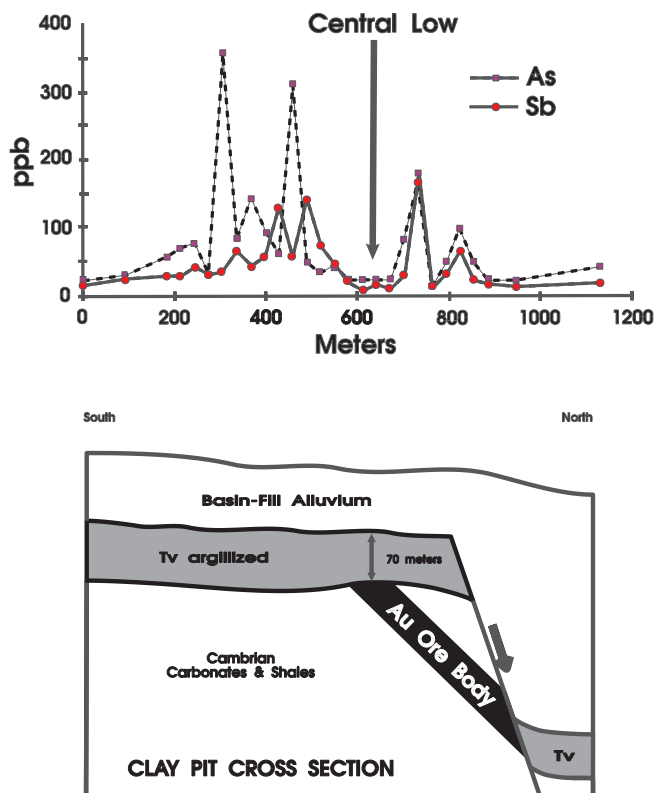


Figure 1: Typical Enzyme Leach oxidation halo over the Clay Pit deposit, an epithermal gold ore body in the Getchell Trend, Nevada. The central low directly overlies the upper end of the mineralized body. The deposit is capped by seventy meters of argillized Tertiary volcanic rock and eighty meters of basin-fill alluvium.

reduced body. For example, a very similar suite of elements forms halos around petroleum reservoirs as is found around porphyry copper deposits, epithermal gold deposits, buried geothermal systems, and barren pyritic bodies. Sometimes, the base metal association in the halo is indicative of the composition of the source. Oxidation anomalies can form above reduced bodies that are covered by either overburden or barren rock. The depth of detection for oxidation anomalies is often too great for the mineralized body to be of economic interest. In arid climates, anomaly-to-background ratios for the oxidation suite commonly range between 5:1 to 50:1, and sometimes anomaly contrast exceeds 100-times background. Oxidation anomalies tend to have more subdued contrasts in humid climates. Because of the difference in the oxidation potential required to oxidize chloride, bromide, and iodide to elemental chlorine, bromine, and iodine (Table 2), you would expect to see a differentiation pattern within oxidation halos. With larger deposits, such as porphyry systems, these patterns are observed about one-third of the time. When a distinct separation of Enzyme Leach Cl, Br, and I is observed, the peak Cl anomaly is closest to the boundary of the central low, and the peak iodine anomaly is farthest out on the margins of the halo.

Table 2: Standard electrode potentials for the oxidation of halides to halogens.

Reaction	E° volts
$2\text{Cl}^- = \text{Cl}_2 + 2\text{e}^-$	+1.39
$2\text{Br}^- = \text{Br}_2 + 2\text{e}^-$	+1.08
$2\text{I}^- = \text{I}_2 + 2\text{e}^-$	+0.62

Apical anomalies

An apical anomaly detected with the Enzyme Leach occurs directly over its source rather than forming a halo around the source. Often these anomalies appear to form as the result of diffusion of trace elements away from a highly concentrated source. The suite of trace elements represented in the anomaly is indicative of the chemical composition of the ultimate source of those trace elements. That source can be the actual source of the anomalous trace elements, or it can be a structure such as a fault that facilitates the movement of trace elements to the surface. Simple apical anomalies that lie directly over a buried mineral deposit often will not show dramatic halogen contrast, as is typically found with oxidation anomalies. Where a metallic mineral deposit is the source of such an anomaly, there sometimes is something in the overburden or overlying rock retarding the gradual formation of an oxidation anomaly. In a laterite terrane where the near surface portion of the deposit has been intensely weathered an apical anomaly will often be observed. In one case study in southern Brazil, where Precambrian schists containing shear-hosted Au deposits have been deeply lateritized, an apical 2.5 ppb Enzyme Leach Au anomaly occurs directly over the mineralized bedrock (Figure 2). The anomalous contrast in this case is twenty-five times background, where other geochemical methods did not reveal any anomaly. In some cases that “something” is an actual barrier, but in many cases it is simply depth. A “fault-related” anomaly will occur almost directly over the subcrop of the fault. Most of the anomalies

detected with the Enzyme Leach are fault-related. However, where a buried reduced body is intersected by a fault, an oxidation suite of elements, including one or more halogens, can form an extremely high-contrast anomaly directly over the trace of the buried fault. Otherwise, apical anomalies usually exhibit a diminished contrast above background, compared to oxidation anomalies. Fault-related anomalies commonly contain very high-contrast concentrations of zirconium and other supposedly “immobile” elements.

Combination anomalies

Metallic mineral deposits can present a complete gradation of Enzyme Leach anomaly patterns from oxidation halos to apical anomalies. Many anomaly patterns are combination anomalies, in that they exhibit the characteristics of both oxidation halos and apical anomalies. In these cases, many of the members of the oxidation suite occur around the sides of the buried deposit, and one or more commodity metals are found in the center of the anomaly, directly over the source. Any trace elements added to the host rocks of the deposit may also produce an apical anomaly over the alteration zone. With increasing efficiency of the oxidation process, several changes are observed in the morphology of these anomalies:

1. Initially, a weak halo comprised primarily of bromine and/or iodine is produced by a weak oxidation cell. The number of trace elements in the oxidation halo increase and the anomalous contrast of those elements tends to rise with increasing strength of a cell.

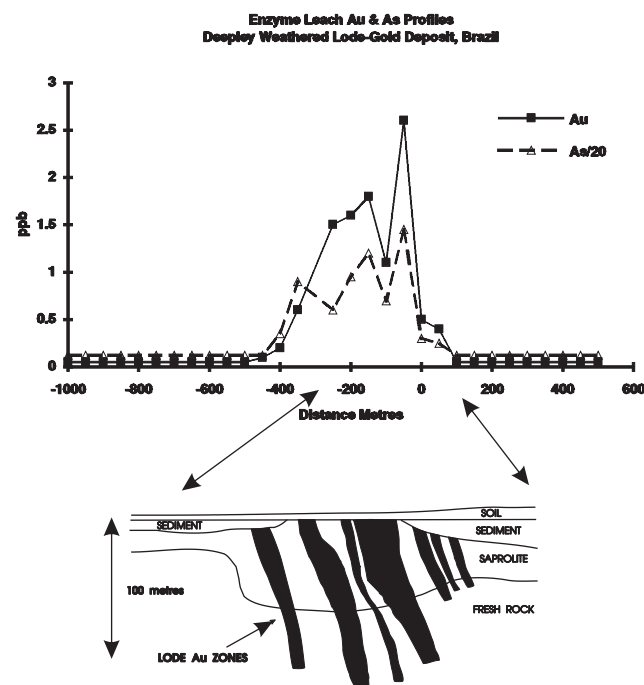


Figure 2: An apical Au anomaly over deeply lateritized lode-gold deposit in southern Brazil. Conventional geochemical analyses failed to produce an anomaly.

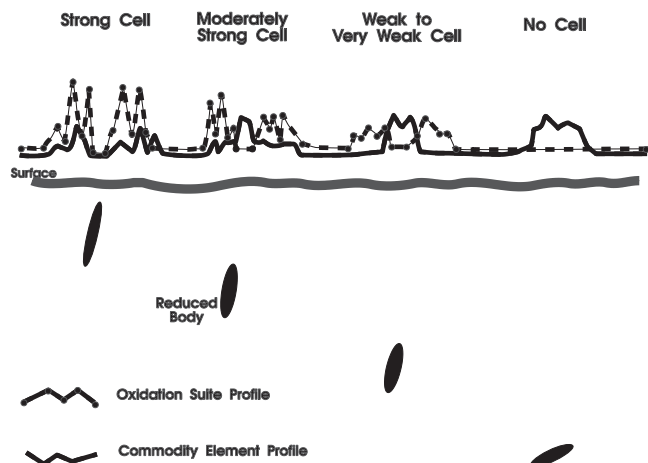


Figure 3: Typical anomaly profile variations related to strength of the oxidation cell. The shifts from one anomaly form to another in some instances is a function of depth below the surface. The depths at which these shifts occur vary from one region to another.

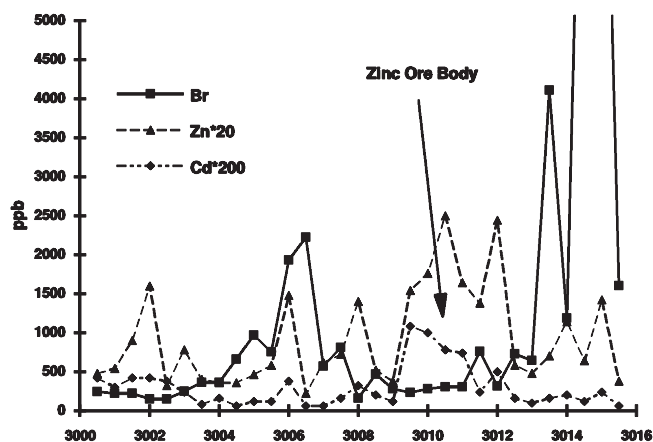


Figure 4: Combination anomaly in forested terrain over a blind MVT deposit located 1200 feet beneath the surface.

2. In weak cells, commodity metals in the concealed deposit form an apical anomaly over the source. In moderately strong cells, the commodity metals migrate into both the halo and into an apical anomaly over the source. In a strong cell, the commodity metals in the deposit are enriched at points within the halo of a strong cell.

In many areas, these morphological changes are a function of the depth of the deposit (Figure 3). The greater the depth, the weaker the cell. In one area where a mineralized trend plunges into the basement, a progression from one anomaly type to another has been observed along the plunge of the trend. The critical depths at which these morphological changes occur changes from one geological terrane to another. Host rock composition, geochemical barriers, and climate variations also affect the depths at which these transitions take place. In northern Chile, deposits at a depth of about one kilometer typically produce a moderately strong to strong oxidation cell. In the Canadian Shield, sulphide deposits often will produce weak oxidation cells when they are at a depth of less than one kilometer. Graphitic host rocks have a very strong quenching effect on the strength of oxidation cells. A good example of a combination anomaly is from a study of the Elmwood Mine in central Tennessee. A Mississippi Valley-type Zn deposit is hosted by Paleozoic carbonate rocks, at a depth of 1200 feet beneath the surface. Halogens form halos on the sides of the ore bodies, and trace elements associated with the ore often form apical anomalies over the ore bodies (Figure 4).

SUMMARY

The Enzyme Leach has been applied in exploration for four years, and more than fifty successful drill tests of anomalies have been reported. The Enzyme Leach has its greatest value in situations where conventional geochemistry has little chance of being used successfully; i.e., in areas of thick or areally extensive overburden, or in areas where potential deposits lie deep within the bedrock. As the body of information on anomaly morphologies and mechanisms of trace element migration has grown, the interpretive models have become more refined. Soil anomalies conforming to the models described here have been found in permafrost regions, mid-latitude deserts, glacially-buried terranes, tropical deserts, savannahs, mid-latitude rain forests, tropical rain forests, mid-latitude woodlands, and in areas that have been intensively cultivated.

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