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Concepts and models for interpretation of enzyme leach data for mineral and petroleum exploration

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Concepts and Models for Interpretation of Enzyme Leach Data for Mineral and Petroleum Exploration

by

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Abstract

The Enzyme Leach is a highly selective analytical extraction used primarily for detecting extremely subtle geochemical anomalies in *B*-horizon soils. Pattern recognition is the key to proper interpretation of Enzyme Leach data, since anomaly patterns are quite different from conventional geochemical data.

Many ore bodies are buried beneath thick sequences of overburden, lake beds, or younger volcanic rocks. In other situations ore bodies or petroleum reservoirs lie deep within rocks that contain no evidence of the resource below. Given geologic time, extremely small amounts of trace elements related to the underlying body can migrate by various mechanisms to the surface, where they would tend to be trapped by various oxide precipitates coating mineral grains in the soil. One of the most effective of these traps is amorphous MnO_2, which is a very small portion of the total manganese oxides in the soil. Amorphous precipitates of MnO_2 should be a very effective trap for a wide variety of cations, anions, and polar molecules that may be migrating to the surface. Because of the efficiency of this trapping material, the locations of Enzyme Leach anomalies are generally independent of the quantity of leachable Mn in the soils. The Enzyme Leach makes use of an enzyme-catalyzed reaction to selectively dissolve the most reactive form of MnO_2 in soils, the amorphous form of the compound. Consequently, a very small portion of the MnO_2 in the samples is dissolved, and the presence of traces levels of H_2O_2 in the leach solution helps lower the solubility of Fe over what it normally would be. Because of this selectivity, the background leachable concentrations of many trace elements that are determined are in the low part-per-billion (ppb) range. Thus, the anomalies often have very dramatic contrast above background. Currently Enzyme Leach anomalies can be classified two ways. Morphologically, there are three commonly recognized anomaly forms: 1. halo anomalies; 2. apical anomalies; 3. combination anomalies. Genetically, there are also three classes: A. oxidation anomalies (sometimes referred to as oxidation halos, where they form a morphological halo); B. diffusion anomalies, which result from the gradual thermodynamic dispersal of a highly concentrated source; C. mechanical/hydromorphic dispersion anomalies.

Oxidation anomalies appear to be caused by very subtle electrochemical cells that develop at the top of reduced bodies in the subsurface. These anomalies are characterized by very high contrast values for a suite of elements, the "oxidation suite," which includes Cl, Br, I, As, Sb, Mo, W, Re, Se, Te, V, U, and Th. Often, rare-earth elements will accompany the oxidation suite. Base metals can be anomalous in the same soil samples, but usually with lower contrast. Anomalous contrasts are often quite dramatic, in some cases exceeding 50-times background. Oxidation anomalies often take the form of an asymmetrical halo or partial halo around the buried reduced body, and that body underlies much of the central low within that halo. They have been found associated with reduced bodies located as much as 2

Km below the surface. Generally, the contrast of the anomaly and the number of anomalous elements in the halo decline as the depth of the reduced body increases. They can be associated with any reduced body: porphyry-Cu deposits, base metal massive-sulfide deposits, epithermal-Au deposits, lode-Au deposits, petroleum reservoirs, geothermal systems, barren massive sulfides, barren disseminated pyritic alteration, blocks of barren pyritic shale or black shale isolated as a horse within a fault or occurring as a graben between two normal faults. Any body of rock that contains more oxidizable material than the surrounding rock has the potential to produce one of these anomalies. The suite of trace elements in the halo often is not indicative of the composition of the source. However, relative differences in some trace elements, and the appearance of some quite rare elements, such as Re, in the anomaly can provide clues about the chemistry of the source. Evidence suggests that volatile halide compounds and halogen gases, which can form at the anodes of electrochemical cells, migrate to the surface along joints and faults in rock and through permeable overburden to form these oxidation anomalies at the surface. Base-metal "rabbit ears" anomalies associated with oxidation suite halos may form as a result of cations being pushed along electrochemical gradients. Electrochemical gradients also appear to produce differentiation patterns for the halogens based on the differing electrode potentials required to oxidize chloride, bromide and iodide to Cl_2, Br_2, and I_2. These patterns are seen around some larger mineral deposits and some petroleum reservoirs. A flux of CO_2 generated in the area of the electrochemical cell may act as a carrier to aid in the migration of oxidation suite volatiles to the surface.

Apical anomalies are the most common morphological form of Enzyme Leach anomalies, and most of these are related to faults. Trace elements that are representative of the source are found as an anomaly directly over that source. If the source is a mineral deposit, many of the commodity/pathfinder/alteration trace elements that characterize the source are anomalous at the surface. When an apical anomaly is found associated with a sulfide-rich mineral deposit, it is because something is preventing a strong oxidation halo from forming. The deposit may be too deep for a strong oxidation cell to develop, there may be a barrier, such as permafrost, between the deposit and the surface, or the top of the deposit may have been destroyed by deep weathering. Metals and pathfinder elements enriched in an underlying mineral deposit may be transported to the surface as a consequence of biomethylation of those elements by bacteria. Dimethyl and trimethyl compounds of many elements are highly mobile as gases. Therefore, it is possible that many apical Enzyme Leach anomalies over deep sulfide-rich deposits result from vapor phase transport of trace elements to the surface. Trace elements that characterize the porphyrins in a petroleum reservoir will often form an apical anomaly over the reservoir. Microseepage of hydrocarbons would carry these compounds to the surface. Faults that are mineralized, that intersect mineralization, or that intersect geochemically unusual rocks will produce a linear anomaly at the surface that follows the subcrop of the fault in the subsurface. If a fault passes through or near an oxidation cell, then oxidation suite elements will commonly form a very high-contrast anomaly over the trace of the fault. Supposedly immobile high-field-strength elements, such as Zr, Nb, Hf, and Ta, will often form very high-contrast anomalies over faults in areas where oxidation is going on in the subsurface.

Combination anomalies have characteristics of both apical and oxidation anomalies. They usually are found where there is a weak to moderately strong oxidation cell in the subsurface. As the strength of the oxidation cell increases, the trace elements that characterize the source migrate more and more into the halo anomaly, until the apical anomaly disappears.

A variety of geological situations can complicate Enzyme Leach anomalies, making interpretation more uncertain. Oxidation halos are often irregular in shape, spotty, or highly asymmetrical. Therefore, it would be very easy to misinterpret a pattern, simply because a single traverse passed through the wrong part of an anomalous area. Closely spaced mineralized bodies can produce interference patterns between adjacent oxidation halos. Graphitic host rocks tend to have a strong quenching effect on an oxidation cell, diminishing the contrast of the anomaly and making the source appear to be much deeper than it actually is. Anomaly patterns can shift substantially with time, due to intense weathering of the top of a deposit, changes in the water table, and other factors. Active and relic anomalies in the same areas will complicate the interpretations. Geochemical barriers in the subsurface, such as strongly oxidized sedimentary units, can attenuate or completely block the formation of an Enzyme Leach anomaly.

1. Introduction

The Enzyme Leach is a new highly selective extraction developed for detecting extremely subtle geochemical signatures in surficial geological materials. Many exploration geologists hope for a new exploration technology that can be used as a "black box;" i.e. they are looking for something that will save them from the uncertainties of doing geology. The Enzyme Leach is not a "black box." Rather, it is like conventional geochemistry or geophysics in that it is another tool to help exploration geologists develop geological models about the area that is being explored. It is best employed as an aid in detecting structures and mineralized bodies deep within the subsurface. Regardless of the tools that are used to make geological interpretations, they still must be tested, usually by drilling, to determine how well the model fits the reality of the rocks beneath the surface.

Pattern recognition is the key to interpretation of Enzyme Leach data, and in most situations the patterns are completely different from those produced by conventional geochemical methods. Conventional geochemical concepts for the most part are not useful. In order to understand the patterns, it is necessary to understand how they are detected, what chemical constituents of the soil are being analyzed, and have a model regarding how the anomalies are migrating to the surface, even if that process is only partially understood. Knowledge of the geological problem and the history of the development of the exploration models is important for being able to interpret Enzyme Leach data.

1.1 Nature of geological problem

Layers of glacial till and glaciolacustrine sediments cover large areas at high latitudes in the Northern Hemisphere, and in many areas of the world much of the bedrock has 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 in many areas has stripped the surficial material of the original chemical signature of the parent rock. In some regions blind mineral deposits occur deep beneath the surface where the overlying rocks contain no sign of the underlying ore bodies (Yeager et al., this issue). Conventional chemical analyses would reveal only the composition of the overburden or obscuring rock 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 or cover rock signature, and random variations in this signature often dramatically outweigh any anomalous chemistry emanating from underlying mineralized rocks. In the past, drilling has been the only means of collecting useful geochemical samples in areas of extensive overburden or rock cover. 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 gradual weathering of mineral deposits in the bedrock can migrate up through overburden or cover rock by such means as groundwater 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 or residual soil. 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 or cover rock 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. Thus, an analytical technique that would tend to preferentially dissolve coating materials rich in amorphous MnO_2 could provide very useful information in exploration for blind mineral deposits.

1.2 Selective analysis

In most cases the chemistry that is done before instrumental determinations are made is critical to the quality of the geochemical interpretations made from the resulting data. Most laboratory procedures for wet-chemical analyses of geological materials employ either a total digestion, strong leach, or fusion of the sample to put the elements of interest into solution in preparation for instrumental determinations. Even though partial digestions and leaches of the sample materials are less destructive than a total digestion or fusion, these methods frequently use relatively strong concentrations of reagents, resulting in a significant dissolution of many of the constituent minerals in the rock, soil, or sediment (Church et al., 1987). When the geochemist is trying to detect very low level trace element anomalies, it is more important to analyze for trace elements "on" the soil particles, not "in" the constituent mineral grains. Trace elements bound "on" the solid matter of the soil are much more likely to have been transported from an obscured source. Partial leaches employing a wide variety of leaching agents have been found useful for selectively analyzing geological materials for weak signatures of transported trace elements. The history of selective geochemical analysis has been reviewed by Chao (1984) and by Hall (this issue).

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, thus:

$$\text{Dextrose} + O_2 + H_2O \rightarrow \textit{(Glucose Oxidase)} \rightarrow \text{Gluconic Acid} + H_2O_2.$$

While concentrated hydrogen peroxide has been widely used as an oxidant in selective leaching processes, it can also function as a reducing agent for several metallic oxides. In an aqueous solution, it will react with manganese dioxide, consuming hydrogen ions, resulting in the manganese being reduced to the divalent state, which is soluble, thus:

$$MnO_{2(s)} + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + O_{2(aq)} + 2H_2O$$

(Robinson, 1929; Rose and Suhr, 1971; Filipek et al., 1981; Filipek and Theobald, 1981). In the process, trace elements trapped in the manganese dioxide coatings are released. Because amorphous manganic dioxide is far more reactive than is the crystalline form of the compound, the trace of H_2O_2 produced by the enzyme-induced reaction tends to selectively dissolve the amorphous MnO_2 present in soils (Clark, 1995). When all the amorphous manganese dioxide in the sample has been reacted, and hydrogen peroxide is no longer being consumed at a rapid rate, the H_2O_2 concentration builds up to a low-part-per-million threshold, the enzyme reaction slows, and the leaching action also slows. Because the enzyme leach tends to be 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. Leachable concentrations for many trace elements in soils are the mid-to-low part per billion range.

1.3 Current level of knowledge

Models for Enzyme Leach anomaly pattern interpretations discussed here in are based on the current level of knowledge after four years of commercial application of the technique. These models are subject to revision as new studies become available for public dissemination. Three morphological types of geochemical anomalies are recognized with the Enzyme Leach: 1. "halo" anomalies; 2. "apical" anomalies (which includes most "fault-related" anomalies); 3. "combination" anomalies (showing attributes of both halos and apical anomalies). Of these, apical anomalies are by far the most common. A genetic classification is also being developed that includes: 1. oxidation anomalies; 2. simple diffusion anomalies; 3. "mechanical/hydromorphic dispersion" anomalies. Vegetation has been observed to play a role in recycling and enhancing Enzyme Leach soil anomalies for some trace elements in temperate climates (Clark, 1993) and in humid tropical climates. In areas where there is a very deep weathering profile, distinct shifts in anomaly patterns have been observed. In a high altitude arid environment, low leachable Mn content of the soils has been observed to produce diminished Enzyme Leach anomaly contrasts. In most cases agricultural activity has little effect on Enzyme Leach anomalies. One notable exception is described in Yeager (this issue). Using the Enzyme Leach in areas of thick glacial overburden has been covered in detail by Jackson (1995), Rogers and Lombard (this issue), and Bajc et al. (this issue).

2. Methods

The preferred sample material is *B*-horizon soils, where they are available. Generally, the greatest concentration of active amorphous manganese dioxide is in the upper ten to thirty centimeters of the *B* horizon. Usually, 100 to 200 grams of sample material is adequate. In coarser grained soils, more sample material maybe needed. 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 can be usable sample media, with lower anomaly contrast than would be found with the *B*-horizon. Samples, collected from the "bleached" A_0-horizon usually are not suitable. Dense layers of caliche, calcrete, and gypcrete cannot be used as sample media and are to be avoided. A detailed description of sampling protocols is in the Appendix. Samples should be air dried if at all possible. If they are artificially dried, the temperature should not exceed 40° C. Samples should not be exposed to excessive heat (such as in an enclosed truck camper shell, a closed trailer, or a shed exposed to intense sunlight in hot weather). When overheating occurs, halogens and trace elements that associate with halogens in oxidation anomalies are lost, while leachable concentrations of certain other trace elements may increase (data presented in Appendix). Sample preparation commonly consists of sieving the samples for the minus-60-mesh fraction (<0.25 mm). In some cases, the minus-80-mesh fraction, the minus-240-mesh (silt and clay fractions), or the minus-60-mesh/plus-240-mesh fraction (fine-sand and very-fine-sand fractions) are used, depending upon what has been found to work best for the soils in the area where the grid of samples was collected.

A detailed description of the Enzyme Leach process can be found in Clark (1995). In summary, 1.00 g is leached for one hour with 15 mL of 1% (w/v) dextrose and 0.1 mL of glucose oxidase solution. All stock solutions are prepared in 18 M-ohm water. After leaching, 10 mL of the solution is removed and saved for analysis. Leach solutions are immediately stabilized with 0.1 mL ultrapure nitric acid. An isotopically pure spike of an internal standard solution is added. Determinations are made by inductively coupled plasma-mass spectrometry (ICP-MS) for a package of 60 elements: Li, Be, Cl, Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Pt, Au, Hg, Tl, Pb, Bi, Th, and U. Of these, Li, Be, Cl, Sc, Ti, and Hg are determined semiquantitatively, due to limitations of the instrumental technology. Inductively coupled plasma-optical emission spectrometry (ICP-OES) can be used to determine B or Fe.

Enzyme Leach data can be presented in a variety of ways. By the far, the most effective is to sample on a regular grid, where the sample spacing will be suitable for the scale of deposit that you are looking for. The data for each element that shows interesting contrast above background are then contoured. If sampling is done along isolated traverses, then the best method of data presentation is to use a spreadsheet program to graph the data, producing a geochemical profile for each element that shows contrast. Most of the data that are presented in this paper are shown as geochemical profiles, because many of the projects shown here were pilot studies, where the traverses to be sampled were often selected by the host companies.

3. Observations and Discussions

3.1 Leach selectivity

Only a small portion of the total manganese oxides in a typical soil is dissolved by the Enzyme Leach. A typical *B*-horizon soil sample from northern Minnesota contains >400 μg/g (parts per million or ppm) total Mn, and most of the Mn in these soils would be present as manganese oxides. In a study of 1670 soils from northern Minnesota with the three leaches, the Enzyme Leach removed about five-times more Mn than a simple water wash (1.5 ppm vs. 0.3 ppm), while a stronger version of the Enzyme Leach dissolves about 10-fold more (17 ppm) than the Enzyme Leach leach (Clark, 1993, p. B22). The strongest of these three leaches typically dissolves less than 3% of the manganese oxides in these soils. Thus, it is logical that the Enzyme Leach is dissolving the most reactive forms of MnO_2. Interestingly, the anomalous threshold for Co in this sample set was 42 ppb for the Enzyme Leach, and it was 675 ppb in for the stronger version of the Enzyme Leach (Clark et al., 1990; Clark, 1993). In some soils certain trace elements will produce similar ranges of values with the Enzyme Leach and a water wash. However, the populations produced by the two leaching techniques for those elements will usually be quite different (Clark et al., 1990, p. 196).

Hydrogen peroxide also tends to oxidize ferrous iron to the less soluble ferric form. Thus, the presence of a trace of hydrogen peroxide in the leaching solution tends to reduce the solubility of Fe over what it would normally be when the sample is soaked in water. In a regional mineral assessment project, both the mean and anomalous threshold for Fe in a large sample set were distinctly lower for the Enzyme Leach than for a water wash (Table 1). This reduced solubility for Fe tends to make the Enzyme Leach even more selective.

Table 1. The univariate statistics for Mn and Fe in *B*-horizon soils collected in a regional geochemical program in the International Falls and Roseau 1°x2° quadrangles, northern Minnesota. All samples were subjected to three leaching procedures: a water wash; the Enzyme Leach; a stronger version of the Enzyme Leach employing a small proportion of ascorbic acid in the leaching solution (Riddle et al., 1992).

Element/ Method	n[1]	Mean	Minimum	Maximum	1st Quartile	Median	3rd Quartile	Populations[2]	Threshold[3]
Water wash:									
Mn (ppm)	1523	0.3	<0.05	23	0.2	0.3	0.6	3	1.7
Fe (ppm)	1646	21	< 0.8	250	10	21	42	2	118
Enzyme Leach:									
Mn (ppm)	1624	1.5	<0.05	72	0.8	1.5	2.8	3	7.4
Fe (ppm)	1645	15	< 0.3	725	9	15	25	1	63
Enz+Asc[4]:									
Mn (ppm)	1657	17	0.1	480	8.5	19	39	2	124
Fe (ppm)	1657	61	2.8	520	26	62	120	2	251

[1] Number of samples above detection limit.

[2] Number of populations determined, using power transformed data and the PROBPLOT program (Stanley, 1987).

[3] Anomalous thresholds determined using power transformed data and the PROBPLOT program.

[4] Method employing a small proportion of ascorbic acid in conjunction with the Enzyme Leach.

Often with selective extractions, the geochemist "hopes" that the chemical process is selectively leaching the desired phase or compound from the geological samples. "Hope" is the appropriate word, because there is often no direct way to prove that the leaching process is 100% efficient or 100% selective. In all likelihood, it is neither. This is probably the case with the Enzyme Leach. The fact that this leaching technique dissolves copious quantities of freshly precipitated amorphous MnO_2 in as little as thirty minutes can be demonstrated in a simple experiment (Clark, 1995). The very slow dissolution of crystalline MnO_2 phases can also be easily demonstrated in the same manner. In nature there is no pure amorphous MnO_2 coating on a mineral grain, or for that matter of any other compound or phase in coatings. Mineral grain coatings produced by weathering are mixtures of various amorphous compounds (such as oxides and hydroxides of Mn, Fe, and Al) and mineral precipitates (such as calcite, gypsum, goethite, limonite, manganite, psilomelane, pyrolusite, gibbsite, boehmite, diaspore, and silica). It would be expected that the amorphous compounds occur in relatively small quantities compared to the crystalline phases present, and that amorphous materials are really a complex mixture of components, including a large proportion of water. In fact, when the Enzyme Leach is selectively dissolving amorphous MnO_2, it is probably to a degree physically dismantling a complex material that includes hydroxy precipitates of Fe and Al.

During leaching trace elements from a variety of components of the soil are probably brought into solution by the Enzyme Leach: 1. trace elements trapped in amorphous MnO_2; 2. trace elements associated with other amorphous compounds that are stripped as the material is physically dismembered; 3. trace elements occurring in water soluble salts; 4. trace elements brought into solution by hydrolysis of silicates; 5. trace elements stripped from ion exchange sites on clay minerals. In some cases, you can get an idea of what trace elements are coming from which sources. For instance, in anomalous soils associated with a very strong oxidation cell, roughly one-half of the Cl would be water soluble. In the case of the Enzyme Leach, it is "hoped" that the background values for many elements are derived from the hydrolysis of silicate minerals in the soil, and that the anomalies for those trace elements come from amorphous MnO_2. It is also "hoped" that the volume of those amorphous materials in the coatings is sufficient to trap all the trace elements emanating from mineralized sources in the subsurface. If this is so, then the locations of anomalies would generally be independent of the quantity of leachable Mn in the soils. Except for a few rare cases, this appears to be the case. One exception is described in Yeager et al. (this issue).

3.2 Oxidation anomalies

Oxidation anomalies appear to be caused by very weak electrochemical cells that develop at the top of reduced bodies in the subsurface. 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 (geology, geophysics, geochemistry, etc.) 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 includes Cl, Br, I, As, Sb, Mo, W, Re, Se, Te, V, U, and Th. Often, rare-earth elements will accompany the oxidation suite. Base metals can be anomalous in the same soil samples, but usually with lower contrast.

Oxidation anomalies often take the form of an asymmetrical halo or partial halo around the buried reduced body, and that body underlies much of the central low within that halo. The Clay Pit deposit in the Getchell trend of Nevada is a typical example (Fig. 1). Clay Pit, an epithermal-gold deposit hosted by Paleozoic carbonates and shales, was uplifted, exposed by erosion, and then covered by a volcanic flow. Immediately after this flow was laid down, there was a geothermal event, and the volcanic rocks were altered to nearly pure clay. Currently the deposit lies under an approximately 70-meter-thick layer of clay and another 80 meters of basin-fill alluvium. Prior to running the Enzyme Leach survey at that location, Clay Pit had been a test site for the U.S. Geological Survey. Neither CHIM, nor any of the other analytical procedures applied to soils at that site detected the ore body in the subsurface. At the time that this study was begun, it was presumed that the thick clay layer was an impermeable barrier blocking migration of trace elements to the surface. Profiles for Enzyme Leach As and Sb (Fig. 1) show high-contrast "rabbit-ears" patterns at the surface, over the Clay Pit ore body. Other oxidation suite elements are anomalous at Clay Pit (Cl, Br, I, V, Mo, W, and rare earth elements), but they do not bracket the top of the deposit as tightly as do As and Sb, and some of them form distinctly asymmetrical anomalies with broad central lows. A base metal, Co, also shows a narrow central low that lies directly over the top of the deposit. A biogeochemical study done by James Erdman concurrently with this study did reveal a broader, much lower-contrast, less structured anomaly than the Enzyme Leach anomaly shown here.

Frequently, one or more elements will very tightly bracket a central low that is close to the same dimensions as the top of the end of the deposit, and that central low will be directly over the reduced body in the subsurface. It does not matter which direction the ore body is dipping or which direction groundwater is flowing, even in areas of relatively strong groundwater flow, the central low is always found over the upper end of the reduced body that is responsible for generating the oxidation halo.

If part of the ore body is oxidized and part is reduced, the central low of the oxidation cell does not cover the entire ore body. Instead, the location and size of the central low is controlled by the location of the reduced part of the ore body. The Rodeo epithermal-Au deposit, located in the northern end of the Carlin trend in Nevada, is a partly oxidized body. A set of soil samples collected across the Rodeo while it was being drilled revealed an Enzyme Leach oxidation halo anomaly that bracketed the reduced ore at depth, not the entire ore body (Fig. 2). In this case, much of the ore lies under or outside the "rabbit ears" portion of the anomaly pattern.

The trace element suite in oxidation anomalies, although often enriched in many types of metal deposits, frequently is not representative of the composition of the buried reduced body. For example, a very similar suite of elements forms halos around petroleum reservoirs, porphyry copper deposits, epithermal gold deposits, buried geothermal systems, and barren pyritic bodies. Sometimes the base metal association or the presence of rare members of the oxidation suite (Re, Se, and Te) in the halo are 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. An oxidation halo anomaly has been drilled where the reduced body was 950 to 1050 meters beneath the surface. 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.

Oxidation anomalies characteristically have high site variance. At one site, Mo might have an anomalous contrast of 80-times background, while a duplicate sample collected 5 meters away may have a Mo anomalous contrast of only 7-times background. Both sites are highly anomalous, but there is a huge difference between the two. This is very common in oxidation halos, to the point that it is positive evidence of the presence of the oxidation anomaly. It is also evidence that can be used to argue of vapor-phase transport of the elements in the oxidation suite.

In some cases central lows, located over a deposit, can have site variance so low that it is within the instrumental variance. In an early pilot study done over the Mike epithermal-Au deposit, north of Gold Quarry, in the Carlin Trend, Nevada, a central low was found where 17 consecutive samples had an Enzyme Leach-Sb mean value of 10.2 ppb with a variance of 2.5 ppb. In that concentration range, that was the determination variance of the analytical instrument that was used. In some cases, site variance within a central low for a few elements, such as Sb, As, or V, is so incredibly low that it falls within the range of instrumental variance. In background areas, outside the area affected by the oxidation anomaly, the site variance will typically be much higher for the same elements. Whenever this is observed, some geochemical process has to be altering the soils within the central low in such a way that it results in a very peculiar lack of variance in certain leachable trace elements.

3.2.1 Discovery and evidence of possible origin of oxidation anomalies

Oxidation anomalies were discovered in 1989 during a test of the Enzyme Leach using soils collected at the Sleeper bonanza-gold deposit, north of Winnemucca, Nevada. A set of *B*-horizon soils was collected along two traverses across the mineralized structure, but outside the boundaries of the open pit (Fig. 3). Overburden along both traverses was roughly 15 meters thick at the east end and 37 meters thick at the west end of the traverses. Overburden consisted of typical clastic basin-fill sediments. Sample spacing along the lines was roughly 30 meters, and all soils were collected at a depth of 0.25 to 0.4 meters. Five "background" soils were also collected on overburden, but upslope from known mineralization (Fig. 3). Along the traverse south of the pit a single-sample apical anomaly was found directly over the mineralized structure. North of the Sleeper pit a broader anomaly was found along traverse 2. The data set that is presented here is the discovery data for oxidation anomalies. The original line for traverse 2 was not long enough to close off the anomaly west of the mineralized structure. Also, it was not expected that the halogens would be anomalous, so only raw counts were measured on the ICP-MS instrument for Cl, Br, and I. All other elements measured were standardized. Follow-up sampling at Sleeper along longer traverses ratified the patterns of this original set of data.

Anomalies for a number of elements were found on the north traverse. In Figs. 4 and 5, the trace element values for background sample sites (c00 through c04) are shown on the left side of the graphs, while the geochemical profile for that element is shown to the right. The vertical dashed line represents the approximate position of the center of the mineralized structure in the subsurface. Chlorine, Br, Re, and Se present multi-site extremely-high contrast anomalies on traverse 2 (Fig. 4). Selenium was known to be enriched in this deposit. Rhenium is a very rare element, which is often enriched in molybdenite, and molybdenite was known to occur in the Sleeper deposit. Thus, it is likely that these Se and Re anomalies formed by some type of dispersion from the bedrock to the surface. Six elements produced anomalies that had a peak on either side of the mineralized structure. Molybdenum, W, Ag, Pb, Th, and have what is often referred to as a "rabbit-ears" profile (Fig. 5). "Rabbit-ears" anomalies are thought of as resulting from and electrochemical process (Govett, 1976; Smee and Sinha, 1979; Smee, 1983; Govett et al., 1984; Govett and Atherden, 1987). Thus, it would appear that an electrochemical process was in some way involved in generating these anomalies.

Fig. 6 is a graph of the maximum anomaly contrast ratio for each of the anomalous elements in the initial Sleeper study. The maximum contrast ratio is the highest value for that element divided by its background concentration. Data for two other partial leaches are also included in Fig. 6. Both the oxalic acid leach and the KI+ascorbic acid leach (described in Viets et al., 1984) failed to produce as good anomaly contrast as the Enzyme Leach or show the "rabbit-ears" profiles. The elements are sorted according to decreasing Enzyme Leach anomaly contrast. If differences in anomaly contrast are a function of relative mobility, then the Enzyme Leach reveals two groups of trace elements in Fig. 6. Those elements that most geochemists would consider to be chemically mobile in the surficial environment as cations have the lowest contrasts. Those that commonly would be assumed to be mobile as anions under near surface conditions have the highest contrast. For example, most geochemists would think that the halogens would be mobile as chloride, bromide, and iodide ions, Mo as the molybdate ion, Se as selenate or selenite ions, etc. However, this probably is not the case for these high-contrast elements.

First, if the "rabbit-ear" anomalies at Sleeper are really related to an oxidation cell, as described by Govett (1976), Tilsley (1978), Smee (1983), Govett et al. (1984), and Govett and Atherden (1987), then you would not expect both anions and cations to be migrating into anomalies in the same places. Anions and cations should be migrating in opposite directions where a current is flowing. Second, it would not be expected that anions would show apparent rates of migration more than ten-times greater than cations. Why is an extremely rare element, Re, showing anomaly contrast at the surface four-times higher than are Cu or Ni, which are much more abundant in the deposit. Why are U and Th, which are not enriched in the deposit, producing greater anomaly contrasts than metals that are enriched in this mineralized system. Thus, it appears that two transport mechanisms are involved in the migration of these trace elements to the surface. The high-contrast group is moving to the surface much more efficiently than is the low-contrast group, the cations, but both groups are being concentrated in or near the same places at the surface. Furthermore, elements derived from the country rock or overburden, such as U and Th, can be enriched in the same anomalies.

The "rabbit-ears" anomaly profile for Ag and Pb can be explained by the conventional model for an electrochemical cell as described by Bolviken and Logn (1975), Govett (1976), Tilsley (1978), Smee (1983), Govett et al. (1984), and Govett and Atherden (1987). Electrochemical transport of ions is a very inefficient process, and a substantial length of time would be necessary to produce an anomaly at the surface through thick overburden. The erosional surface at Sleeper was determined to be approximately 3 million years old (William Utterbach, personal communication). If an electrochemical cell existed in the subsurface at Sleeper, then several million years probably would be sufficient time to generate a Ag anomaly three-times higher than background at the surface through 30 meters of overburden by means electrochemical transport.

The high-contrast suite (i.e. the "oxidation suite") of elements is a different story. Existing models for electrochemical cells in the crust (Bolviken and Logn, 1975; Govett, 1976; Tilsley, 1978; Smee and Sinha, 1979; Smee, 1983; Govett et al., 1984; and Govett and Atherden, 1987) do not explain "oxidation suite" anomalies. A plot of As and I together on the same profile for traverse 2 at Sleeper shows a strong degree of correspondence for the two elements (Fig. 7). When the data for arsenic and iodine from all the sample sites are plotted together on a scatter diagram, the background sample sites plot in a small cluster near the origin of the graph, and the anomalous sites tend to line up in a linear trend going away from the origin (Fig. 8). Either As and I are being mobilized and migrating to the surface together, or they are being trapped sympathetically by the same mechanism in the soil. Most likely, As and iodine are traveling to the surface together. If that is the case, then there is a strong possibility that they are traveling as AsI_3. A scatter diagram of Mo and Cl shows a similar relationship for five of nine anomalous sample sites (Fig. 8). Rhenium and Br also tend to follow each other (Fig. 8). Since 1993, these linear relationships between members of the oxidation suite have been observed numerous times in exploration projects and pilot studies in many parts of the world, most commonly where the overburden is dry. In some locations Mo and Br correlate with each other, sometimes a strong correlation is found between Se and Cl or Se and Br, sometimes W and Cl correlate with each other, and in several projects Sb and Br (Fig. 8) have been observed to follow each other. Frequently, contour maps of exploration grids will produce very similar patterns for As, V and iodine near mineralized bedrock, indicating that V often associates with As and iodine. In each of these cases, it seems that each pair of elements is migrating together to the surface from a source in the subsurface.

Metals and metalloids of the oxidation suite (Mo, W, Re, V, As, Sb, Se, Te, Th, and U) form halides and oxyhalides that have relatively low boiling points (Table 2). The halogens also have low boiling points. These elemental gases and volatile halide compounds would tend to form under the acid/oxidizing conditions of the anode of an electrochemical cell. Geochemical analysts have long been aware of the tendency to loose these elements from digestions that evolve elemental halogen gases. Each of the compounds listed in Table 2 has a significant vapor pressure under ambient conditions near the surface of the Earth. For instance, the volatility of $MoCl_5$ can be demonstrated on an analytical balance that weighs to 0.0001 g, in that the reading of the last digit is declining too fast to record the number. There is a strong tendency for gases in the subsurface to diffuse vertically toward the surface (Klusman, 1993). Thus, if these volatile compounds formed at the anode of an electrochemical cell in the subsurface, they would tend to diffuse vertically away from that anode, toward the surface. These are not charged species, and they would not diffuse along electrochemical gradients. In fact, the oxidation suite appears to form apical anomalies over their sources, anodes. Because these apparent anodes are located irregularly around the sides of the upper ends of reduced bodies, asymmetrical "rabbit-ears" anomalies are found at the surface bracketing the upper ends of these bodies at depth. These volatile halides would be metastable in the soils at the surface, and the trapping efficiency of the coatings on mineral grains in the soil for the various trace elements probably would vary considerably. Fig. 9 is a model for the anomaly pattern produced at the surface over a reduced body, where "oxidation suite" anomalies occur over the anodes (oxidizing poles) that flank a buried source. The reducing pole (cathode) would correspond to the "central low" of these anomaly patterns. It appears that a wide variety of factors come into play in establishing the symmetry, or lack thereof, of these oxidation cells. These would include, geometry of the deposit, faulting and fracturing of the deposit and host rocks, variations in the chemistry of the host rocks, chemistry and zoning of the reduced body, relative depth of the water table, and direction of groundwater flow.

Table 2. Boiling points of elemental halogens and some halide compounds of some elements belonging to the "oxidation suite" and Zr.

Compound	Boiling Point °C
Cl_2	-35
Br_2	59
I_2	184
VCl_6	152
$VClO_3$	127
WCl_5	288
$WClO_4$	220

Compound	Boiling Point °C
$AsCl_3$	130
$AsBr_3$	221
AsI_3	403
$MoCl_5$	264
$ReCl_5$	330
$SeCl_4$	subl. @ 196
$ZrCl_4$	331

In the classic model for electrochemical cells in the earth's crust (Govett, 1976) a steeply dipping electronic conductor, such as a massive sulfide body, facilitates the flow of electrons from a more reduced depth in the crust to an area of less reducing conditions nearer the surface. The bottom of the conductor is the anode, and the top end is the cathode. Oxidation suite data from a variety of studies and projects indicate that there are two problems with applying this model to the oxidation anomaly phenomenon. First, as described above, the anodes appear to be on the sides of the body, not at the bottom. Second, none of the reduced bodies at depth in the examples shown here are "electronic conductors." An electronic conductor is a mass that has unbroken electrical conductivity from one end to the other. In the case of a sulfide body, it would have to be massive sulfide. The vast majority of bodies associated with oxidation halos are not electronic conductors. Petroleum reservoirs, porphyry copper deposits, epithermal gold systems, geothermal cells, and barren bodies of disseminated pyritic alteration do not have a continuos connection of electronic conductor minerals from one end of the body to the other. The ones that do contain sulfides, are characterized by disseminated sulfides, which make up a small proportion of the mineralized rock. In fact, many of the oxidation anomalies that have been observed are associated with reduced bodies that do not contain sulfide minerals.

Petroleum reservoirs often produce oxidation anomalies. Located about twenty miles north of Houston, Texas, the Indian Hills field produces from a sand unit of the Yegua formation, at a depth of about 1700 meters (5600 feet) beneath the surface. Soil samples were collected along a roughly N-S traverse that followed the paved county road at an interval of 0.16 Km (0.1 mile) between sample sites. Samples were collected from the *B* horizon of the soil, at a depth of about 25 cm (10 inches) from the surface. Humid subtropical weathering of the sandy surficial material produced a buff-colored to reddish-brown *B* horizon beneath a very thin *A* horizon. The Tamina oil field is located several miles to the north, and the Huffsmith oil field is located about one mile south of the Indian Hills field. Production from these fields is also from the Yegua formation. The proximity of the Huffsmith field was found to have an effect on the Br anomaly pattern for the Indian Hills field. Enzyme Leach analysis of the samples revealed patterns for several trace elements that delineated the reservoir. Most of these elements tend to form a rough anomalous halo, with the strongest peaks near the edges of the field. Bromine produces a sharp anomaly with a contrast of 800-times background at the north edge of the field, and south of the field, in the area between Indian Hills and Huffsmith, there is a broad Br anomaly with a contrast of 80-times background (Fig. 10). No chlorine anomaly was detected around Indian Hills, and the iodine anomaly, which has a maximum contrast of 9-times background, is confined largely to the south side of the field. Thorium produces weakly anomalous values over much of the area of the field, but the strongest values are near the edges (Fig. 10). Zinc forms a halo, with peaks near the edge of the field (Fig. 10).

An alternative model for the formation of halo anomalies at the surface around petroleum reservoirs at depth calls upon a zone of reduced permeability above the reservoir to be responsible for the central low over the reservoir (Sandy, 1987). This barrier would be formed by petroleum microseepage-induced alteration and microbial deposition of carbonates and sulfides in the section directly overlying the reservoir. There are three problems with this model. If such a barrier was responsible for diverting microseepage to the flanks of the reservoir, then why does not the barrier continue to propagate laterally eventually extinguishing the microseepage of hydrocarbons to the surface. Second, it does not explain oxidation suite anomalies on the flanks of reservoirs, often coincident with hydrocarbon anomalies. Third, stratiform layers of chemical precipitates are not impermeable. Dense layers of caliche in the subsurface do not block the migration of oxidation suite elements to the surface. Why should a similar layer over a reservoir be any more effective at blocking the migration of hydrocarbons.

If an electrochemical process is responsible for the formation of volatile compounds that migrate to the surface, then it is possible that variations in oxidation potential within the electrochemical cell will cause differential migration of volatiles that form at different electrode potentials. The halogens would be a likely candidate for this differentiation, because of the difference in the oxidation potential required to oxidize chloride, bromide, and iodide to elemental chlorine, bromine, and iodine (Table 3). In most instances, no differentiation pattern is observed for the halogens, and the peaks often closely coincide. However, about one-third of the time larger mineralized systems produce iodine peaks farthermost from the central low, chlorine peaks adjacent to the boundary of the central low, and Br peaks between Cl and iodine. In a pilot study in western Alaska, a test line, which was not long enough to show the entire anomaly on one side of the central low and barely crossed the central low at the other end, revealed a coincident central low for Cl, Br, and iodine (Fig. 11). On the one flank, which included one side of the halo, a typical differentiation pattern was observed in the geochemical profile. This apparent differential migration of Cl, Br and iodine has been observed around several porphyry prospects in North America and Chile. Stan Keith (personal communication) has suggested that this may be primary halogen zoning produced by the mineralizing event, rather than electrochemical differentiation. The fact that this pattern has also been observed around some petroleum reservoirs argues strongly against a primary zoning interpretation. The Hillman oil field in southern Ontario shows Br/I zoning on each side of the field. (Fig. 12).

Table 3. Standard electrode potentials for the oxidation of halides to halogens.

Reaction	E° volts
$2Cl^- = Cl_2 + 2e^-$	+1.39
$2Br^- = Br_2 + 2e^-$	+1.08
$2I^- = I_2 + 2e^-$	+0.62

Halide compounds of metals and metalloids of the oxidation suite could easily migrate to the surface by diffusion through dry overburden. The problem is that these compounds are highly soluble in water. For reduced bodies located below the water table, other factors have to come into play to allow members of the oxidation suite to migrate to the surface. It is highly unlikely that the halogens and volatile halides would be generated in sufficient quantities to form their own microbubbles, which would migrate vertically through groundwater. Even if microbubbles of these compounds did form, they would likely disappear rapidly as the gas dissolved in water. Of several suggestions that have been made to explain transport of halogens and halide gases through groundwater, the most plausible to date has been made by Ronald W. Klusman. Carbon dioxide is likely being generated as the reduced body at depth is gradually oxidized. A flux of carbon dioxide microbubbles streaming to the surface could act as a carrier for volatile oxidation suite elements.

3.3 Apical anomalies

Anomalies that are apical over their source, rather than forming a halo around their source, are the most common form of Enzyme Leach anomalies. 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. These anomalies can form over the actual source of the anomalous trace elements, or they can develop above a structure such as a fault that facilitates the movement of trace elements to the surface.

Simple apical anomalies that lie directly over reduced bodies in some cases will not show significant contrast for oxidation suite elements, apparently indicating that for some reason an electrochemical cell is not present. Sometimes a factor can be identified that would retard the flow of oxygen from the atmosphere to the reduced body in the subsurface. In some cases that factor is an actual barrier, but in many cases it is simply depth.

3.3.1 Apical anomalies over bodies at great depth

Several cases have been observed where a purely apical anomaly is found over a very deep reduced body, both for sulfide mineral deposits and petroleum reservoirs. Unfortunately, the details of these mineral deposit examples must remain confidential. One petroleum example has been released for publication. Reservoirs in at least part of the Permian Basin of western Texas have a Ni signature that can be detected as an Enzyme Leach anomaly at the surface, usually in association with a suite of other trace elements that include several members of the oxidation suite and other base metals. It is likely that the petroleum in that area is characterized by Ni porphyrins. Porphyrins are a product of the transformation of chlorophyll deposited in sediments. During diagenesis, Ni often replaces the Mg and Fe in the original chlorophyll (Tissot and Welte, 1978), and porphyrins are found in petroleum. If there is any leakage from a petroleum reservoir, it is likely that the chemical signature of the porphyrins in the oil will be detectable at the surface with the Enzyme Leach. Most of the prior reservoirs and exploration targets in the Permian Basin were located at depths up to roughly 2000 meters below the surface. These produced oxidation halos of varying strengths. However, one reef structure was identified by 3-D seismic techniques at a depth of 2956 meters (9700 feet) in the Lower Permian Wolfcamp formation. An Enzyme Leach survey over the target revealed a purely apical Ni anomaly, the dimension of which corresponded exactly to the potential reservoir nearly 3000 meters below the surface (Fig. 13). Of all the 59 other elements determined in the Enzyme Leach analyses, none showed any anomalous contrast. Based upon similar observations over other deep targets, the trace element signature at the surface found with the Enzyme Leach reflects the chemistry of the source at great depth, and in these cases no evidence was found of any oxidation anomaly. Thus it appears that the formation of an oxidation suite anomaly is an inverse function of depth.

3.3.2 Apical anomaly over body within a "barrier" (permafrost)

An example of an obvious barrier retarding oxidation is provided by the Lik deposit in northern Alaska, an exhalative base metal deposit situated in a steeply dipping sequence of sea floor sediments. It subcrops beneath twenty meters of alluvial cover, and permafrost is present from about a meter beneath the surface on down for some unknown depth. Every analytical method that was applied to the soils collected at Lik detected a geochemical anomaly associated with the deposit (Karen Kelley, personal communication). The Enzyme Leach data from Lik show a zoning that is related to the chemical stratigraphy of the underlying rocks (Fig. 14). Cobalt and Mn vary sympathetically and produce an anomaly to one side of where the base-metal horizon occurs in the subsurface. At first this was interpreted as a bog, until it was learned that the area was characterized by good drainage and similar soils all along this traverse (Karen Kelley, personal communication). In fact, stratigraphic "up" is to the left in Fig. 14. The Mn and Co anomalies are located over what is apparently the oxide faces of the subcroping exhalative sequence. A Cu anomaly occurs mostly over the sulfide faces, while the strongest Zn high is near the top of the sulfide faces (Fig. 14). Uranium and Tl anomalies are present over the most reduced part of the underlying stratigraphy (Fig. 14). Cadmium is enriched near the top of the sulfide faces, and Ag is anomalous directly over the most sulfide-rich sediments (Fig. 14). Each of the anomalies for these elements occurs at the surface, directly over the underlying part of the chemical-sedimentary sequence where it would be expected that element would be most concentrated. It appears that the Enzyme Leach data map the underlying chemical stratigraphy. There is no distinguishable anomaly for any of the members of the oxidation suite on that line. Therefore, it seems that no electrochemical cell is present at this point along the strike of the sulfide-rich strata (at some other location down strike, a cell may be active). The development of an electrochemical cell may be inhibited by the sulfide body being encased in a block of ice. Cold temperatures tend to dramatically slow many geochemical reactions, and the oxidation of sulfide minerals is aided by the presence of liquid water or water vapor. Ice is not a perfect barrier to oxidation. Therefore, over time some breakdown of sulfides would be expected, and the metals that are released could eventually diffuse to the surface through the permafrost as the ice almost continuously undergoes recrystallization.

3.3.3 Apical anomaly over extensively weathered deposit (laterite)

In a laterite terrane where the near surface portion of mineral deposit has been deeply and intensely weathered, an apical Enzyme Leach anomaly will often be observed. At the Fazenda Nova deposit, Goas Province, Brazil, owned by Santa Elina Mineracao Ltda. and Echo Bay, Pre-Cambrian 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 (Fig. 15). The anomalous contrast for Au and As in this case are twenty-five-times and twelve-times background, respectively, where conventional geochemical methods did not reveal any anomaly. Although As is a member of the oxidation suite, this anomaly is not a product of an oxidation cell. None of the halogens are anomalous, and none of the other members of the oxidation suite form a halo anomaly. In order to interpret an anomaly as being caused by an electrochemical cell, at least one halogen must be anomalous, commonly along with As, Sb, and/or Mo, and the morphology of the anomaly should have some resemblance to a "rabbit-ears" pattern. In this study, conventional geochemical analyses produced an anomaly with substantially lower contrast.

3.3.4 Fault-related anomalies

Apical Enzyme Leach anomalies that follow the subcrop of faults are probably the most common anomalies detected with this technique. Some faults have a unique signature and often can be traced for many kilometers under basin-fill alluvium. The faults that have the strongest signatures are those that either intersect chemically unique rocks or mineralized bodies somewhere at depth, or that contain mineralization. If that mineralized rock is under going subtle oxidation, or if the fault plane passes close to an active oxidation cell, then trace elements of the oxidation suite will produce an extremely-high-contrast apical anomaly over the trace of the fault. An example is the fault that intersects the Rodeo epithermal-Au deposit in the Carlin Trend, NV (Fig. 2). The oxidation suite and most of the other elements in the periodic table were found in the fault-related anomaly over the trace of this fault. Cases have been observed where a mineralized structure with a specific signature crosses another mineralized structure with a different signature. At these intersections, sometimes the anomaly patterns open up into oxidation halos. In some instances, where a large fault with a distinct signature cuts a reduced body in the subsurface, the fault-related anomaly crosses the oxidation halo at the surface, and the fault-related anomaly can retain its unique signature within the halo. One possible explanation is that the crossing fault is providing plumbing for oxygen to get into the reduced body, in effect splitting the electrochemical cell in two. The Clearville oil field in southern Ontario appears to have one of these split oxidation halos (Fig. 16). Copper forms an anomalous halo that brackets the area underlain by the reservoir. The halogens are weakly anomalous in the halo, and Cl and Br form a very sharp anomaly over what is apparently a fault. There is also a halogen differentiation pattern in the halo and around the apparent fault in the center of the field.

The Meikle epithermal-Au deposit located in the northern part of the Carlin trend of Nevada is situated at a depth of about 250 meters (Fig. 17). It is cut by four faults of the Post Fault system. The extensive faulting of the deposit has apparently altered the anomaly pattern produced by the buried deposit. Many trace elements of the oxidation suite form strong apical anomalies over these faults instead of producing an oxidation halo. Vanadium produces a high contrast anomaly over these faults and a lower contrast anomaly in the flanking areas where an oxidation halo would be expected (Fig. 17). This V pattern is quite similar to the pattern for Cl and Br at the Clearville oil field (Fig. 16).

3.3.4.1 High-field strength elements in fault-related anomalies

Trace elements that are supposedly geochemically "immobile," such as Zr, Nb, Hf, Ta, and rare-earth elements, are often found in fault-related anomalies. It appears that chemically resistate minerals, which are enriched in these elements, such as zircon, are crushed and exposed to fluids in the gouge zones of these faults. In the presence of Cl_2, Zr is mobile as $ZrCl_4$ (Table 2). The rare earth elements can also be mobilized as volatile halides (Gunsilius et al., 1987; Murase et al., 1992). Gouge zones of faults would provide a highly permeable pathway for the migration of oxidation suite elements to the surface. If Cl_2 and/or halide compounds are migrating up a fault, then it is likely that these "immobile" elements in the gouge zone will be entrained into the dispersion process and carried to the surface and will contribute to anomalies over the trace of the fault. Where faults either intersect or lie close to oxidation halos, high-field strength elements will commonly form extremely-high contrast fault-related apical anomalies. For instance, the Post Fault, shown in Fig. 2, has a very high contrast Zr and rare earth anomaly over the trace of the fault at a number of locations along its strike (Fig. 18). A Zr contour plot from a Nevada exploration grid shows how these high-field strength elements can be used to map fault systems under basin-fill cover (Fig. 19).

3.4 Combination anomalies and the gradations between apical and halo anomalies

Metallic mineral deposits and petroleum reservoirs 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/pathfinder/alteration metals are found in the center of the anomaly, directly over the source (Fig. 20). A good example of a combination anomaly is from a study of the Elmwood Mine in central Tennessee, a Mississippi Valley-type Zn deposit hosted by Paleozoic carbonate rocks, at a depth of 370 meters 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 (Yeager et al., this issue).

With increasing efficiency of the oxidation process, several changes are observed in the morphology of Enzyme Leach anomalies. When the oxidation process of a reduced body is too weak to produce an oxidation anomaly, its expression at the surface is an apical anomaly for commodity/pathfinder/alteration trace elements. The trace elements in the apical anomaly are characteristic of the source in the subsurface. As the oxidation process gradually intensifies, a halo at the surface comprised primarily of bromine and/or iodine is produced by a very weak oxidation cell. The number of trace elements in the oxidation halo increases and the anomalous contrast of those elements tends to rise with increasing strength of a cell. In weak cells, commodity/pathfinder/alteration metals in the concealed deposit continue to form an apical anomaly over the source. In moderately strong cells, the commodity/pathfinder/alteration metals migrate into both the halo and into an apical anomaly over the source. In a strong cell, the commodity/pathfinder/alteration metals in the deposit are enriched at points within the halo, and the apical anomaly is gone. In many areas, these morphological changes are a function of the depth of the deposit (Fig. 20). 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 moderately strong to strong oxidation cells. In the Canadian Shield, it appears that sulfide deposits often will produce weak oxidation cells when they are at a depth of much less than one kilometer.

3.5 Mechanical/hydromorphic anomalies

In terranes where the bedrock is buried by extensive deposits of glacial overburden, mechanical/hydromorphic anomalies are observed, often in close association with oxidation-halo anomalies and apical anomalies. Applying the Enzyme Leach in glacially buried terranes has been discussed by Jackson (1995). Mechanical dispersion trains 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 groundwater flowing through the till. Vegetation with roots tapping into either the mineralized till or anomalous groundwater 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 glacial overburden situations, including areas where the glacial till is blanketed with a thick layer of 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 often reflect at least part of the chemical signature of the bedrock source. Anomaly contrasts in soils developed on glacial till often range from 2-times to 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 in similar situations with conventional chemical analyses. Also, it is not uncommon to find oxidation halos bracketing a lode-Au zone, while a low contrast W and/or Bi anomaly can be detected for several hundred meters down ice from the prospect. Similarly, low contrast base metal anomalies can be found on the down-ice side of an oxidation halo or apical anomaly associated with a massive sulfide.

3.6 Complicating factors and interpretation problems

3.6.1 Interference patterns

When mineralized bodies lie in close proximity to each other, interference patterns between adjacent anomalies will often produce a confused picture to the exploration geologist. A good example is found at the Pinson Mine, in the Getchell Trend, Nevada. The Mag epithermal-Au deposit is covered by about 80 meters of basin-fill alluvium (Fig. 21). At the time that the original pilot study was done in 1992, it was found that the original line was too short to encompass the entire oxidation halo. A year later, the line was extended, and the sample spacing was increased on the east end of the line to be sure to get far enough out from the Mag body to get into background. Subsequently, a second subeconomic mineralized body was discovered down slope from the Mag deposit, in the area where a wider sample spacing had been employed. Plots for several oxidation suite elements shows a central low over both mineralized bodies (for example: Fig. 21). If the geologist only had this traverse to use to select drill targets, the first target choice would be put a vertical hole into the apparent central low between the two highest peaks (Fig. 21). If the drill hole went deep enough, eventually it would intersect the Mag ore body. However, if it did not intersect a mineralized body, the geologist would still be left without an explanation for a very attractive anomaly. The logical second choice for a drill target would be the central low over the Mag deposit, because this is where the overburden would be expected to be thinner, rather than the central low downslope with a higher contrast halo. Ambiguities such as this are often cleared up when sampling is done on a grid and the data are contoured.

3.6.2 Graphitic horizons

Graphitic host rocks can have a very strong quenching effect on the strength of oxidation cells. Massive sulfide occurrences hosted by graphitic rocks seem to produce much weaker oxidation anomalies than would be expected. Similar mineralized bodies hosted by altered volcanic rocks in the same locality often will produce much stronger oxidation cells, even though they might be substantially deeper beneath the surface. It would appear that graphitic host rocks tend to short out the electrochemical cells, preventing the oxidation potentials from getting high enough to generate strong anomalies.

3.6.3 Au and Hg Enzyme Leach anomalies

Metallic Au and Hg are not soluble in the Enzyme Leach. And, yet Au or Hg anomalies can turn up within areas affected by oxidation anomalies. The Enzyme Leach-soluble Au and Hg has to be present in some nonmetallic, oxidized, form that can be dissolved during the leaching process. The pilot study done over the Rabbit Creek deposit (now part of the Twin Creeks Project, in the Getchell Trend of Nevada) in 1990 shows examples of this kind of Au anomaly. The northernmost sampling traverse is in an area where the overburden is about 50 meters thick and the southern traverse is about 200 meters above the bedrock Fig. 22). Several of the samples around the sides of the Rabbit Creek deposit were found to have detectable Au above the 0.1 ppb level (Fig. 22). One sample was as high as 0.6 ppb.. These same samples are also anomalous in oxidation suite elements, like Cl, Br, I, or Mo. Gold trichloride sublimes at only 265° C. Therefore, it is possible that $AuCl_3$ migrated as a volatile through as much as 200 meters of overburden. However, the soils in this area have a total Au content of about 3 ppb. If a subtle flux of substances like Cl_2, Br_2, I_2, or $MoCl_5$ pass through such a soil, it would be not be surprising if part of the Au in the soil was oxidized, making it soluble to the Enzyme Leach.

The Happy Creek Prospect, also located in Northern Nevada, is another location where Enzyme Leach-Au anomalies are found (Fig. 22). The Au anomalies in Fig. 22 are at a much higher level, 2 to 5 ppb. At these levels it is doubtful that the Au anomaly is produced from background Au that is being oxidized in place. After this initial pilot study, a detailed soil sampling program was conducted using a regular grid pattern, the samples were analyzed using the Enzyme Leach, and the data were contoured. Several of the central lows in the sampled area were drilled, and zones of epithermal mineralization with subeconomic Au grades were found more than 300 meters down. In a recent pilot study, it was shown that the geologist should begin to suspect that Enzyme Leach-Au is originating in the bedrock when the values go above the 0.6 ppb level.

Mercury behaves similarly to Au. When either Au or Hg anomalies are detected with the Enzyme Leach, it is most often a positive indication of oxidation anomalies. If the values go high enough, a bedrock source for the anomaly should be suspected. Occasionally, an apical Enzyme Leach-Au anomaly will be found in the center of an oxidation halo along with Sb, or sometimes As. There is not yet an adequate explanation for the formation of these apical Au/Sb anomalies, but they have led to more than one discovery.

3.6.4 Collapsed Oxidation Halos

Where an extremely deep weathering profile has resulted in the total destruction of the sulfides in the upper portion of a mineral deposit, the oxidation halo is often observed to have collapsed inward, and at present specific features within the deposit are the centers of oxidation cells. Most commonly in these cases the gouge zones within faults that cut the deposit control the locations of oxidation cells. Typically, the quite narrow central lows of these collapsed halos are centered over the deeper weathering crevices along the faults. The clearest publishable example of this to date is at the Radomiro Tomic deposit north of Calama, Chile, where the current oxidation cell is controlled by a single fault.

Radomiro Tomic (RT), located along the east side of the "West Fissure" and just north of Chuquicamata, is a deeply buried porphyry copper deposit. The upper portion of the primary sulfides is very deeply weathered, typically to depths of well over one hundred meters (Figure 23). The weathered subcrop is covered by gravels that are in some places up to one hundred meters thick. Secondary copper sulfides are present near the bottom of the weathering profile. Exotic copper ore is also present in the section above the unweathered sulfide zone. The post-ore fault is a splay off of the West Fissure. A series of extensive pilot studies were conducted over this deposit using a variety of conventional and new geochemical techniques in late 1994. Rather than forming a halo around the deposit, the oxidation suite anomaly is found over the deposit (Figure 23). The central low for this anomaly is less than 200 meters wide, and it is situated directly over the large post-ore fault. If the sample spacing had been wider than 100 meters, this central low may not have been identified. That would have made it appear that the oxidation suite anomaly is apical over the source, rather than forming a halo around the source, which in this case is the narrow gouge zone in the fault.

Evidence of two stages of weathering are present at RT. When collapsed halos are observed, weaker oxidation suite anomalies are often found at points around the mineral deposit where you would expect to find the halo under normal circumstances. These small outlying anomalies could be due to a weaker larger-scale oxidation cell, or they could be "relic halos" left over from an earlier period in the weathering history of the deposit. If these are genuine relic halos, then you would expect the halogen halo to collapse much more rapidly than the base metal halos, because of evidence discussed earlier (Fig. 6) that suggests that the oxidation suite is transported into anomalies much more rapidly than the base metals. If oxidation suite elements are transported into the anomalies more rapidly, then their anomalies will probably dissipate first in the old location and redevelop first in the new location. A Enzyme Leach-Cu halo is often found lying outside the sulfide-rich part of porphyry systems. It is not unusual for this Cu halo to be more than one kilometer outside the primary Cu-enriched area. If Cu is being moved by electrochemical processes laterally over such are large distance, then a substantial amount of time would be required to form these halo anomalies. The higher magnitude Cu anomalies at RT halo the deposit, not the currently active part of the oxidation system, and the highest contrast Cu anomaly is actually upslope from the primary sulfides (Figure 24). It has been suggested that these flanking Cu spikes at RT are structurally controlled. That is probably true in part, but essentially the same pattern has been observed at several other porphyries. Within the collapsed halo, weakly anomalous Cu appears to be migrating into the new halo, in the same area as the new halogen anomaly (Fig. 24). Therefore, it would appear that during an earlier stage of weathering and with current weathering of RT, the oxidation process appears to have been characterized by a strong oxidation cell, differing only in the size of the cell.

3.6.5 Smelter smoke and mine dust contamination

One of the possible problems addressed at RT and at Mansa Mina, located south of Chuquicamata, is the potential for false anomalies generated by the dense smelter smoke that frequently blows across the surface in these areas. First, many of the anomalous trace elements detected with the Enzyme Leach would not be found in appreciable quantities in smelter smoke (for example: the halogens, vanadium, and tungsten). Second, if smelter smoke was producing anomalies in the soils of this area, the anomaly would have a broad dispersion pattern. Instead, what you see are sharp anomalies that tie directly to geologically recognized features in the basement. Finally, Enzyme Leach tests in the area around Chuquicamata and in other mining areas indicate that detectable contamination is usually confined to the upper 1 or 2 centimeters of the soil.

3.6.6 Apical anomalies over alteration zones

Any trace elements added to the host rocks of the deposit may also produce an apical anomaly over the alteration zone. These alteration related apical anomalies can also be seen at the Elmwood Mine (Yeager et al., this issue). In some areas Ba anomalies can be found over barite, alunite, or potassic alteration zones. Sometimes, a Cs halo can be found over a phyllic or propylitic alteration zone. Data for elements such as Ba, Cs, Rb, and Sr should be plotted for any exploration grid to see if alteration patterns in the bedrock can be identified.

3.6.6 Geochemical barriers in section above body

Where a geochemical barrier occurs in the rock column above a mineralized body, the signal of that body can be blocked from reaching the surface. Several instances have been observed where the presence of highly oxidized sediments in the section above a mineral deposit appear to attenuate the anomaly from the deposit at depth. For instance, the Carlin formation appears to have an attenuating effect on the contrast of Enzyme Leach anomalies. Other instances have been reported indicating that thick red beds in the overlying section can completely block the development of Enzyme Leach anomalies.

4. Conclusions and Process Models

4.1 Role of fractures in anomaly formation

Fracturing facilitates the migration of Enzyme Leach anomalies to the surface from a bedrock source. These anomalies can only reach the surface because the overlying rocks have some degree of permeability. One of the commonly held myths in geology is that hard rocks and fine-grained sediments are impermeable. All rocks are permeable to one degree or another. For dense, seemingly impermeable rocks, such as varved glaciolacustrine sediments, limestones, shales, or volcanic flows, the path of least resistance through these rocks is going to be joints. It does not matter if it is varved lake beds or ignimbrite flows, they are all jointed. Regardless of whether the exploration target is a Mississippi Valley-type deposit located beneath 400 meters of limestones and shales in North America or a porphyry located beneath a thick section of ignimbrites in Chile, the anomaly over the deposit can only reach the surface because there is a permeable route to the surface, and in most cases that route would be along joints in the overlying rock.

A common thread that is found in the interpretation of Enzyme Leach data in exploration projects, regardless of the types of anomalies that are found, is the strong degree of structural control that is frequently observed in plots of the data. Even in oxidation halos, where the sampling density in a grid or traverse is sufficiently dense, the highest contrast anomalies for the oxidation suite elements appear to line up over joints or faults. On a larger scale, structure can help control the development of oxidation cells. On an even larger scale, the reduced bodies that produce oxidation anomalies are frequently located along structures that controlled their genesis, and these genetic structures can often be identified in contour plots of Enzyme Leach data.

4.2 Role of vapor transport in oxidation anomalies

Vapor phase transport appears to play an important role in the genesis of many geochemical anomalies detected with the Enzyme Leach. With regard to oxidation anomalies, a number of observations and principles have already been discussed that support this interpretation. Electrochemical cells in the subsurface could generate electrical potentials sufficient to cause the oxidation of chloride, bromide, and iodide ions to $Cl_{2(g)}$, $Br_{2(g)}$, and $I_{2(g)}$. Concurrently, there would be a tendency for certain metals and metalloids that are present to form halides that easily migrate in a vapor phase with halogen gases. Because of the relatively low boiling points of these halogens and halide compounds, they would have significant vapor pressures under ambient conditions in the subsurface, in most geographic areas. This would explain the strong correlation between some trace elements and the halogens found in a number of projects. The site variance in oxidation anomalies fits the vapor-phase transport model. Because of the tendency of volatile compounds to migrate vertically toward the surface with little lateral dispersion (Klusman, 1993), a soil sample collected directly over a joint in the bedrock, could have a much higher contrast anomaly than a sample collected five meters away. Hundreds of exploration projects and pilot studies have shown repeatedly that the oxidation suite of elements has a much higher anomaly contrast than do trace elements that would be mobile as ions. Therefore, it appears that the oxidation suite of elements is traveling as something other than charged ions. Vapor phase transport of volatile compounds in microbubbles would be a much more efficient means of moving these trace elements to the surface than would ionic diffusion or dispersion along lines of electromotive force. Fracture control of microseepage of volatiles has been called upon by other researchers to account for analogous observations (Klusman, 1993; Sikka, 1959).

4.3 Electrochemical processes

Evidence supporting the electrochemical interpretation for oxidation anomalies comes from several observations. The central low, as defined by the elements that most tightly bracket the low, is always over the upper end of the reduced body, not the entire body. This is what would be expected if there was a flow of current between the reduced body and the surface; i.e. the current would flow from the end of the body closest to the surface. The observation that groundwater flow does not move these anomalies off the top of the reduced body located in the subsurface, also suggests that something capable of having an effect within a short time frame is holding these anomalies in place. Electrical discharges would tend to hold the system in place. These anomalies are associated only with geological features that have a contrast in oxidation potential with the surrounding rock. If part of an ore body is reduced and part oxidized, then the anomaly is associated with the reduced part. Many cations form anomalies that resemble the "rabbit ears" pattern, predicted with the classical model for an electrochemical cell associated with a massive sulfide body (Bolviken and Logn, 1975; Govett, 1976). With some notable exceptions, oxidation anomalies consist of similar trace element suites regardless of the type of reduced body that appears to be causing the apparent electrochemical cell. Porphyry-Cu deposits produce a suite of anomalous elements at the surface that is similar to the suite produced by a petroleum reservoir. However, the contrast of the various elements does vary considerably depending on the source. Anomaly patterns found with the Enzyme Leach are similar to those modeled for an electrochemical cell associated with a petroleum reservoir (Tompkins, 1990). Apparent patterns of differentiation of Cl, Br, and I around mineral deposits and petroleum reservoirs are strong evidence of oxidation potential gradients in these electrochemical cells. The high oxidation potentials that would account for these halogen patterns would also promote the formation of volatile halide compounds at the anodes of electrochemical cells. This would allow for the migration of the oxidation suite of elements to the surface by a relatively efficient vapor-phase microseepage mechanism. A flux of carbon dioxide, which could be generated as a result of the break down of carbonated minerals during this process, could act as a carrier for volatile compounds of the oxidation suite (R.W. Klusman, personal communication).

4.4 Unified hypotheses and anomaly evolution

4.4.1 Apical metal anomaly hypothesis

Apical metal anomalies associated with petroleum reservoirs can be explained by microseepage of hydrocarbons from the reservoir. Those hydrocarbons would contain porphyrins that are rich in trace metals (Tissot and Welte, 1978), and the petroleum in each reservoir would have a metal signature that would be carried vertically to the surface by microseepage. In a weak to moderate strength electrochemical cell those trace elements would likely show up as apical anomalies at the surface, over the reservoir. In a case where a strong cell developed, the trace metals may be found in the halo at the surface, around the reservoir.

Apical metal anomalies over deep sulfide mineral deposits require a different dispersion mechanism. It is quite possible that bacteria play a role in the formation of these anomalies. Even when a sulfide mineral body is located at too great a depth for an oxidation anomaly to form, it is still possible for bacteria to very gradually begin the process of oxidation of sulfide minerals in the deposit. This bacterial oxidation might be imperceptible to the miner working underground in a deep deposit, but it would explain how commodity metals can reach the surface. Considering the concentration low levels that can be detected with the Enzyme Leach, it would take only a small amount of some metal reaching the surface to produce an anomaly. As sulfur oxidizing bacteria feed on sulfide minerals, they will ingest the metals in the sulfides. In order to rid themselves of elements that they cannot tolerate, these bacteria would methylate the harmful trace elements, and excrete the products (Klusman, 1993, p. 290-291). Dimethyl and trimethyl compounds of metals and metalloids are volatile and could easily migrate to the surface to form Enzyme Leach-detectable anomalies directly over a mineral deposit located several kilometers beneath the surface. The more toxic the trace element is to the bacteria, the more efficiently the bacteria will dispose of that element by means of biomethylation (Klusman, personal communication). Evidence that suggests this can be seen in the Enzyme Leach anomalies over the Elmwood zinc deposit. The maximum Zn anomaly contrast is 5.5 times background, and the maximum anomaly contrast for Cd is 60 (Yeager et al.; Table 1, this issue). Thus, biomethylation can explain the very subtle dispersion of metals like Zn, Cd, As, Sb, Cu, and Pb to the surface, over deep mineral deposits. It does not explain Enzyme Leach-Ba anomalies at the surface over deep occurrences of barite in the subsurface.

4.4.2 Oxidation cell hypothesis

As a deep mineral deposit or petroleum reservoir is slowly unroofed by erosion, it will be easier for atmospheric oxygen to diffuse downward to the deposit. Whether the subtle oxidation of the deposit is accomplished by biological or inorganic reactions is irrelevant. Anytime a reduced substance is oxidized electrons are produced. In the case of a sulfide mineral, each sulfur atom will give up six electrons when it oxidizes from sulfide to sulfate. Thus, there is the possibility for generating an electrochemical cell with the accompanying current discharges. With an oxidizable body at depth, atmospheric oxygen at the surface, and a semipermeable material in the middle, all the elements are in place to form an electrochemical cell, with currents flowing from the reduced body to the source of oxygen.

Most published models for electrochemical cells in the crust can explain some of the features observed in these Enzyme Leach oxidation anomalies (Bolviken and Logn, 1975; Govett, 1976; Smee and Sinha, 1979; Sivenas and Beales, 1982a; Sivenas and Beales, 1982b; Smee, 1983; Govett et al., 1984; Govett and Atherden, 1987). For instance, base metal anomaly patterns often fit these models. However, these models do not explain oxidation suite halos. These models also call upon the reduced body to be an electronic conductor. Most of the reduced bodies, where Enzyme Leach evidence of oxidation has been found, are not electronic conductors. Therefore, earlier electrochemical models cannot explain many of the observations associated with Enzyme Leach oxidation anomalies. Futhermore, whatever model is employed, it has to explain similar empirical observations for both petroleum reservoirs and deep mineral deposits.

For the most part, the reduced bodies are electrically resistive media. In the case of the reduced bodies that contain sulfide minerals, as the sulfides break down in the mineral bodies, the ionic strength of water within the body will increase, lowering electrical resistance. But, they still are not "electronic conductors." The rock and overburden overlying these reduced bodies also are electrically resistive media. Consequently, one of these electrochemical cells also would be a capacitor. The electrical potential (voltage) has to build until it is high enough to discharge across the resistive barrier. When the discharge occurs, electrons will flow from the reduced body in the subsurface toward the source of oxygen, the atmosphere, following the path of least resistance. Oxidation suite anomalies appear to form over the anodes of these cells. These anomalies are found at the surface, around the sides of the reduced bodies at depth. Therefore, contrary to previous models (for example: Govett, 1976; Sivenas and Beales, 1982a; Smee, 1983), the anode is not at the bottom of an electronic conductor. Instead, there are probably multiple anodes, located around the sides of a reduced body, and if that body has a vertical extent (dipping vertically or at an angle), anodes are near the top end of the body. The active anodes form where the electrical current returns to the reduced body. Oxidation occurs at the anodes: sulfide oxidizes to sulfate, metal ions and H^+ form, and electrons are generated. Reduction reactions would characterize the cathodes, the points at which electron discharges would be leaving the reduced bodies. Central lows of oxidation anomalies probably occur over the cathodes of these electrochemical cells (Fig. 25).

Since that voltages that build up would be discharging through a resistive media, the electrochemical potentials that are involved are not small. Those voltage differentials would likely be sufficient to electrolyze water; i.e. the voltage differential between the anode and cathode would be at least 1.229 volts. Under the acid conditions that would accompany the breakdown of sulfide minerals, water could dissociate at the anodes into O_2 and H^+, while at the cathode H_2 would form at the expense of H^+. If chloride is being oxidized to Cl_2, then the electrical potential at the anode is at least 1.36 volts. The formation of a reducing gas, such as H_2, at the cathode would help explain the phenomenon of the central lows of oxidation anomalies. Because of their buoyancy, H_2 microbubbles would rise through groundwater at a relative rapid rate. A weak flux of hydrogen or biogenic methane rising from the cathode as microbubbles would produce a "reduced chimney" above the deposit (Fig. 25). In the case of a petroleum reservoir, leakage of hydrocarbons from the reservoir, combined with H_2 formed at an electrochemical cathode at the top of the reservoir, could produce the same effect. Such a column of reduced gas would alter the overlying rocks and soil. This would account for authigenic magnetite and pyrite being found over petroleum reservoirs. Furthermore, a very subtle flux of hydrogen gas rising through a reduced chimney, given a sufficient amount of time, could reduce leachable As and Sb in the soils to forms which are not leachable, and cause the unusually low and uniform values for these elements found in some central lows. In a few cases, apical As and/or Sb anomalies that accompany an apical Au anomaly have been observed in what is otherwise a central low for the other members of the oxidation suite. Under acid conditions and in the presence of H_2, oxidized forms of As and Sb will be reduced to arsine and stibine (AsH_3 and SbH_3), both of which are gases under near surface conditions, and both of which would migrate with the flux of H_2. Thus, stibine and arsine could form at the cathode of an oxidizing mineral body and be swept to the surface. Therefore, it would appear that As and Sb can be members of the oxidation suite of elements, as well as of a less well defined "hydride suite." Research needs to be done to determine if Au is mobile in a vapor phase in the presence of stibine or arsine.

4.4.3 Apical anomaly to oxidation halo to apical anomaly

A mineral deposit or petroleum reservoir that is too deep to form an electrochemical cell can develop an apical anomaly at the surface due to leakage of the reservoir or the very subtle destruction of sulfide minerals by bacteria. The chemistry of the apical anomaly would reflect the composition of the source at depth. In some cases, a barrier will retard oxidation. As the deposit or reservoir is unroofed over time, and the fugacity of O_2 in the area of the reduced body will increase to a point that oxidation reactions and/or microbial activity intensify to the point that electrical charges can develop and currents can discharge. Initially, because of mineralogical inhomogeneities within most sulfide bodies, oxidation cells would be small and irregularly distributed around the top of the reduced body. These would rapidly grow and coalesce. At this early oxidation stage, anomalies of a few oxidation suite elements (probably including Br and/or I) would develop at the surface, forming a rough halo around the apical anomaly, and together making a combined anomaly. Spotty anodes would occur around the sides of the deposit, and the cathode would expand to cover the top of the deposit. A plume of reduced gases, probably including H_2, would develop over the cathode and produce a "reduced chimney" that would extend to the surface. As more of the rock overlying the reduce body is removed by erosion (or the barrier blocking the flow of oxidation breaks down) the intensity of the oxidation process would increase concurrent with increasing complexity of the oxidation anomaly at the surface. The strength and frequency of subterranean electrical discharges would increase, and some of the metals liberated by the breakdown of sulfides that had been migrating into the apical anomaly, would begin to migrate laterally, pushed along by electrical potential, opposite to the flow of electrons, into the anomalous halo, and near to where the oxidation suite anomalies would be forming. The electrical discharges would be analogous to miniature underground lightning strikes. They would not necessarily flow from the same point on the cathode or return to the same anode every time. Instead, they would move around, depending on where the greatest potentials had built up at that point in time and upon differences in resistance of different pathways through the semi-permeable media above and around the reduced body.

Eventually the oxidation cell would evolve into a strong cell (Fig. 20), and the apical part of the anomaly would be gone. Up until this point, much of the oxidation of an underlying mineral deposit would be almost imperceptible to a mine geologist. At some point in the process of unroofing and oxidation, more intense weathering and possibly supergene enrichment would take place. As the top of a mineral deposit is consumed, anomaly patterns would shift dramatically. If a deposit underwent multiple periods of weathering and/or supergene enrichment caused by stages of erosion, climatic shifts, and changes in the water table, there could be multiple periods of oxidation-anomaly formation and destruction. Collapsed halos (Fig. 23) or apical anomalies could form in more than one of these stages. Once the top of the deposit is exposed at the surface or totally oxidized for some considerable depth below the surface, an apical anomaly is frequently all that is left (Fig. 15).

It must be kept in mind that all of this is a very slow process requiring many millions of years, even if erosion is accelerated by geological events. The quantities of trace elements that are mobilized to form apical anomalies and oxidation anomalies are incredibly small. If it were not for the sensitivity and selectivity of the analytical methodology, most of these anomalies would be impossible to detect. It is only when the reduced bodies are either relatively close to the surface or an oxidation cell is extremely active that these anomalies can be quantified with conventional analytical techniques. Because only very small amounts of material are transported to the surface to form these anomalies, most Enzyme Leach anomalies probably form at a very slow rate. In areas buried by glacial overburden, anomalies have apparently reformed since the last glaciation. In a project in Ecuador, it was found that anomalies were reforming subsequent to the landscape being buried by 10 to 30 meters of volcanic ash in historical times. However, the length of time that is required for these anomalies to equilibrate is not known.

4.5 Additional data and comparative data

Full sets of data plots the Clay Pit deposit, the Mag deposit, Sleeper, Rabbit Creek, the Lik deposit, Indian Hills, Hillman, and Clearville can be obtained by sending an E-mail to the author at clark@actlabs.com. Conventional analytical techniques were tested in many of the pilot studies mentioned in this paper. Analytical data using other methods at Clay Pit are the property of the U.S. Geological Survey. Aqua regia/ICP-OES data from the pilot study at the Rodeo and Meikle deposits are the property of Barrick Goldstrike. The oxalic acid leach and KI+ascorbic acid leach data from the Sleeper pilot study can be obtained from the author by sending an E-mail to clark@actlabs.com. Comparative analytical data from the Happy Creek prospect are the property of Gerle Gold Company. Data for other analytical techniques at the Lik deposit are the property of the U.S. Geological Survey. Comparative analytical data for the RT deposit are the property of Codelco. Additional information regarding the Brazilian laterite study can be obtained form Dr. Peter Rogers, (E-mail address: proger3@ibm.net).

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5. Appendix - Discussion of Sample Collection and Sample Handling

5.1 Sample collection

Although the Enzyme Leach can be used as a partial-analysis method for virtually any surficial geological material, the sample media most commonly analyzed with this method is *B*-horizon soils. Research to date indicates that amorphous MnO2 in soils is most abundant in the *B* horizon. This horizon is the most chemically active part of the soil, with regard to the formation of oxide coatings on mineral grains. Studies in both arid and humid climates indicate that the sampler should be careful to collect soil samples from the *B* horizon when at all possible.

The following information is based on observations from studies in glacially-buried terrane in northern Minnesota and Canada, desert pediments in Nevada, areas of extensive overburden in South America, test sites in the Colorado Front Range, and over oil fields in western Wyoming and southeastern Texas. Soil horizons vary in appearance and depth, even within relatively small areas. It should be emphasized that the samplers should be collecting material from a consistent soil horizon, rather than a consistent depth. Samplers should be encouraged to expose the soil profile whenever they encounter soil zoning that varies from previous observations. Before beginning, it is a good idea to observe soils profiles in ditches and trenches in and near the area to be sampled. The best potential sample sites are those that appear to be undisturbed and that have mature vegetation growing on and around the site. Samples collected from trenches and pit cuts are also good, as long as a fresh surface is scraped on the face of the soil profile to be sure that you are collecting freshly exposed material. Ditch banks, on the side away from infrequently used roads, under most circumstances can also be good sample sites, after digging into the bank to expose fresh material. The sampler should observe the conditions at such sites and make a judgement about the potential for contamination or of excessive disturbance. Road fill (new or old) is not usable sample material. Also, roads are often contaminated with a variety of pollutants that can linger for centuries. Plowed fields can provide usable samples, if an undisturbed site is not available. It is better to move a sample site a relatively short distance rather than to use a bad site just because it is at the specified spot.

5.1.1 Desert soils.

There is an adage to the effect that desert soils are not zoned (azonal). In many cases this is not true. The appearance of the horizons is different from soils in humid climates, but they are still frequently zoned. The current surface on many desert pediments is more than one million years old, which is more than sufficient time for soil horizons to develop. Relatively little organic matter is found in *A*-horizon soils in desert climates. The *A* horizon is typically a light-gray to light-grayish-tan, loose, fine sand to silt. Descending through the soil profile, the *B* horizon begins where the soil is more cemented and slightly darker in color, often becoming slightly more brown than the overlying loose material. The brown color often becomes darker farther down into the *B* horizon, but in other cases, the color difference between the *A* and *B* horizons is almost imperceptible. Where the color changes are minimal, a key criteria is that the cementing of the grains in the *B* horizon often produces a weak blocky fracture that is absent in the *A* horizon. In areas that have a history of previous mining activity, the upper centimeter of the *A* horizon can be highly contaminated with many trace elements. Rarer elements, such as gold, can be enriched by as much as 10- to 100-times background. The *A* horizon should be scraped from the area around the spot to be sampled for a radius large enough to prevent this contaminated material from trickling into the sample material.

In areas of extreme aridity, such as the Atacama desert of South America, the sampler often will not find soil horizons. At most locations in that region the best level to sample is 25 cm to 40 cm beneath the surface. Most of the projects undertaken in deserts to date have used "*B*-horizon" soils collected above the caliche layer, where something resembling a *B* horizon can be identified. In the Atacama desert a fine granular, almost sugary textured, reddish layer will often be encountered just above the caliche layer. This reddish color results from oxide coatings on granular selenite that has formed in the soil. The presence of granular selenite in the soil does not detract from the results, and this layer is a very usable sample media. Recent aeolian material deposited directly on top caliche is not a suitable media for the Enzyme Leach.

5.1.1.1 Caliche

Do not sample from the caliche layer or immediately beneath it. Caliche will produce extremely erratic Enzyme Leach data, with numerous, unreproducible false anomalies.

Where caliche comes too close to the surface to collect a sample, move the sample site a short distance or abandon it.

5.1.2 Humid climate soils.

Sample sites with the best developed soil horizons are usually found in groves of trees. In northern climates, aspen groves are the best. The *A* horizon consists of an upper humus layer, a dark layer of mixed organic and mineral matter, and there may be a bleached mineral layer at the bottom, the A_0 horizon. The bleached layer results from the reducing action of the overlying organic-rich layers, which dissolves oxide coatings on mineral grains. The top of the *B* horizon is the point below which there is no organic matter and where oxide coatings are found on mineral grains. Iron oxide coatings typically give *B*-horizon soils colors that are some shade of brown or red (dark brown, medium brown, light brown, brick red, tan, orange, etc.). Where the *A* horizon is quite thick, such as around bogs, there is often a faintly gray layer beneath the bleached layer of the *A* horizon. The faint gray color is due to manganese oxides, and this material is usable *B* horizon, if a darker colored *B*-horizon layer is not available. In a humid, forested area all the material comprising the *A* horizon of the soil (decaying leaf litter, humus, and organic-rich mineral layers) should be scraped away to reveal the *B* horizon. The sample is collected from 10 to 30 centimeters into the top of the *B* horizon. *A*-horizon contamination of *B*-horizon samples should be avoided as much as possible.

When driving probes through bogs, a grayish-blue clay layer is often found under the peat. This material is analogous to a fire clay under a coal seam. (Given a few million years, that is what it would be.) It is chemically different from the glacially derived material below it, and it will give different background values for a number of elements determined with the Enzyme Leach.

5.1.3 Hard pan at the surface

In some areas either caliche or laterite is at the surface or so close to the surface that a usable sample can not be collected. There are cases where loose wind blown silt lies directly on top of the caliche. This material cannot be used as a sample media, since it has not been in place long enough to begin to equilibrate with dispersion processes from the underlying bedrock. In order to collect a usable sample in areas like these, it will be necessary to either dig through or drill through the hard pan. The distance below the hard pan layer that you must go to get a valid sample will vary from area to area, and pilot studies must be carried out in each new situation to determine the optimum sampling depth.

5.1.4 Mountain soils and glacially scoured terrane.

Due to the rapid rate of mechanical weathering in mountainous areas, there are localities where the soil is truly azonal. Also, during Pleistocene glaciation, the regolith was completely removed in many areas and a chemically mature soil profile has not had sufficient time to redevelop. In such cases the sampler should dig deep enough to obtain soil material that is as free of organic matter as possible.

5.1.5 Rock-chip sampling

In areas where barren volcanic or sedimentary cover rock is all that is present at the surface, an Enzyme Leach survey can still be done with limitations. Look for joints and fractures that contain oxide coatings just beneath the surface. Use a rock hammer to break up the rock so that you can collect chips from within the fractures. Make sure that the chips you collect have as much of that fracture surface as possible. Sample handling is identical to that for soils. In the laboratory, the chips are dropped into a clean jaw crusher to reduce them to millimeter-scale material. The weathered surfaces from the chips tend to end up in the fines that come out of the crusher. The sample is then screened for the minus-60-mesh fraction and treated as if it were a soil. The Enzyme Leach data from these rock-chip samples have substantially reduced anomaly contrast compared to soils from the same region, but the anomaly morphologies are the same.

5.2 Sample handling

5.2.1 Quantity of sample to collect

Samples should consist of about 100 to 200 grams of material depending on the fineness of the soil. Coarser soils require more material to assure adequate sieved sample material for analysis.

5.2.2 Sample bags

There has been a fair amount of discussion about the type of bags to use with Enzyme Leach samples. Most sample bags are suitable. Polyolefin well cutting bags work very well. They are free of contamination and they allow the samples to dry through the porous material. Polyethylene bags and plastic sandwich bags work well. They are free of contamination, but wet samples will not dry in them, requiring extra sample handling to ensure that the samples dry properly. Craft paper soil-sample bags are sturdy when wet samples are placed in them, and they allow the samples to dry through the paper. Some people are concerned about trace element contaminants in the paper getting into the samples. Several tests have been run in which the outer 1 mm of a clay-rich sample that had been stored wet in a craft paper bag was scraped off and analyzed separately. There was not a discernible difference between the rind in contact with the paper and the core of the sample. If the samples are damp, then the mass flow is out of the sample, through the paper, and into the atmosphere, the wrong direction to take contaminants from the paper and carry it into the sample. Common paper bags tear easily, especially when damp, and are not suitable collecting soils for any type of analysis.

5.2.3 Sample drying

If at all possible, the samples should be air dried. If circumstances require the use of a drying oven, the temperature should not exceed 40°C, and the drying time should not be longer than is necessary to dry the sample. Too high a drying temperature alters the chemistry of the amorphous manganese dioxide coatings and drives out the volatile halogens and halide compounds (Fig. 26). At the same time the leachable amounts of some metals like Cu can increase (Fig. 26). David Cohen (personal communication) attributes this increase in leachable metals to the collapse of amorphous coatings as H_2O is driven out. This would result in metals that are not compatible with the collapsing structure being forced to the outside of the material, where they would be more readily dissolved by the Enzyme Leach.

Most laboratory drying ovens are not suitable for drying Enzyme Leach soil samples. They are designed for drying laboratory glassware, and their thermostats are designed for operating at substantially higher temperatures than 40° C. The interval between heating and cooling cycles of the thermostats can be as large as 15° C. If one of these cheaply thermostats sticks during a heating cycle, the temperature can quickly rise to 60° C, or more. Forced-air drying ovens are prone to do the most damage. Although they do have a more uniform temperature distribution in the oven, the heat transfer rate to the samples is much greater with moving heated air than for slowly convecting air. Moving air is also going to disperse volatiles in the samples at a much higher rate than is stagnant air. The reader should look at Fig. 26 and then make a decision about whether or not to use a drying oven If in doubt, let the service provider perform the sample preparation, or air dry the samples. They know which sieve sizes to use, and what steps must be followed to maintain the geochemical integrity of the sample material.

Pulverized samples have been "cooked" by the heat that is generated in the grinding mill. The grinding process also destroys the coating on mineral grains. Samples which were collected previously for some other purpose and were pulverized during preparation are not suitable for analysis with the Enzyme Leach.

5.2.4 Sample handling in the field

When presented with this information about not overheating samples, many geologists become quite concerned, because the surface temperature on a hot day in many deserts often goes well above 50° C. Earth is an outstanding thermal insulator. Ten centimeters below the surface the temperature will be approaching constant level that is much cooler and will be fairly consistent from day to day. Most samples are collected at 30 cm or greater depth.

Once the samples are collected, they should not be stored in a place where the temperature can rise much above 40° C for several hours. Enclosed trailers and camper shells that are sitting still in the sun are a definite hazard. Samples should be kept in the shade if it is a hot sunny day. Also, samples that are stored together in a pile have greater thermal inertia and will heat up slower than samples that are laid out individually on the ground.

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Figure 24. Enzyme Leach-Cu profile over Radomiro Tomic porphyry-Cu deposit, section 10300 N.

Fig. 25. Model for an electrochemical cell occurring at the top of a reduce body in the subsurface.

Fig. 26. Effect of excessive drying temperature on Enzyme Leach analyses of soils for Br and Cu.

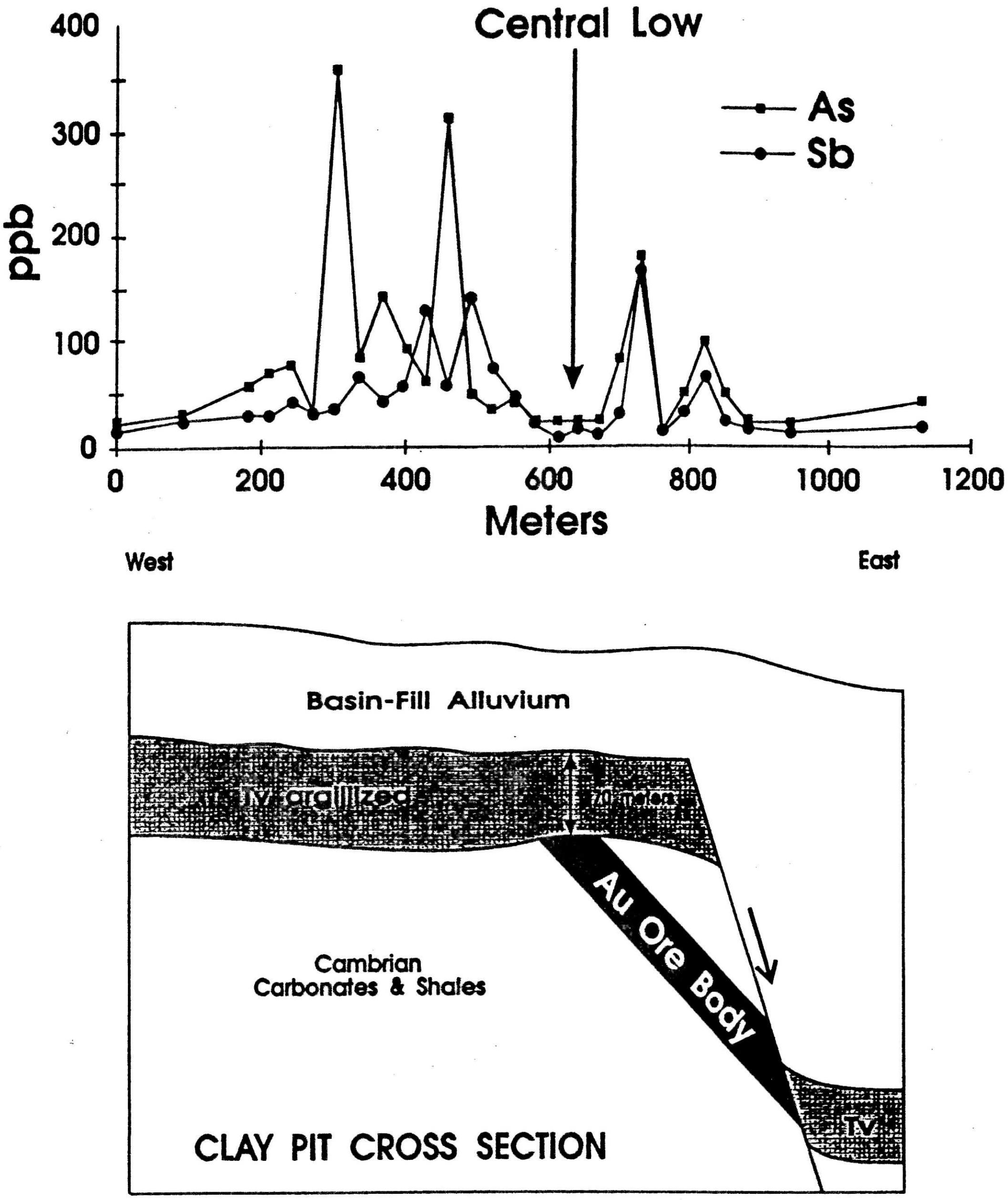
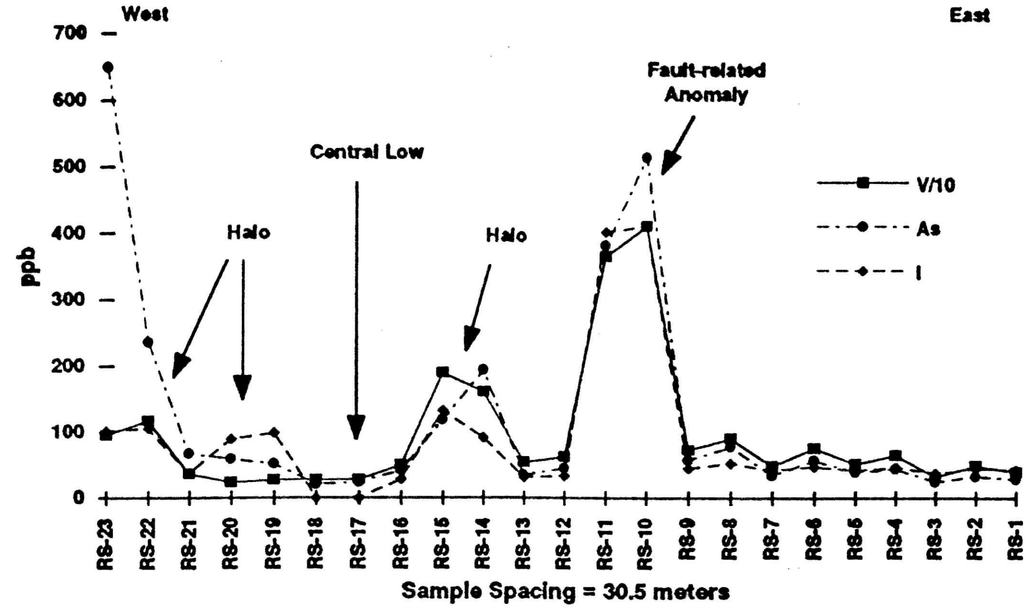


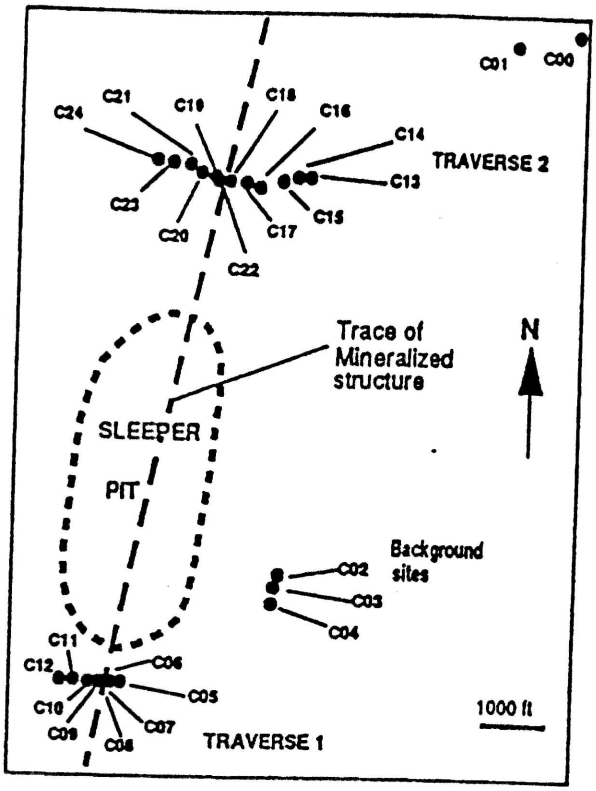
Figure 1. Typical Enzyme Leach oxidation halo over the Clay Pit deposit, an epithermal gold ore body in the Getchell Trend, Nevada. The central low directly overlies the upper end of the mineralized body. The deposit is capped by seventy meters of argillized Tertiary volcanic rock and eighty meters of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



Geology to be included shortly.

Fig. 2. Oxidation halo and central low for As, I and V over reduced part of epithermal-Au ore body and a fault-related anomaly over Post Fault, at the Rodeo deposit in the Carlin Trend of Nevada. The fault-related anomamly is controlled by the Post Fault.

Fig. 3


C01
C00
C24
C21
C19
C18
C16
C14
TRAVERSE 2
C13
C15
C17
C22
C20
C23
Trace of Mineralized structure
N
SLEEPER
PIT
Background sites
C02
C03
C04
C11
C12
C06
C05
C10
C09
C08
C07
TRAVERSE 1
1000 ft

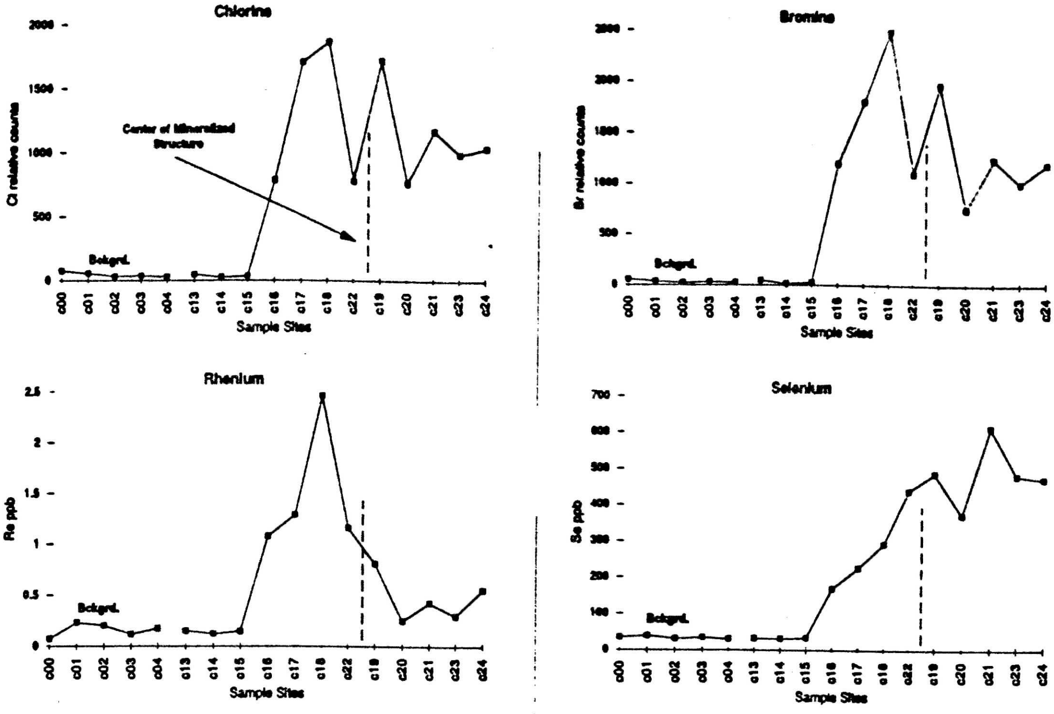


Fig. 4. Chlorine, Br, Re, and Se anomaly patterns along northern sampling traverse, Sleeper Mine, Nevada.

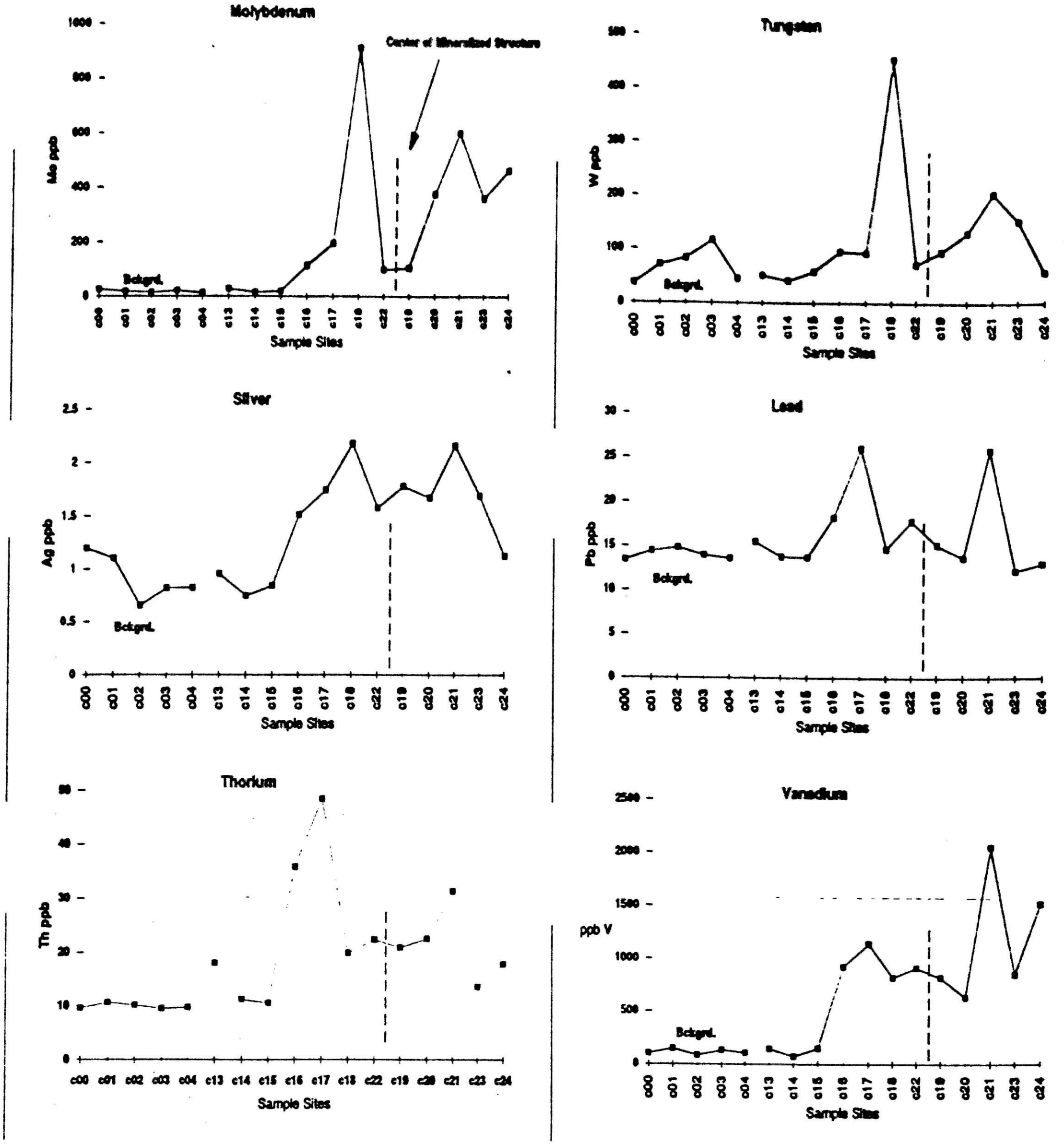


Fig. 5. "Rabbit-ears" anomaly patterns along northern traverse across the controlling structure, Sleeper Mine, Nevada.

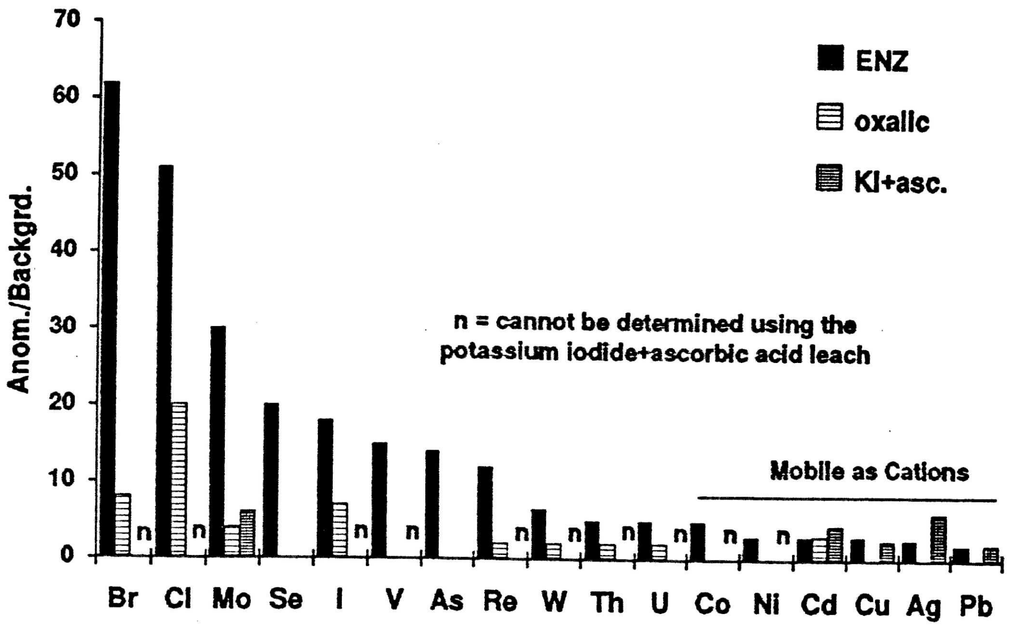


Fig. 6. Maximum anomaly/background contrast for anomalous elements in the pilot study at the Sleeper Mine, Nevada.

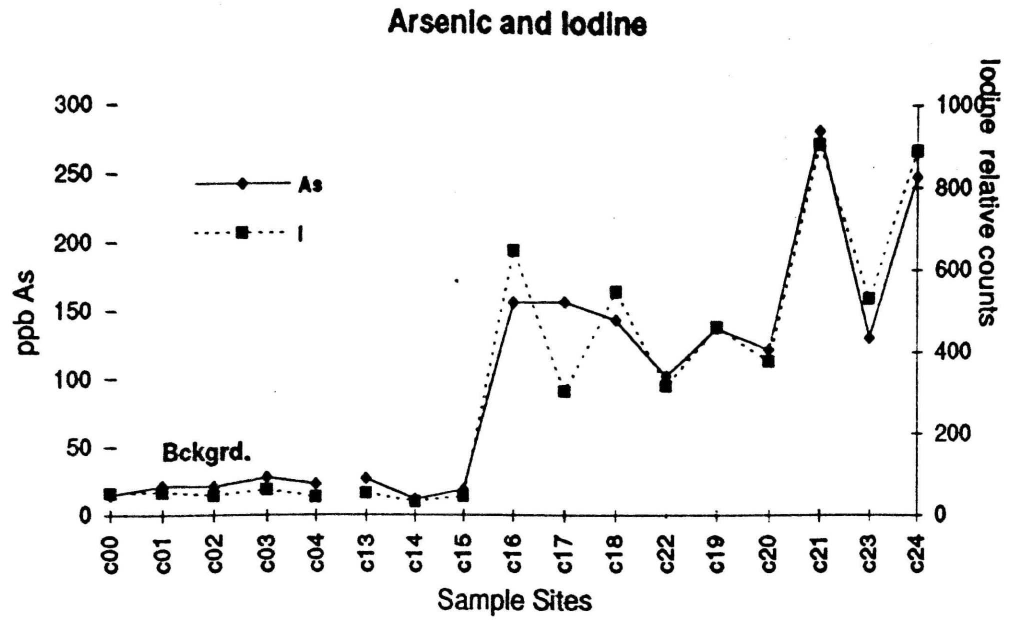
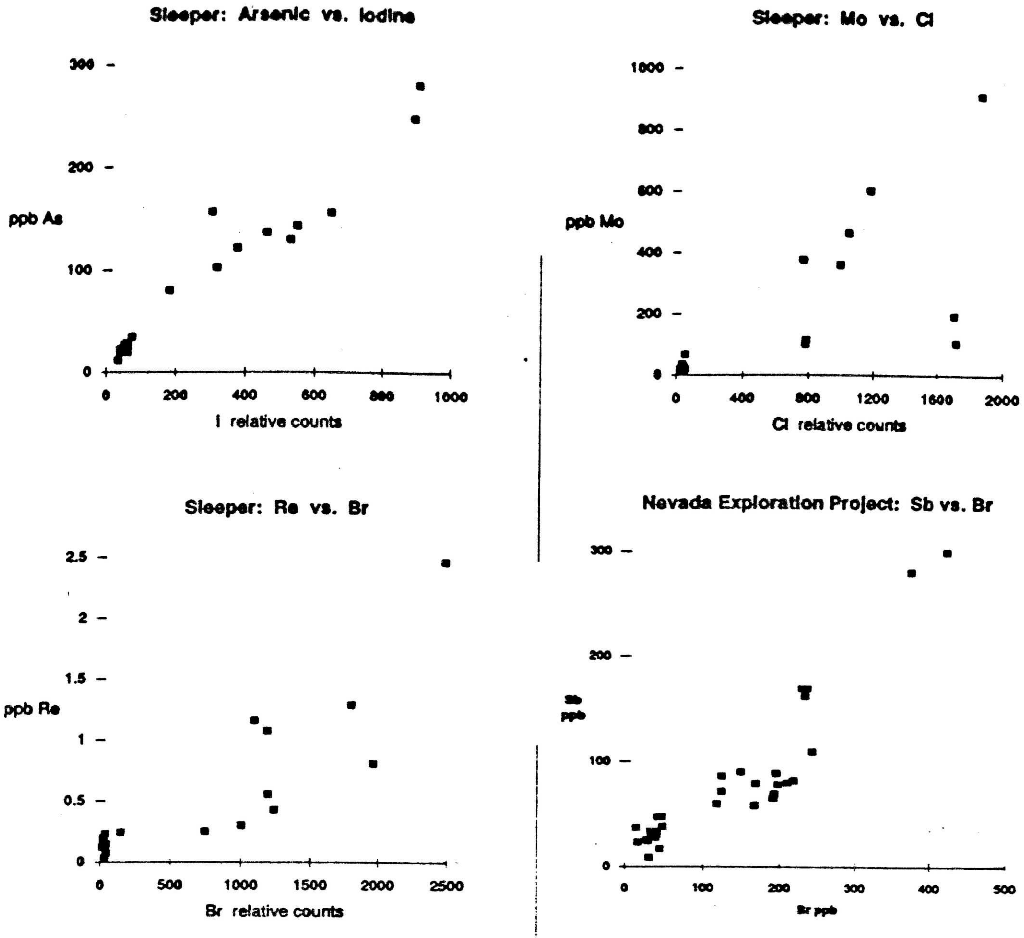


Fig. 7. Close correlation between Enzyme Leach As and iodine along the northern traverse of the pilot study at the Sleeper Mine, Nevada.



Sleeper: Arsenic vs. Iodine

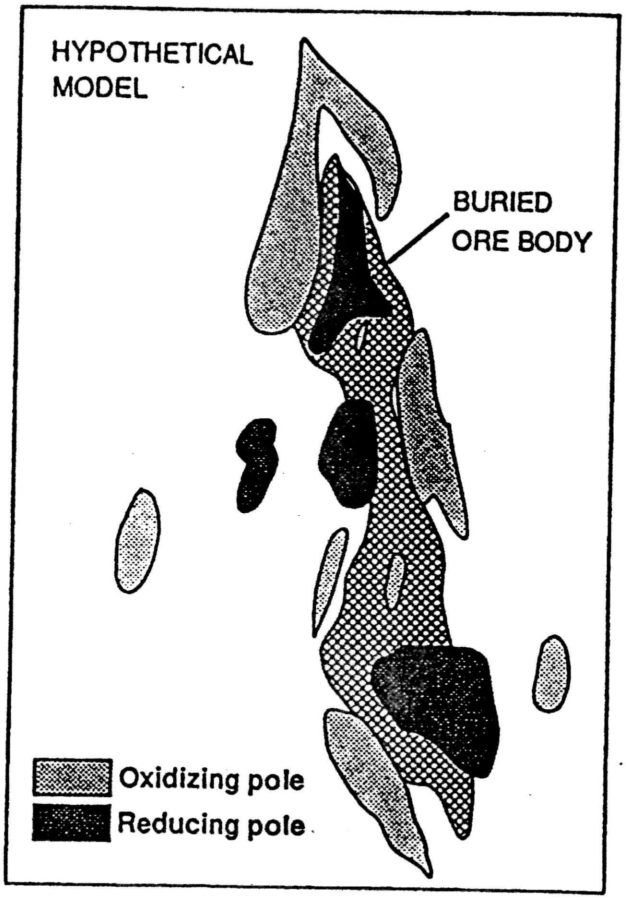
Sleeper: Mo vs. Cl

Sleeper: Re vs. Br

Nevada Exploration Project: Sb vs. Br

Fig. 8. Scatter diagrams showing relationships between some elements that can form volatile halides and halogens at the Sleeper Mine, Nevada, and at an exploration project area in Nevada.

Fig. 9
~~Fig. 10~~


HYPOTHETICAL MODEL
BURIED ORE BODY
Oxidizing pole
Reducing pole

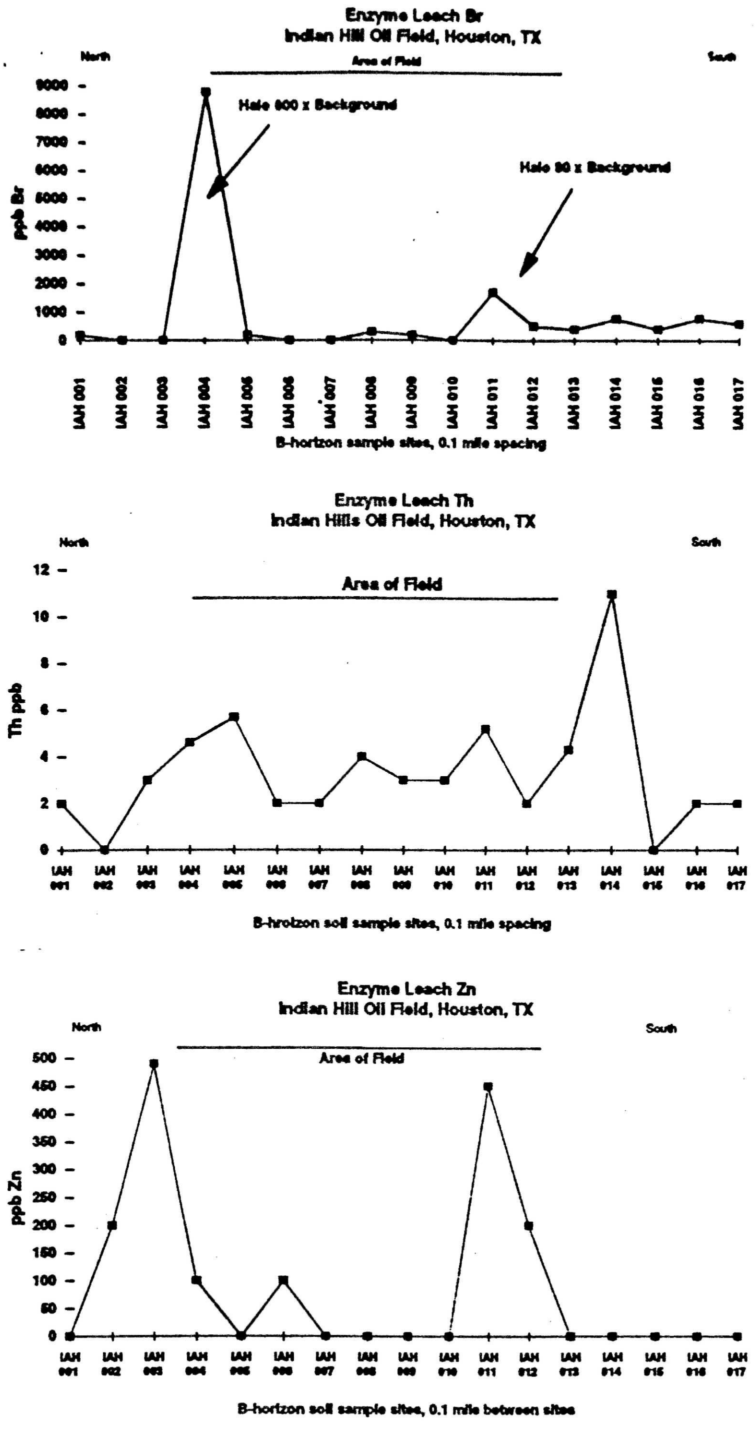
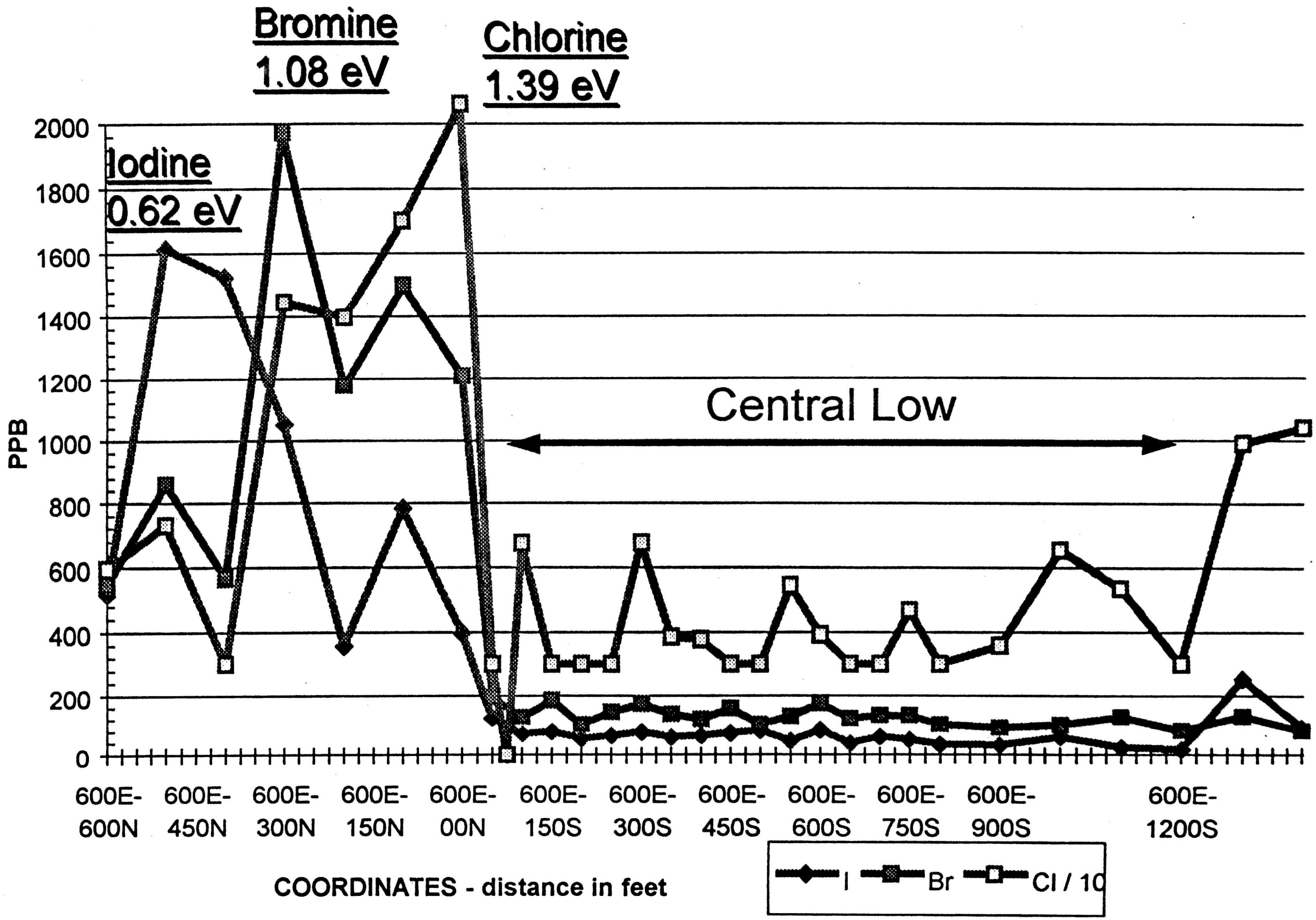


Fig. 10. Enzyme Leach anomalies associated with the Indian Hills Oil Field, north of Houston, Texas.

Fig 11

Alaska Project Cl, Br, & I



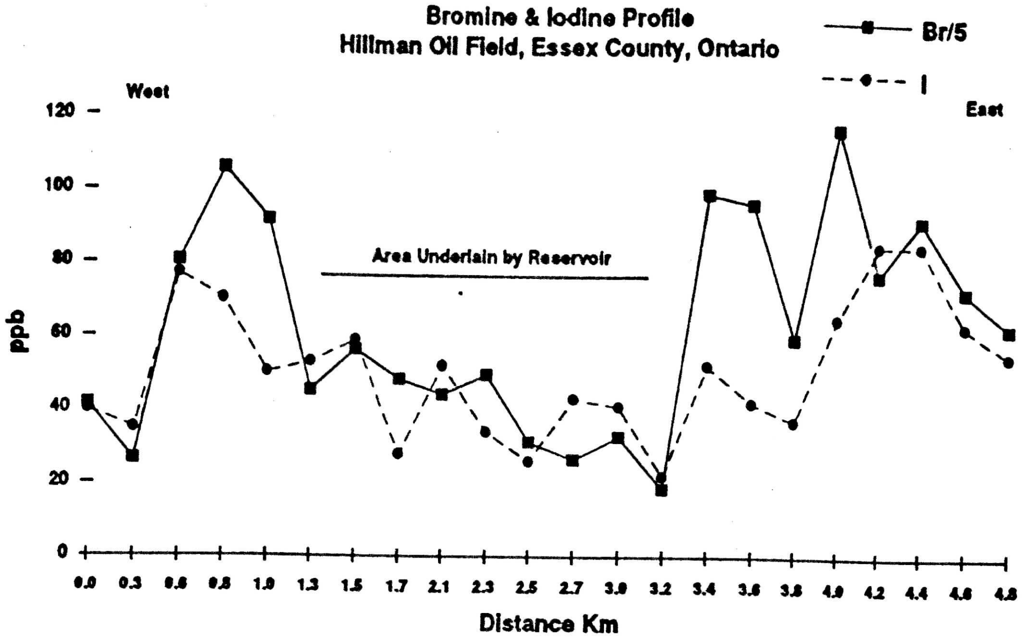


Fig. 12. Bromine/iodine zoning pattern in oxidation halo around the Hillman Oil Field, Essex County, Ontario. Enzyme Leach bromine anomaly in soil peaks closer to edges of reservoir in subsurface than does iodine.

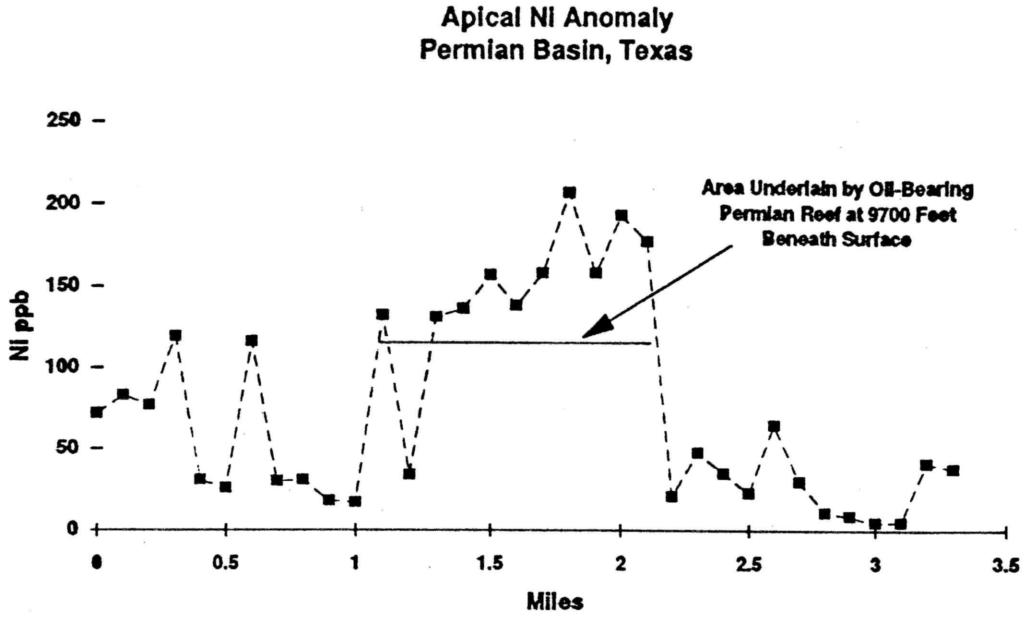
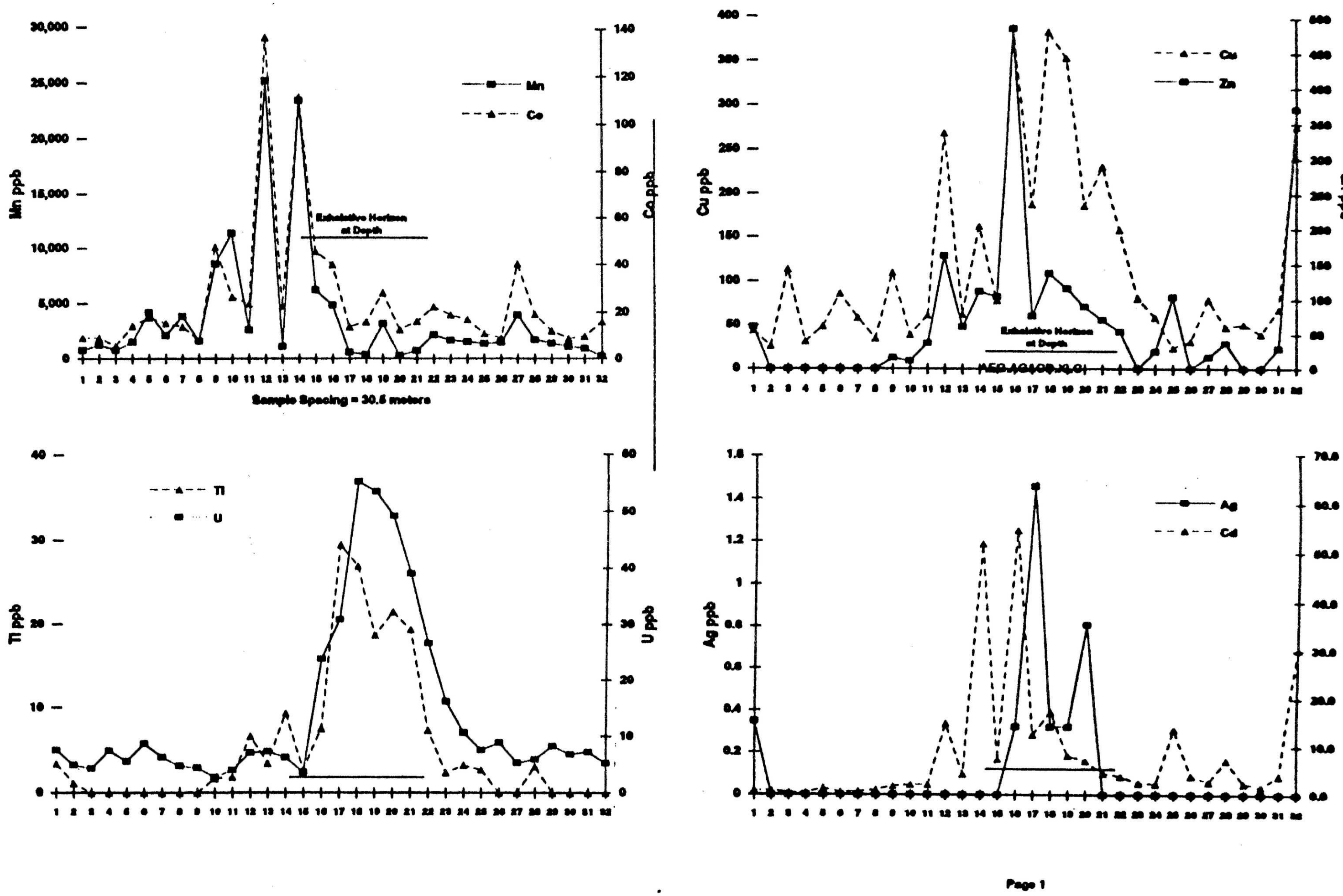


Fig. 13. Apical Ni anomlay over a reef-hosted reservoir almost 3000 meters below the surface in the Permian Basin, Texas.



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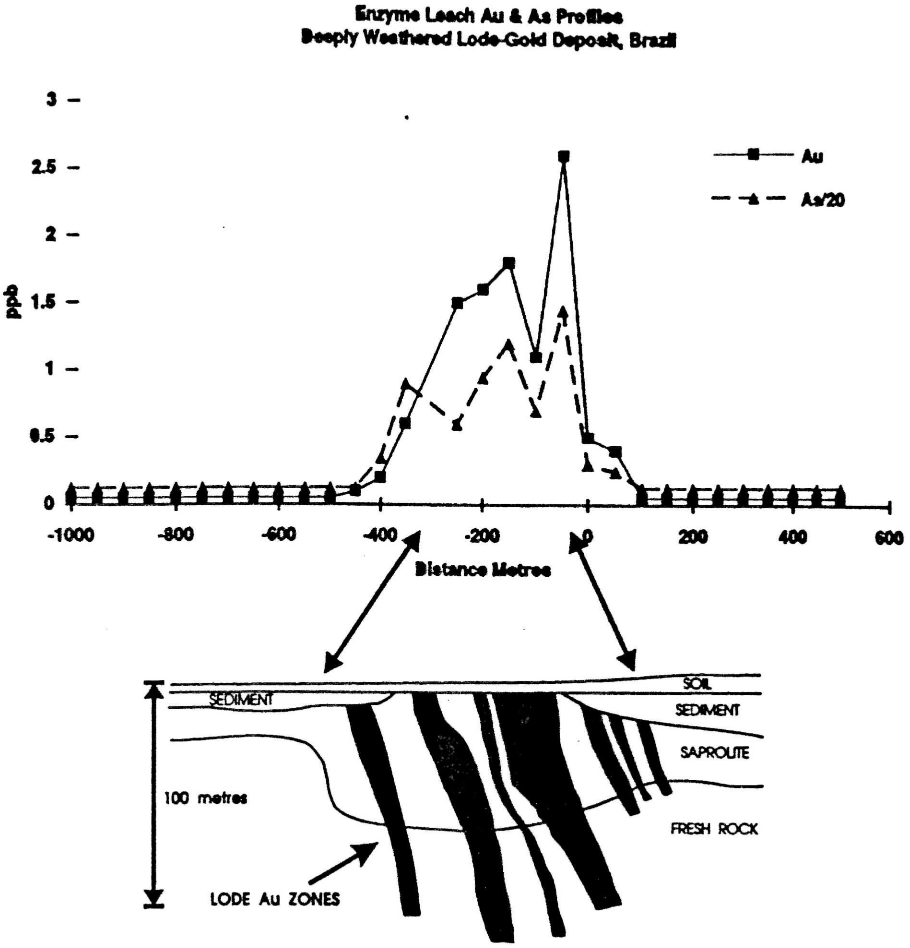
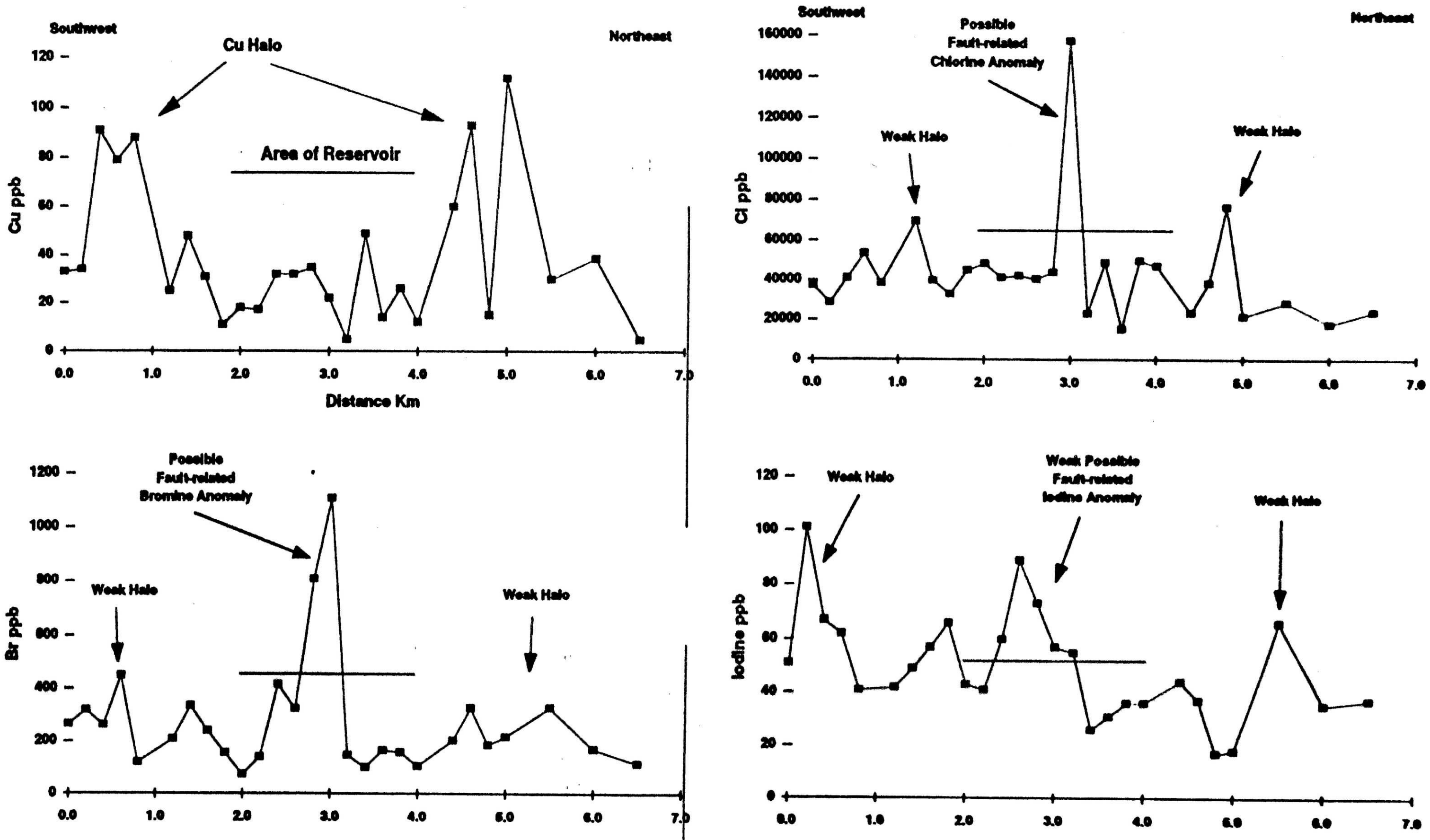


Figure 15. Apical Au and As anomalies over deeply lateritized lode-gold deposit in southern Brazil.



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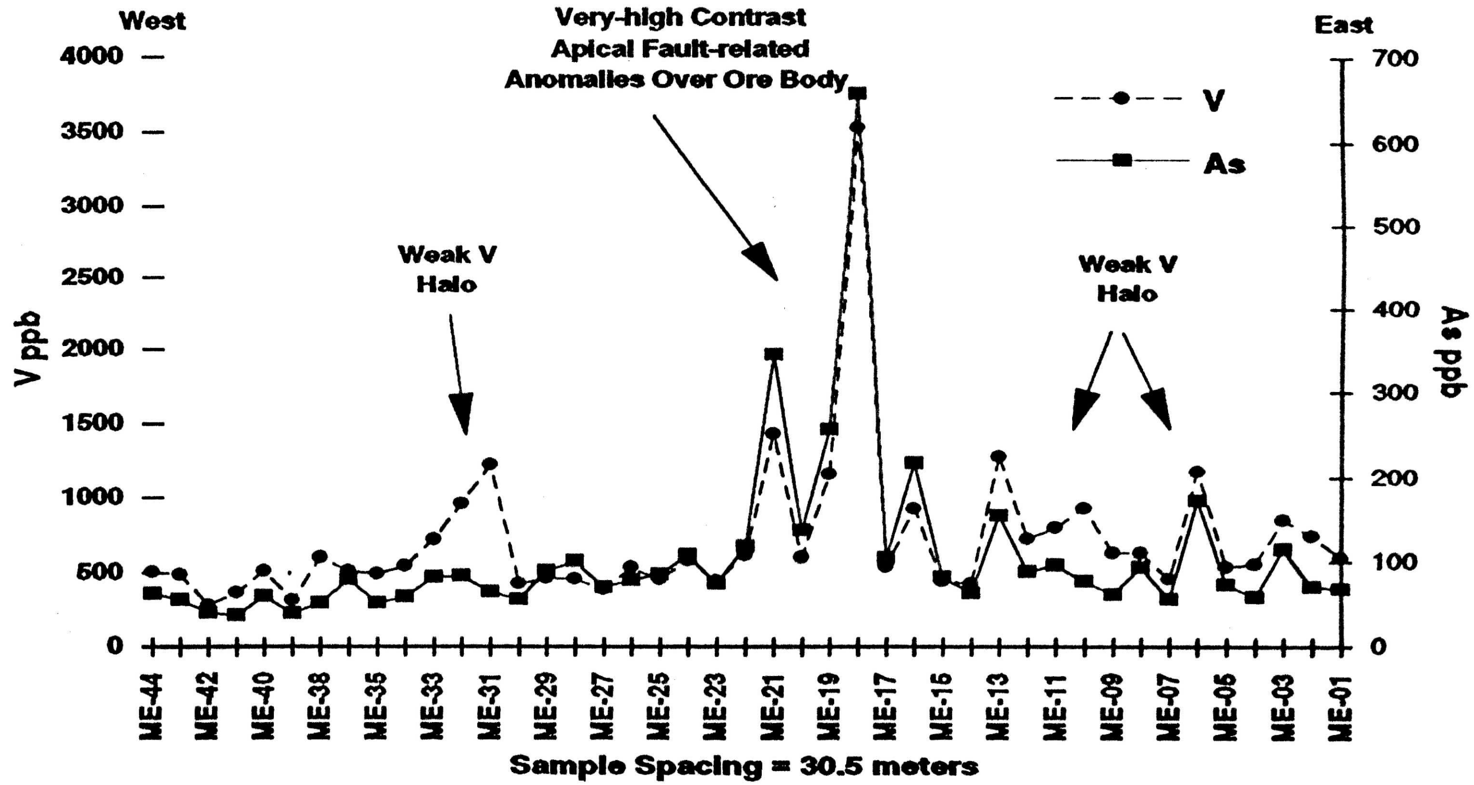

Geologic base to be included shortly.

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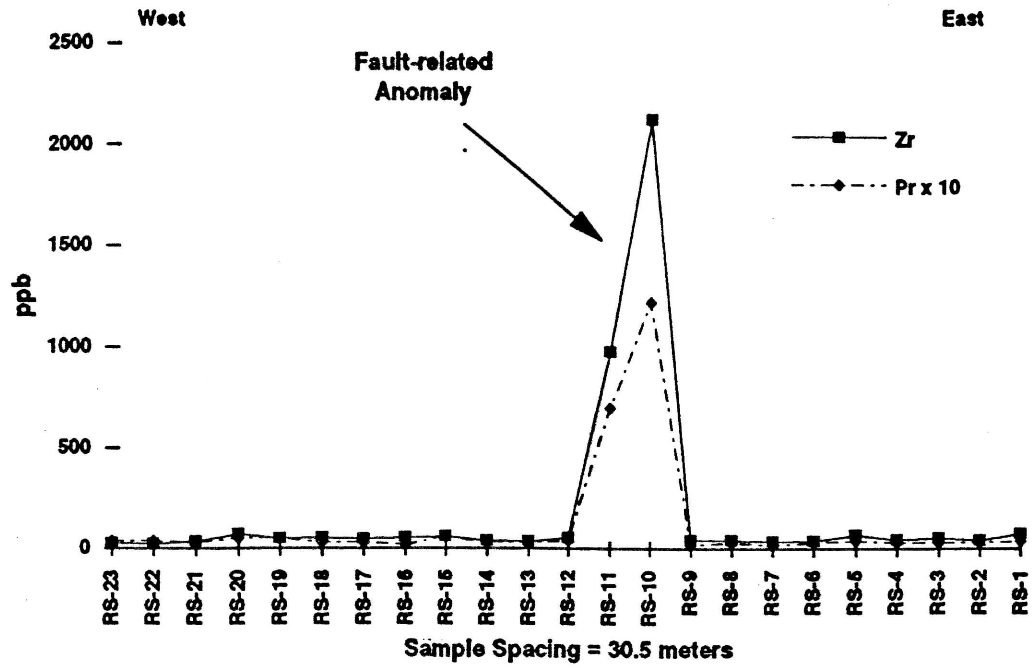


Geologic base to be included shortly.

Fig. 18. Fault-related Zr and Pr anomaly over the Post Fault, near the Rodeo ore body, Carlin Trend, Nevada.

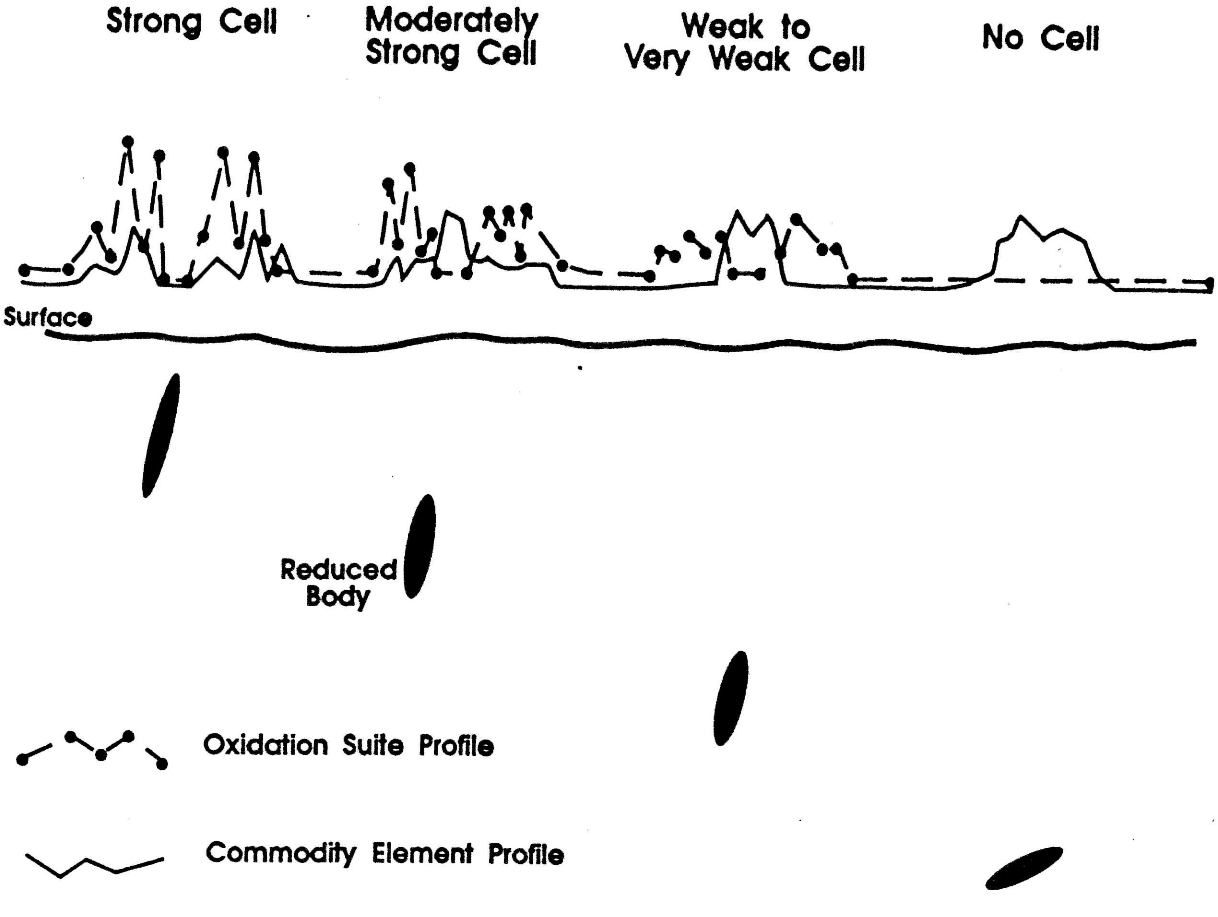
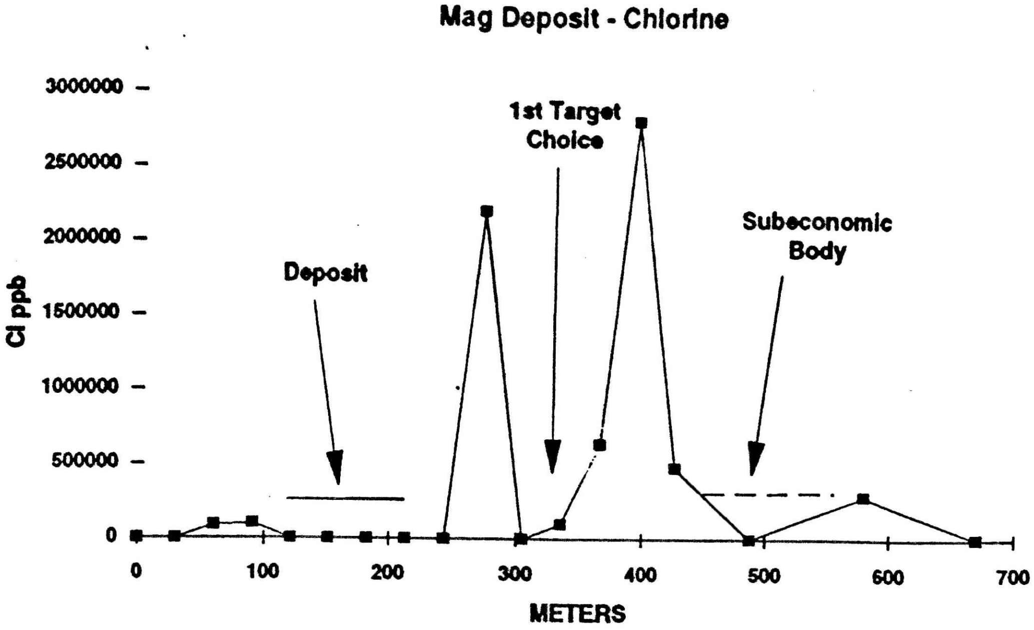


Fig. 20. Typical anomaly profile variations related to strength of the oxidation cell. The shifts from one anomaly form to another in some instances is a function of depth below the surface. The depths at which these shifts occur vary from one region to another.

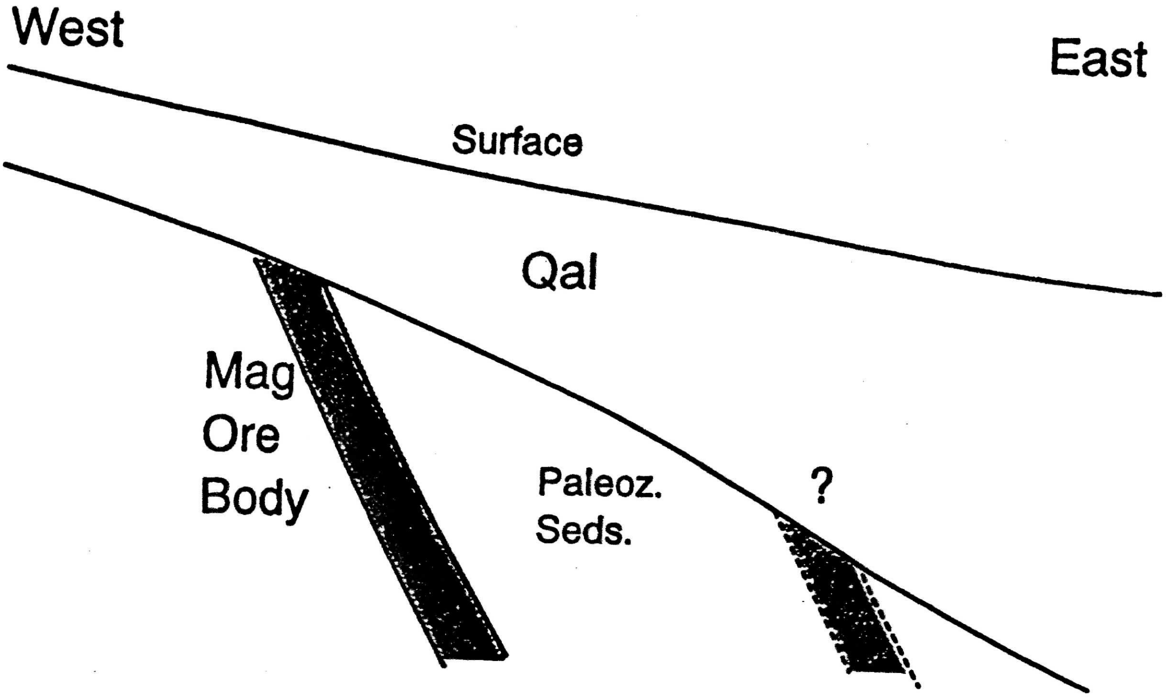


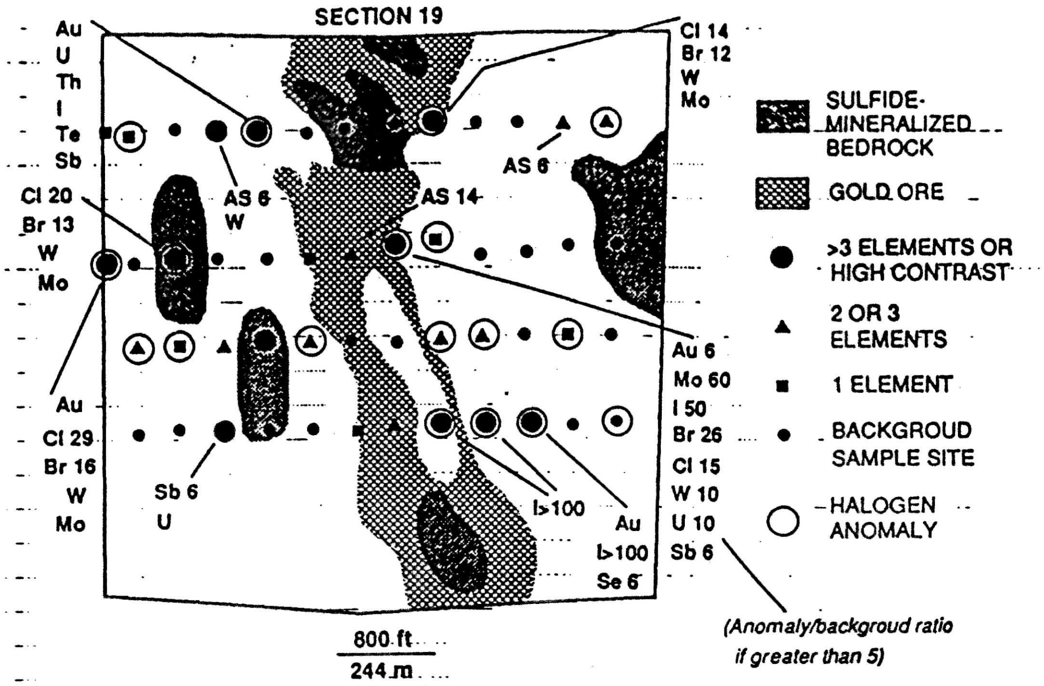
Geology base on next page

Fig. 21. Interferrence pattern between adjacent mineralized bodies, Pinson Mine, Nevada.

Fig. 21, Bottom

Mag Deposit Cross Section





Soil Geochemical Anomalies associated with gold mineralization, Rabbit Creek Mine, Nevada.

(note: computer problem, all bars are the same pattern)

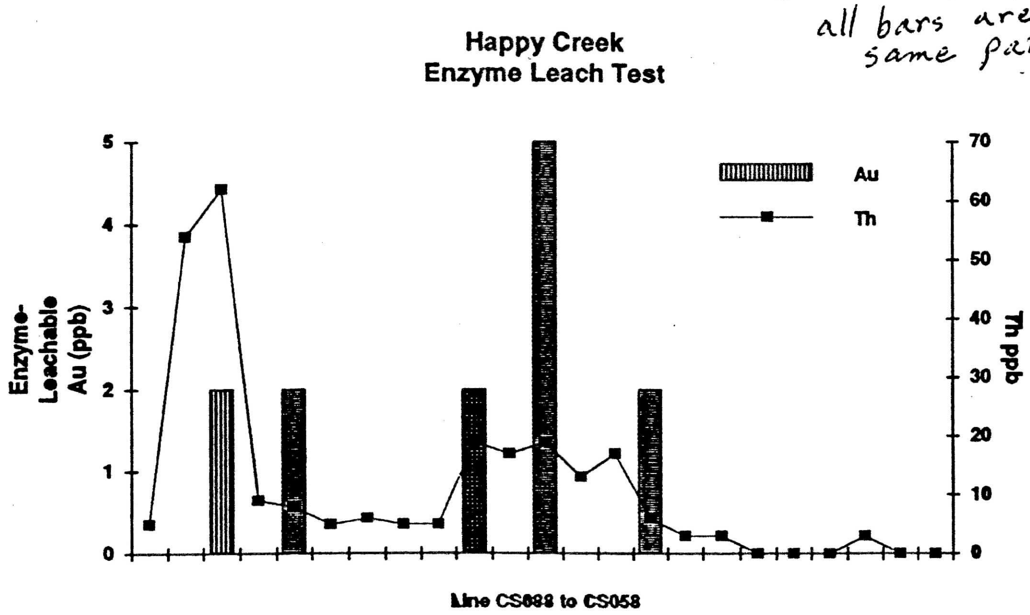
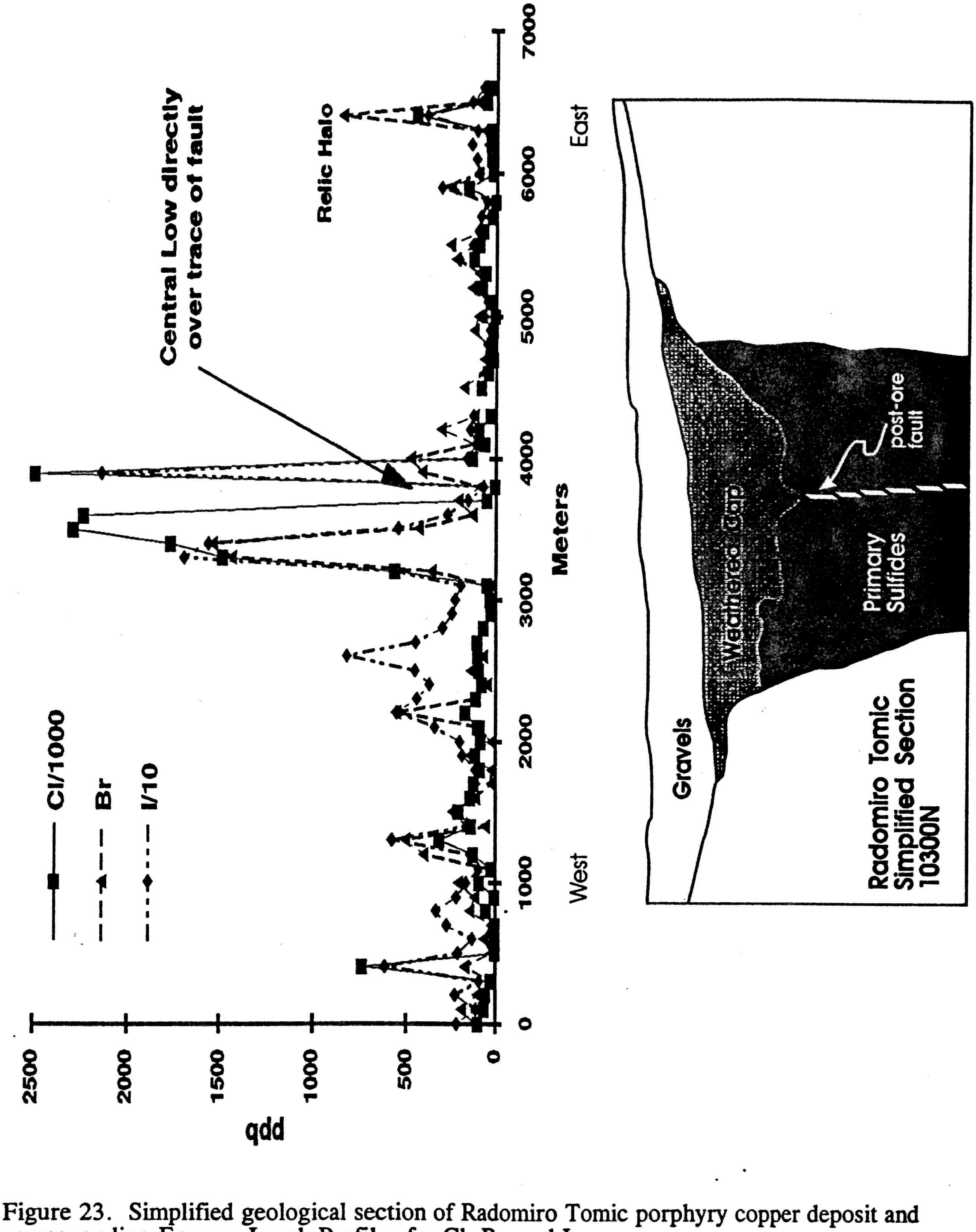


Fig. 22. Enzyme leachable-Au anomalies at the Rabbit Creek deposit and the Happy Creek prospect, Nevada.



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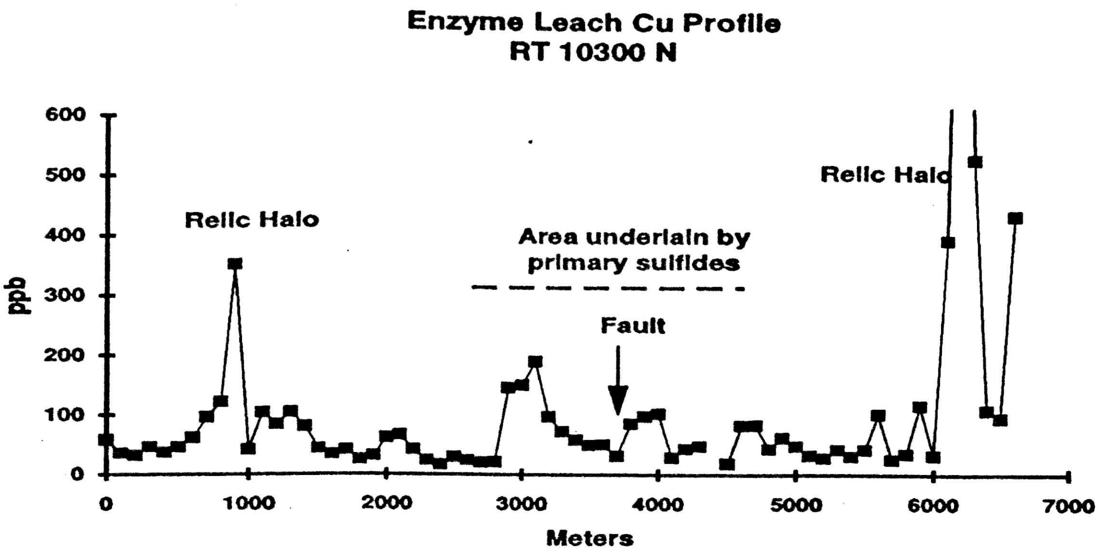
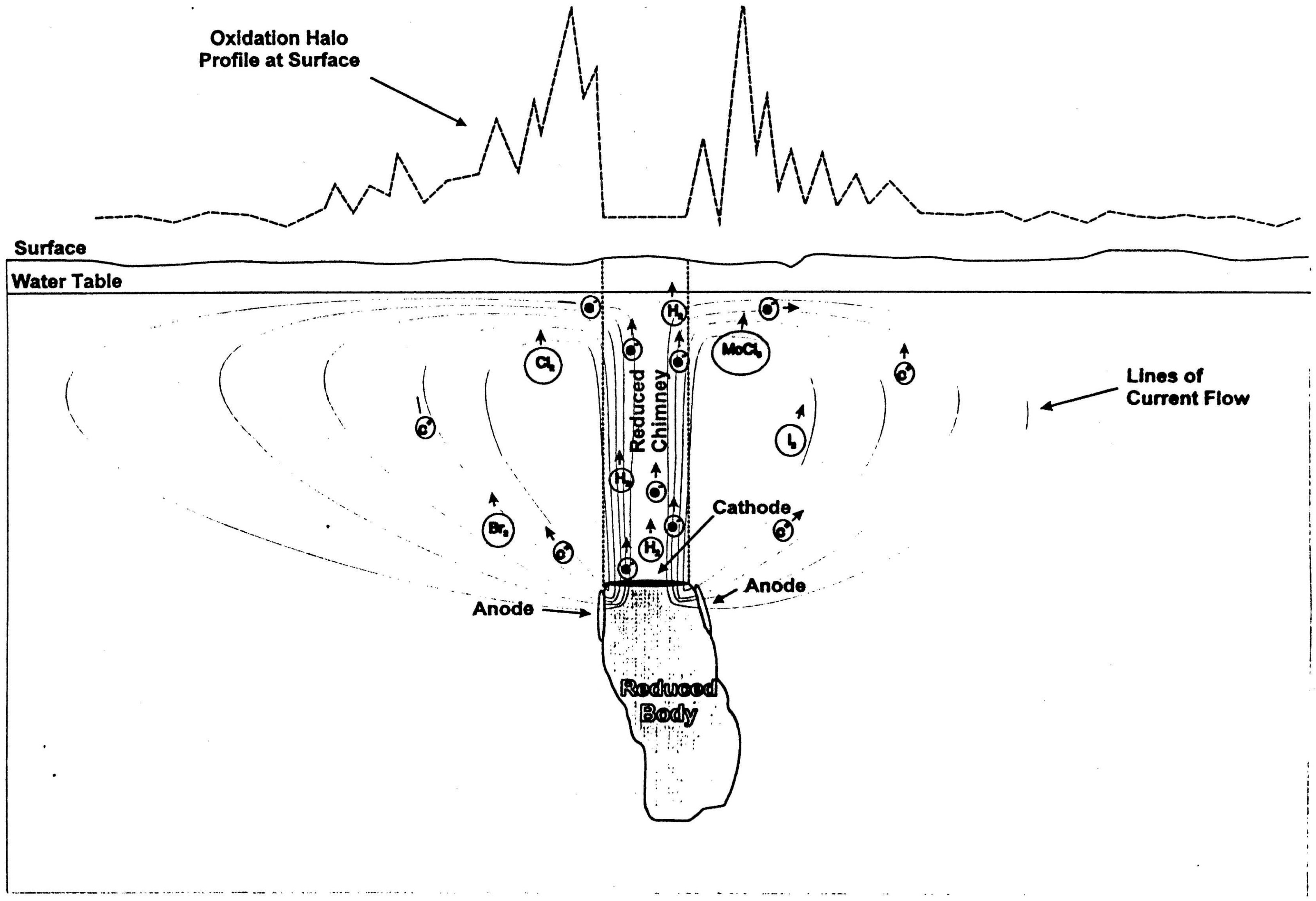


Figure 24. Enzyme Leach-Cu profile over Radomiro Tomic porphyry-Cu deposit, section 10300 N.



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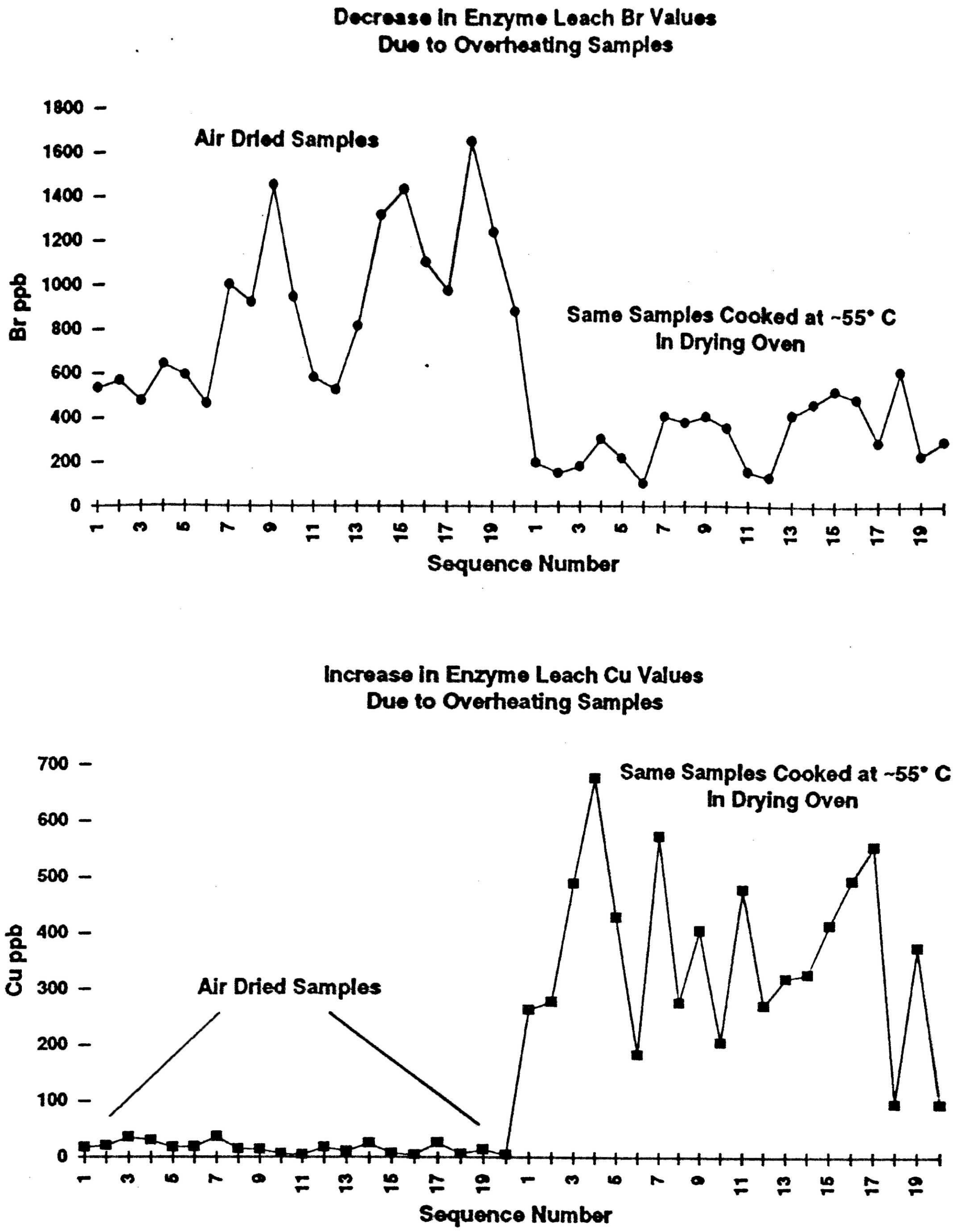


Decrease in Enzyme Leach Br Values
Due to Overheating Samples

Increase in Enzyme Leach Cu Values
Due to Overheating Samples

Fig. 26. Effect of excessive drying temperature on Enzyme Leach analyses of soils for Br and Cu.

Topics of Discussion:

Three Key Concepts:

(i) Conventional Soil Geochemistry vs Enzyme Leach (SM)

(ii) Chemistry of the Enzyme Leach (SM)

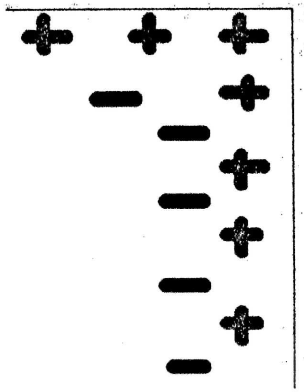
(iii) Anomaly Patterns

Three Key Concepts

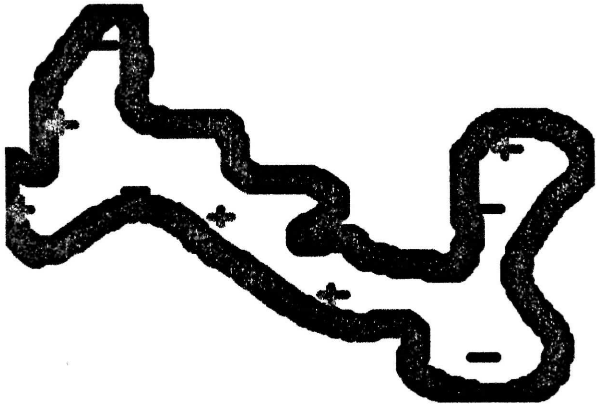
- Vapour Phase Geochemistry
- The Amorphous Phase of MnO_2
- The Electrochemical Cell Model

Forms of MnO_2

- Surface of Crystalline Phase



- Surface of Amorphous Phase



Types of Analyses

Partial or Total Digestions
vs Selective Extractions

- Partial Digestions
- Aqua Regia Digestion with ICP-OES leaches base metals and some silicates
- 30-32 elements
- Detection limits are from 1 to 20 ppm

- These leaches are too strong!

Conventional Geochemical Anomalies

- Conventional chemical leaches extract large portions of trace elements from silicates producing false anomalies
- Cannot determine many volatile anions such as Cl, I and Br
- Detection limits are not sensitive enough
- Anomalies give chemistry of the overburden...not the deposit
- Minimal anomaly contrast, if detected at all

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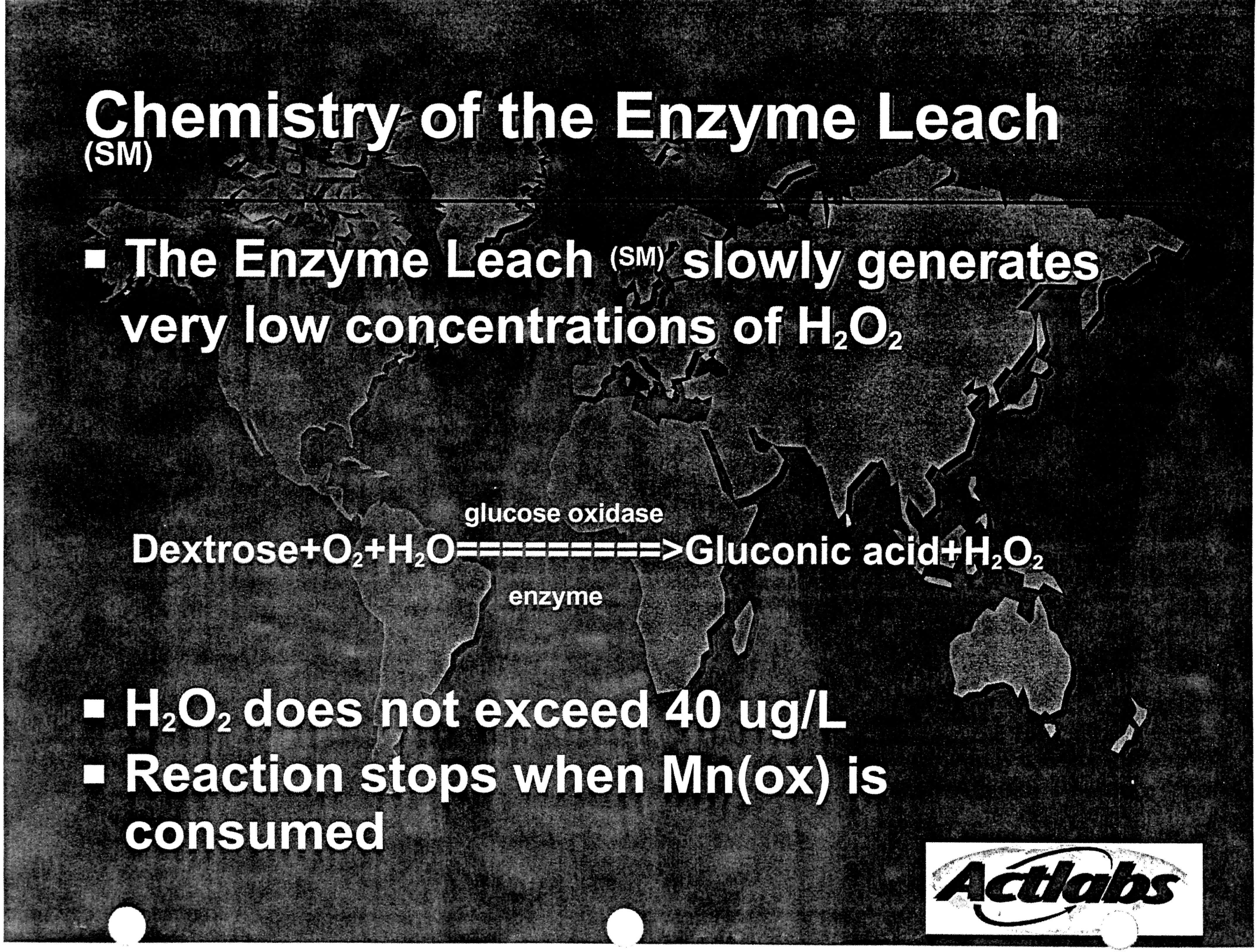


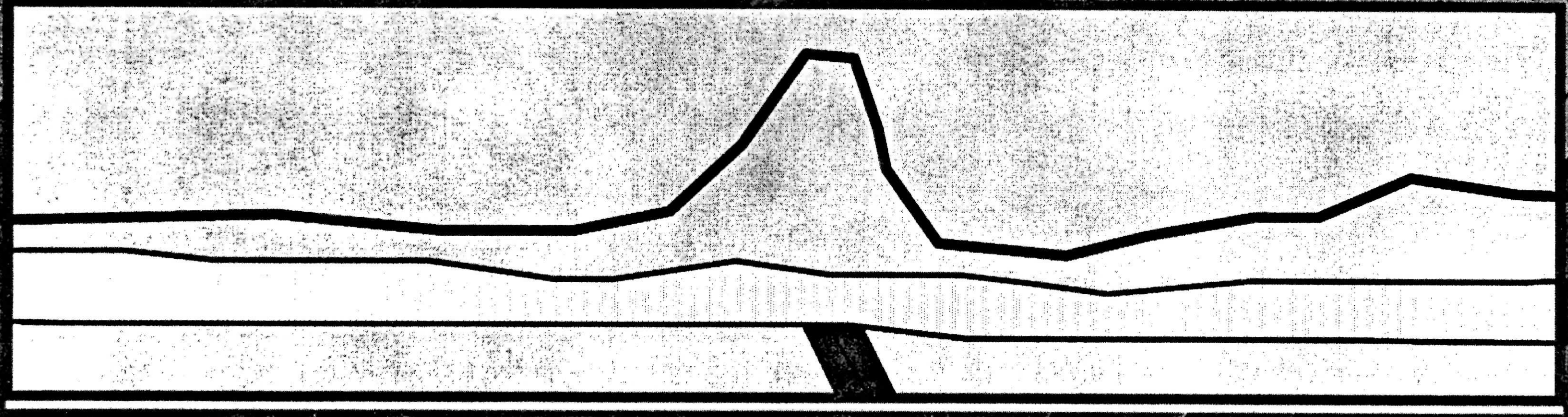
Chemistry of the Enzyme Leach (SM)

- The Enzyme Leach (SM) slowly generates very low concentrations of H_2O_2

$$\text{Dextrose}+O_2+H_2O \overset{\text{glucose oxidase}}{\underset{\text{enzyme}}{==========>}} \text{Gluconic acid}+H_2O_2$$

- H_2O_2 does not exceed 40 ug/L
- Reaction stops when Mn(ox) is consumed

Apical Anomalies



- Apical anomalies can occur over the source resulting from diffusion of trace elements from a highly concentrated source
- Fault related anomalies occur almost directly over the fault subcrop and reflect fault related mineralization
- Fault related anomalies often contain "immobile" elements such as zirconium

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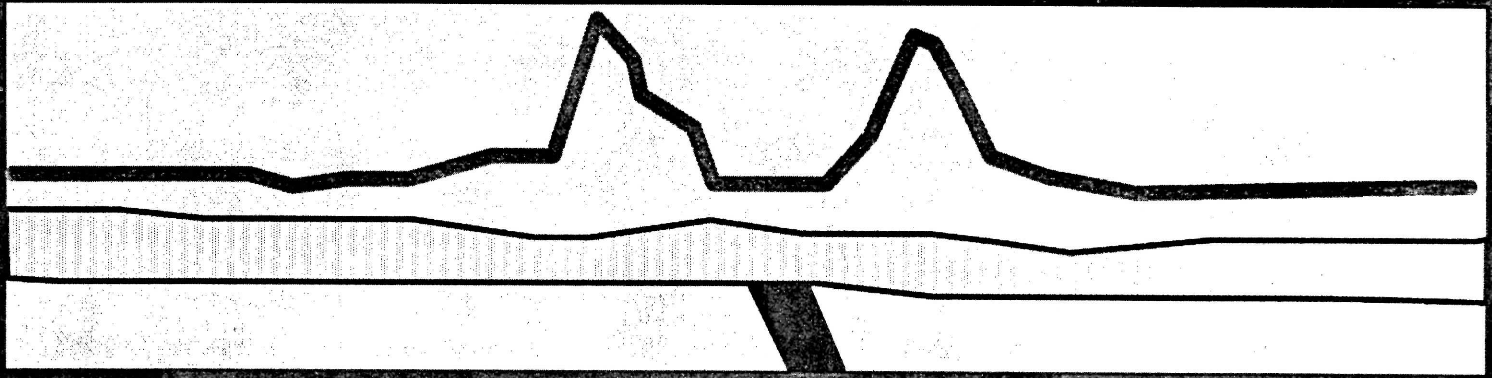
Oxidation Anomaly



- Oxidation anomalies are formed by the generation of an electrochemical cell from an oxidizing orebody
- Oxidation suite consists of: Cl, Br, I, As, Sb, W, Se, Re, Te, V, U and Th
- Form lows directly over the mineralization subcrop, regardless of groundwater flow or glacial transport
- The oxidation suite migrates as gases from volatile halide compounds

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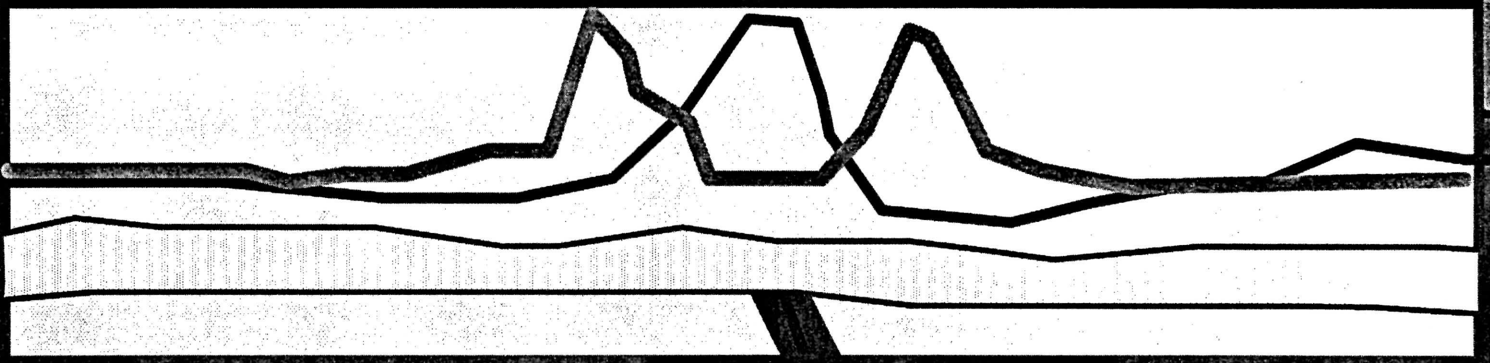
Combination Anomalies



- Combination anomalies result from weak oxidation cells where the halogens form an oxidation anomaly and other elements related to mineralization for apical anomalies over the mineralization
- Common to areas where faults occur within the ore zones
- May indicate a shallow source of anomaly

Enzyme Leach (SM) Instrumentation

- ICP Mass Spectrometry (ELAN 6000)
  Measures mass of the ions using a quadropole mass spectrometer
- More sensitive than ICP-OES
  0.2 ppb for Ag, 1 ppb for most other elements
- Sixty elements:
  Halogens, Oxidation Suite, Metals, Precious Metals, REE, HFSE, Lithophile

Why use the Enzyme Leach $^{\text{(SM)}}$

- Enzyme Leach $^{\text{(SM)}}$ anomalies define a clearer drill target
- Enzyme Leach $^{\text{(SM)}}$ only extracts ions related to mineralization
- Enzyme Leach $^{\text{(SM)}}$ maximizes background to anomaly contrast
- Enzyme Leach $^{\text{(SM)}}$ only attacks weakly bonded ions
- Enzyme Leach $^{\text{(SM)}}$ anomalies occur directly over the mineralization subcrop

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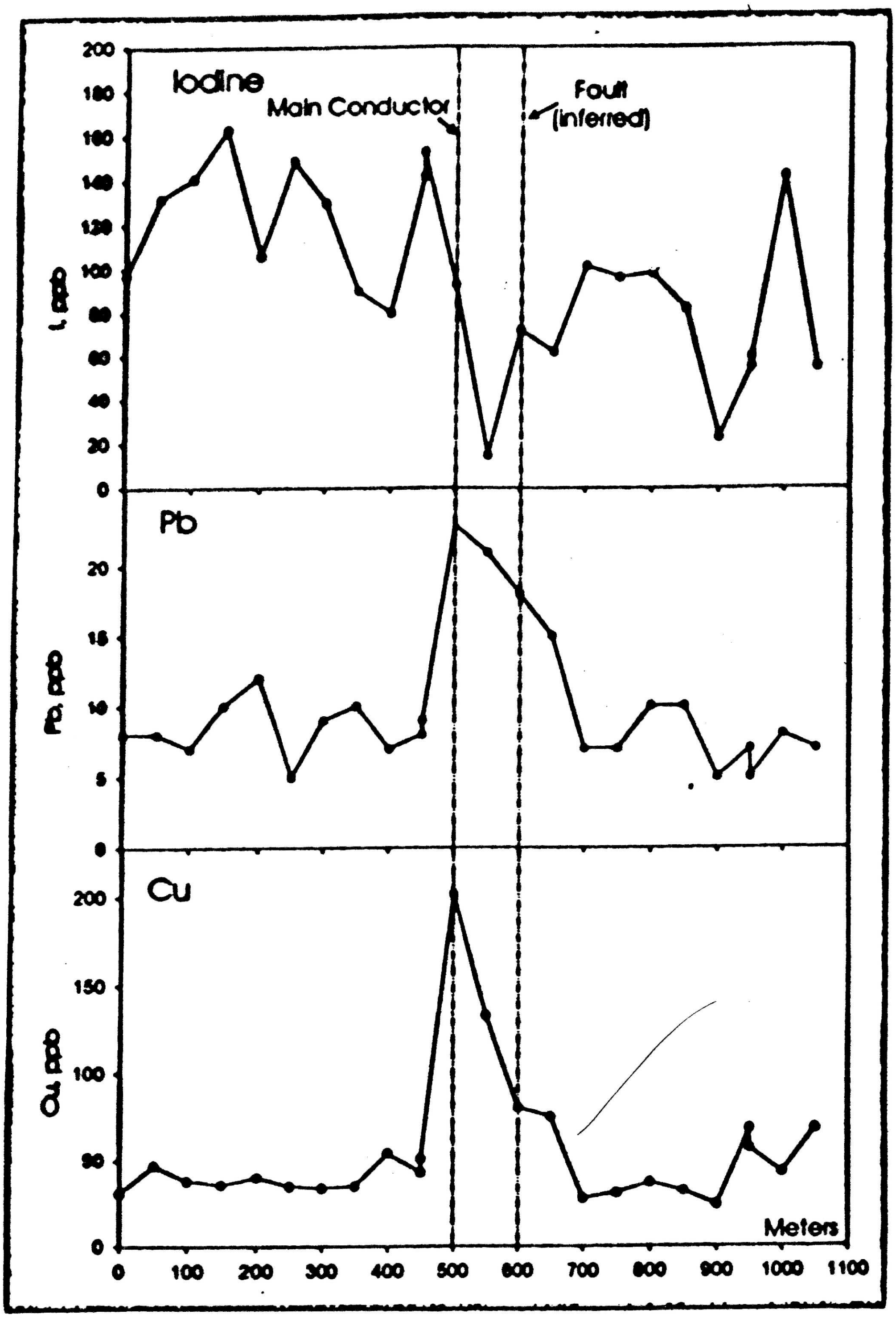
Case Histories:

- Glacial-Assean Lake (NE Manitoba)
  -Stimson Prospect (Abitibi Clay Belt)
- Permafrost-Lik Deposit (Alaska)
- Loess-Brewery Creek (Yukon)
  able to differentiate bedrock geology
- Arid Environment (Northern Mexico)
- Carbonate Terrain-MVT (Tennessee)

Assean Lake-NE Manitoba



From: M Fedikow and D Ziehlke
Manitoba OFR 98-3

Survey Location

- Stimson Prospect (Ontario)

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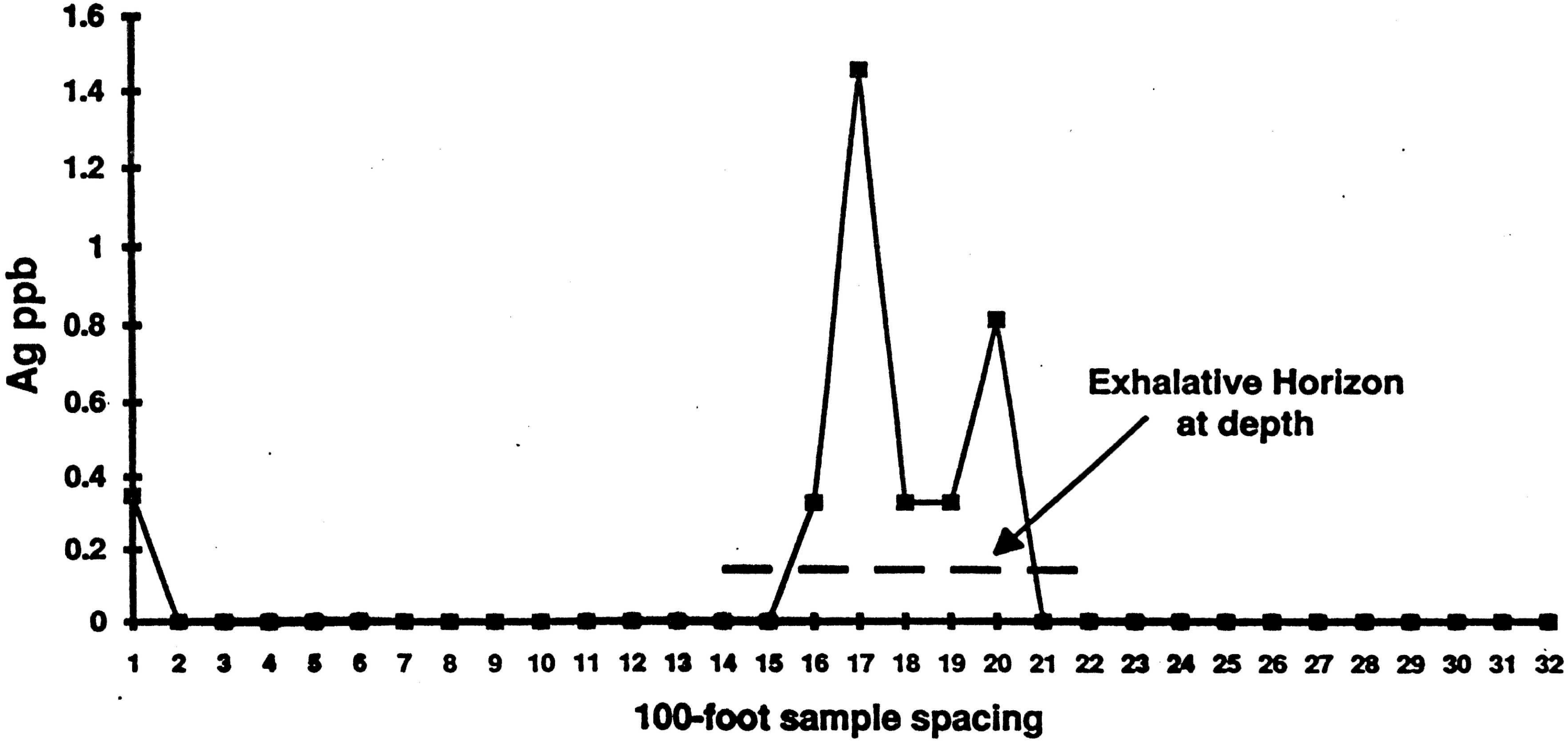
Ontario Geological Survey

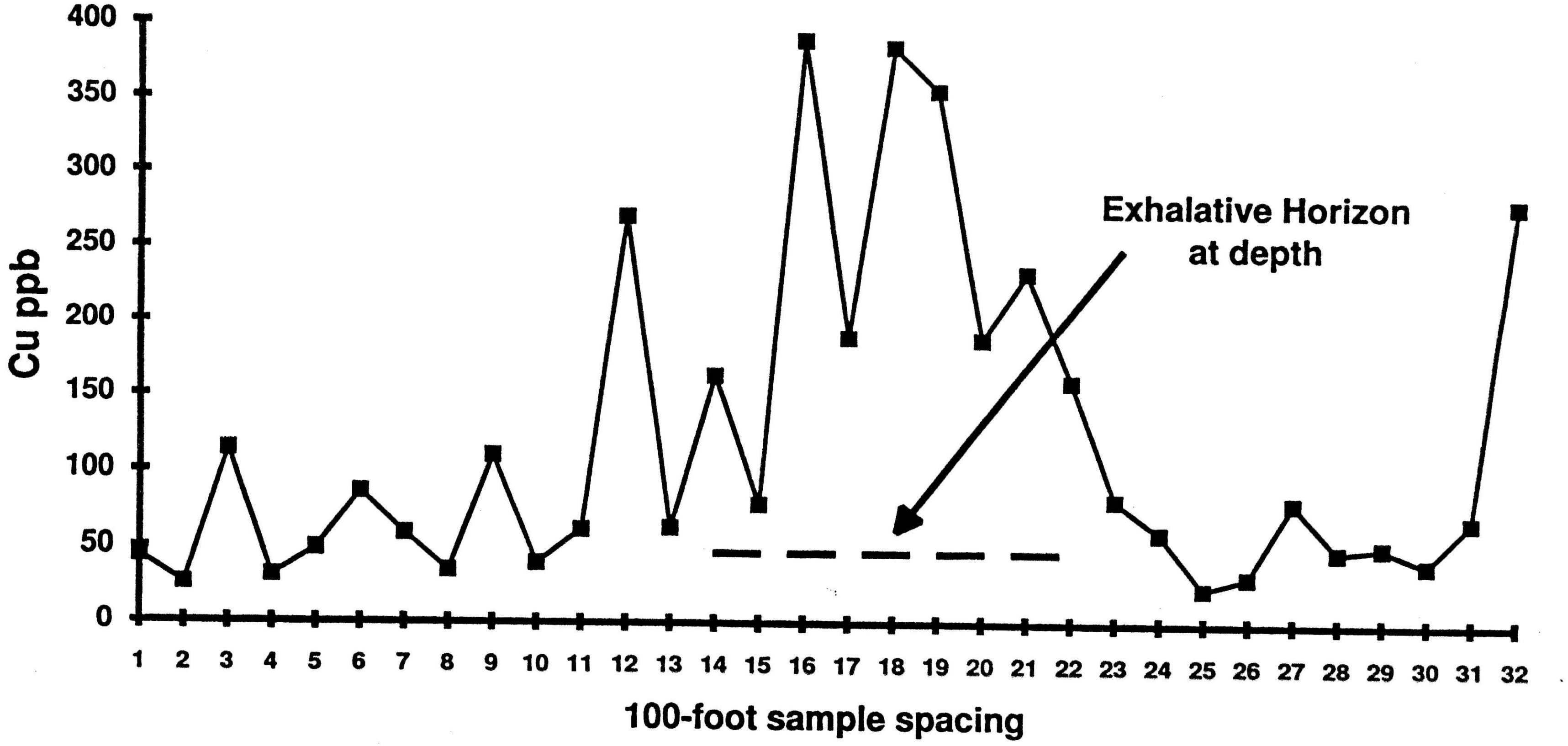
- "The B horizon as analyzed by the enzyme leach ICP-MS method consistently yielded a recognizable response to mineralization under all terrain conditions. No anomalies were obtained when the samples were analyzed by aqua regia ICP-ES"

Jackson, R.G. 1995. The application of water and soil geochemistry to detect blind mineralization in areas of thick overburden; Ontario Geological Survey, Open File Report 5927, 151 p.

Enzyme Leach Test
20 Meters Alluvial Cover with Permafrost



Enzyme Leach Test
20 Meters Alluvial Cover with Permafrost



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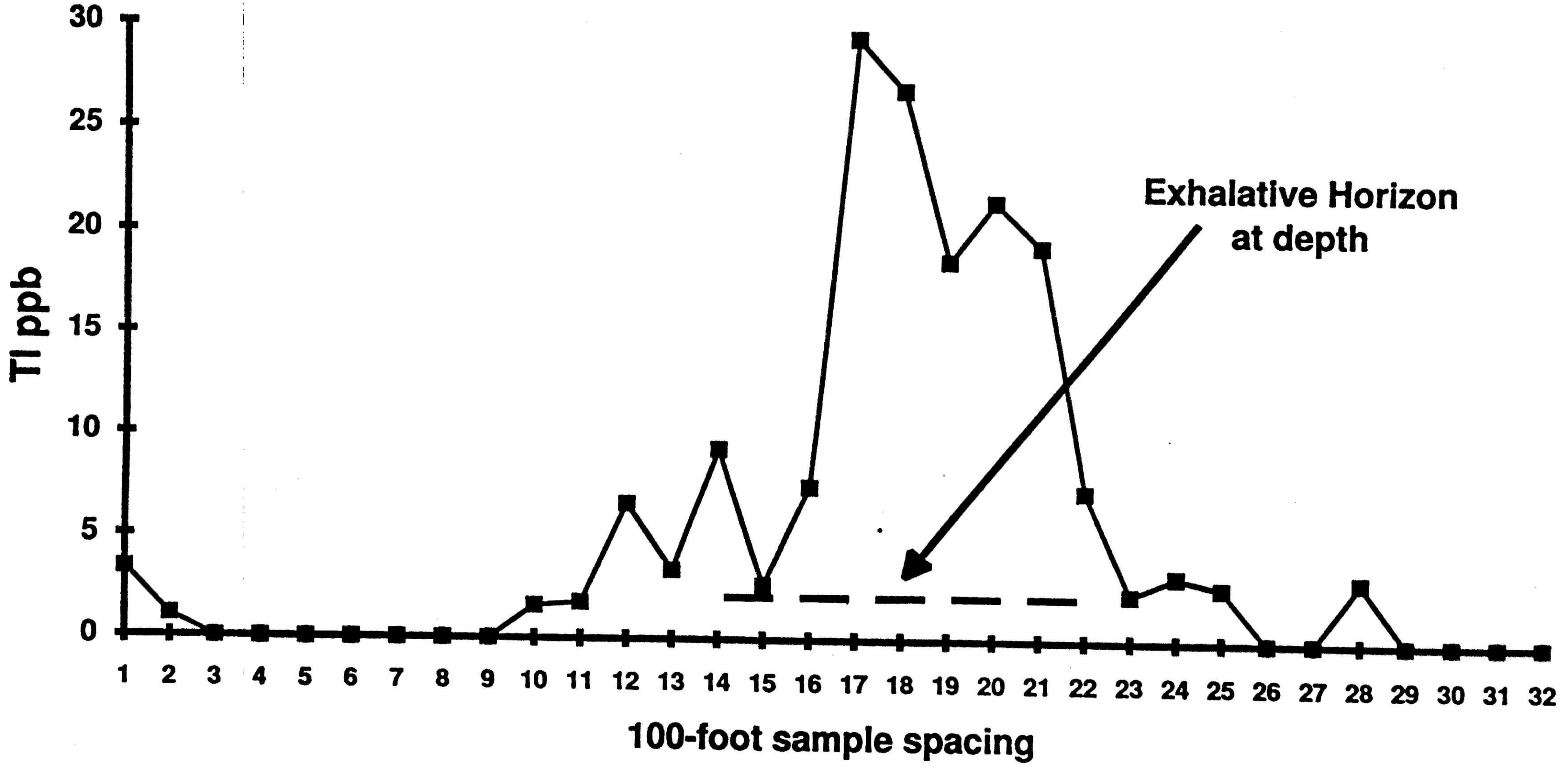
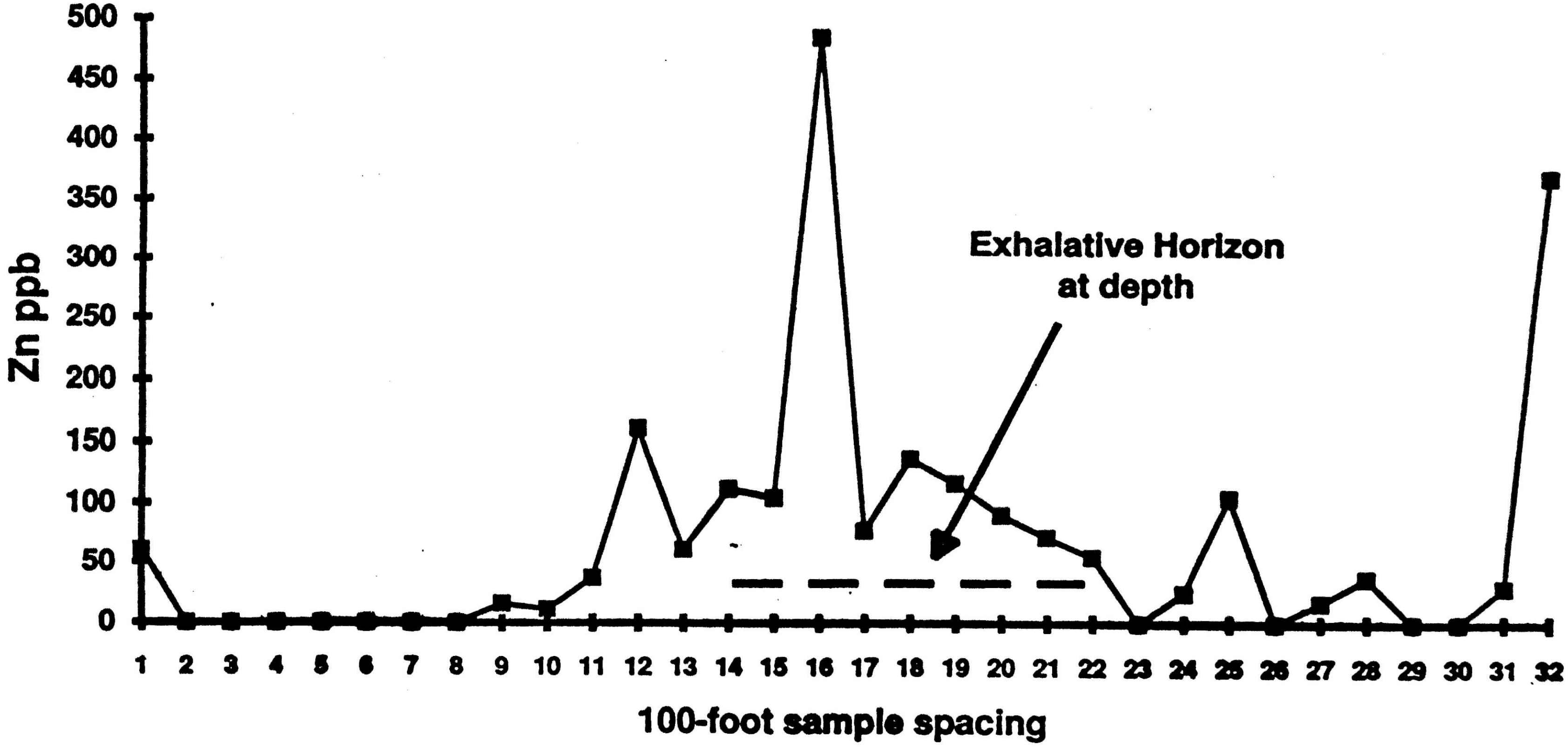
Enzyme Leach Test
20 Meters Alluvial Cover with Permafrost



Enzyme Leach Test
20 Meters Alluvial Cover with Permafrost



Brewery Creek, Yukon (Loki Gold)

- Biogeochemistry and Enzyme Leach (SM)

-discontinuous permafrost and loess cover

Dr Colin Dunn, Robert Shives and Bruce Ballantyne (GSC)
Viceroy International Exploration Inc
GSC Open File Report

Conclusions: Brewery Creek

- "the structural preparation of the ground and subsequent ore solution transport in and through fault zones appears to confine apical and oxidation halo anomalies so that they directly reflect the underlying mineralization"
- "the thickness of the loess cover does not appear to obliterate the enzyme leach anomalies but the concentration levels of As and Sb may be subdued"

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Enzyme Leach (SM) Discovery Detachment Au Deposit-Mexico

- Everything was tried on this deposit conventional geochemistry, geophysics and drilling
- As a last resort, Enzyme Leach (SM) was tried
- Three anomalies were drilled and three gold deposits were discovered below the 3rd detachment sheet 200 m below surface

- This successful Enzyme Leach (SM) survey played a key role in the discovery of these deposits

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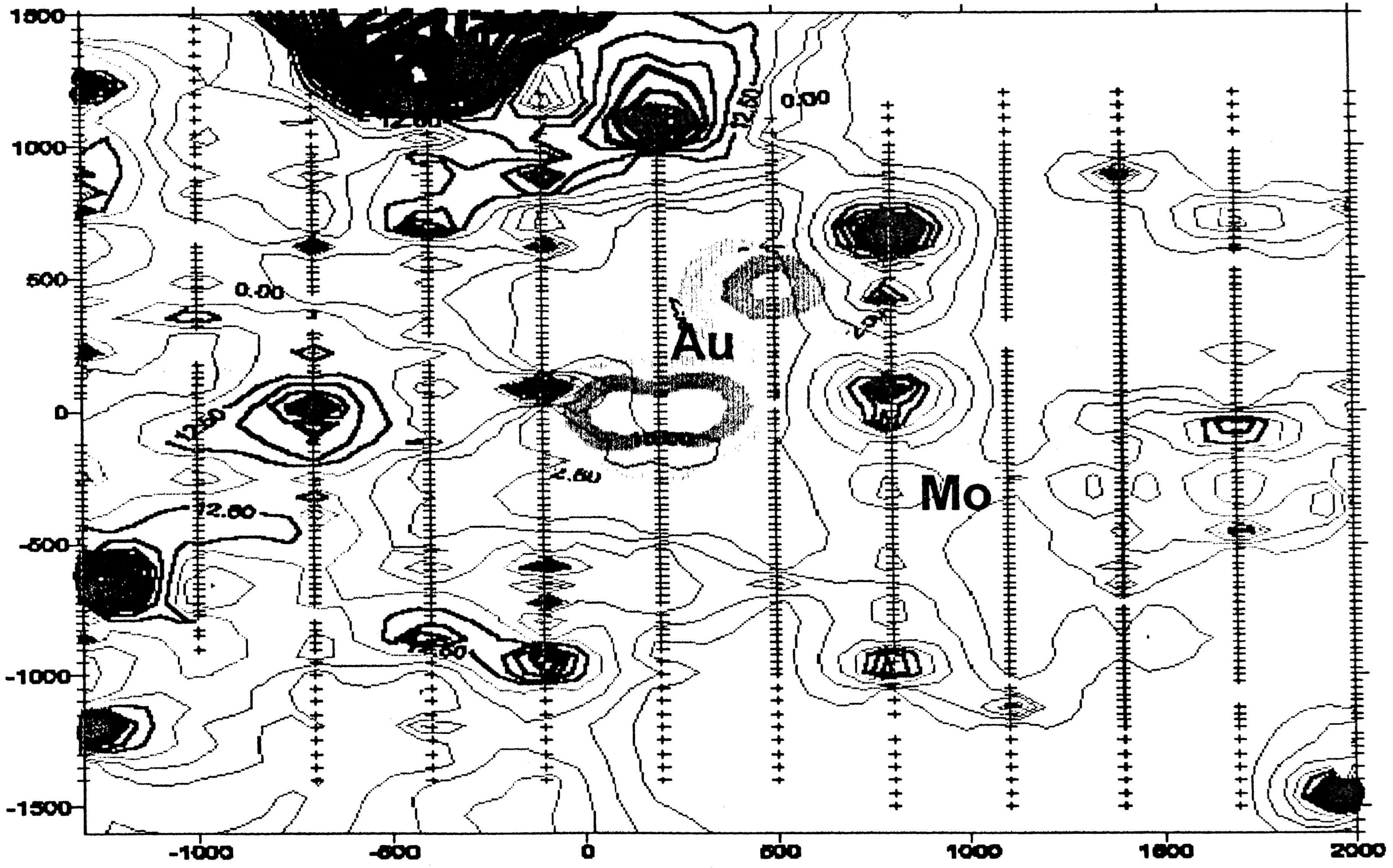
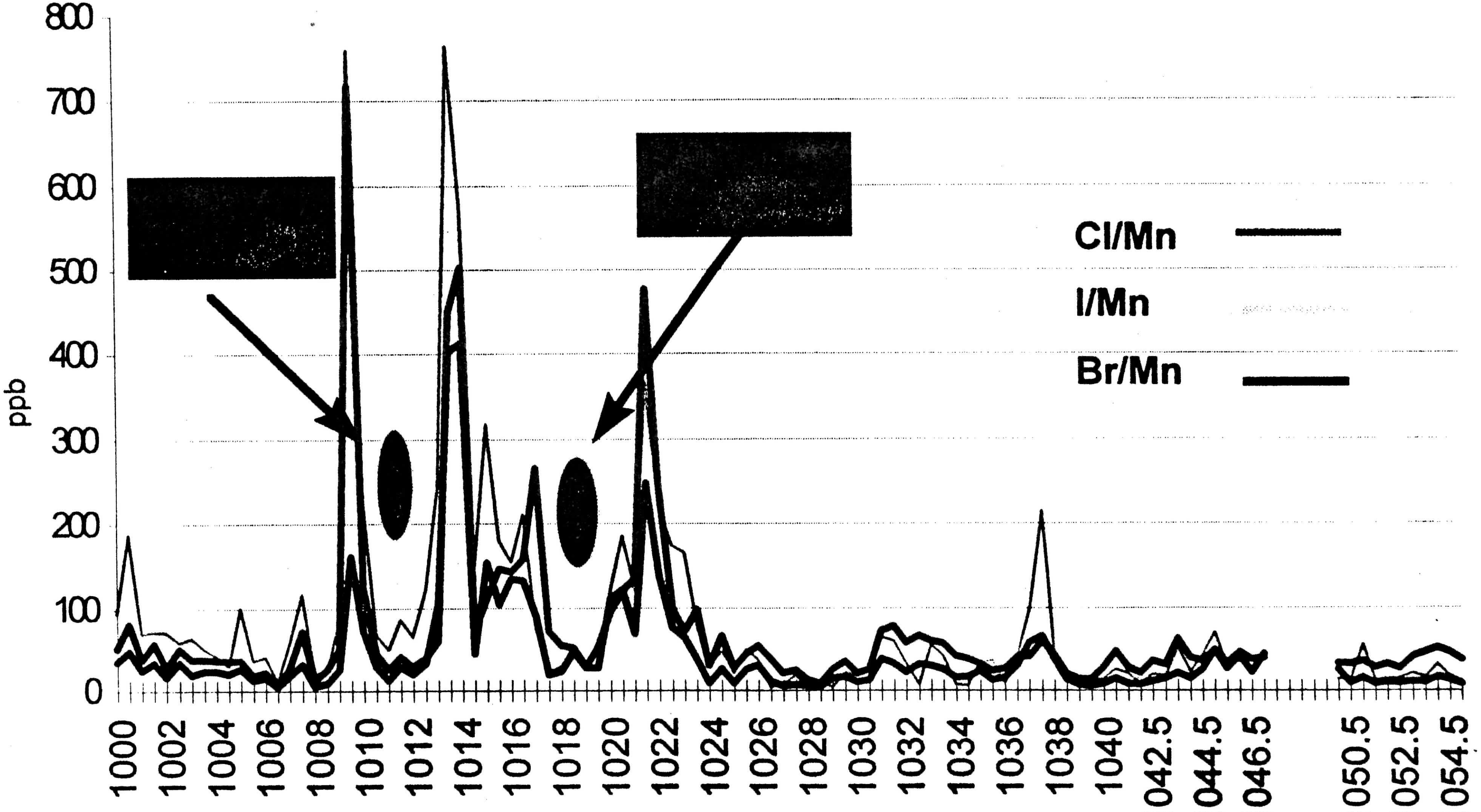
Combination Anomaly Mexico
Au and Mo



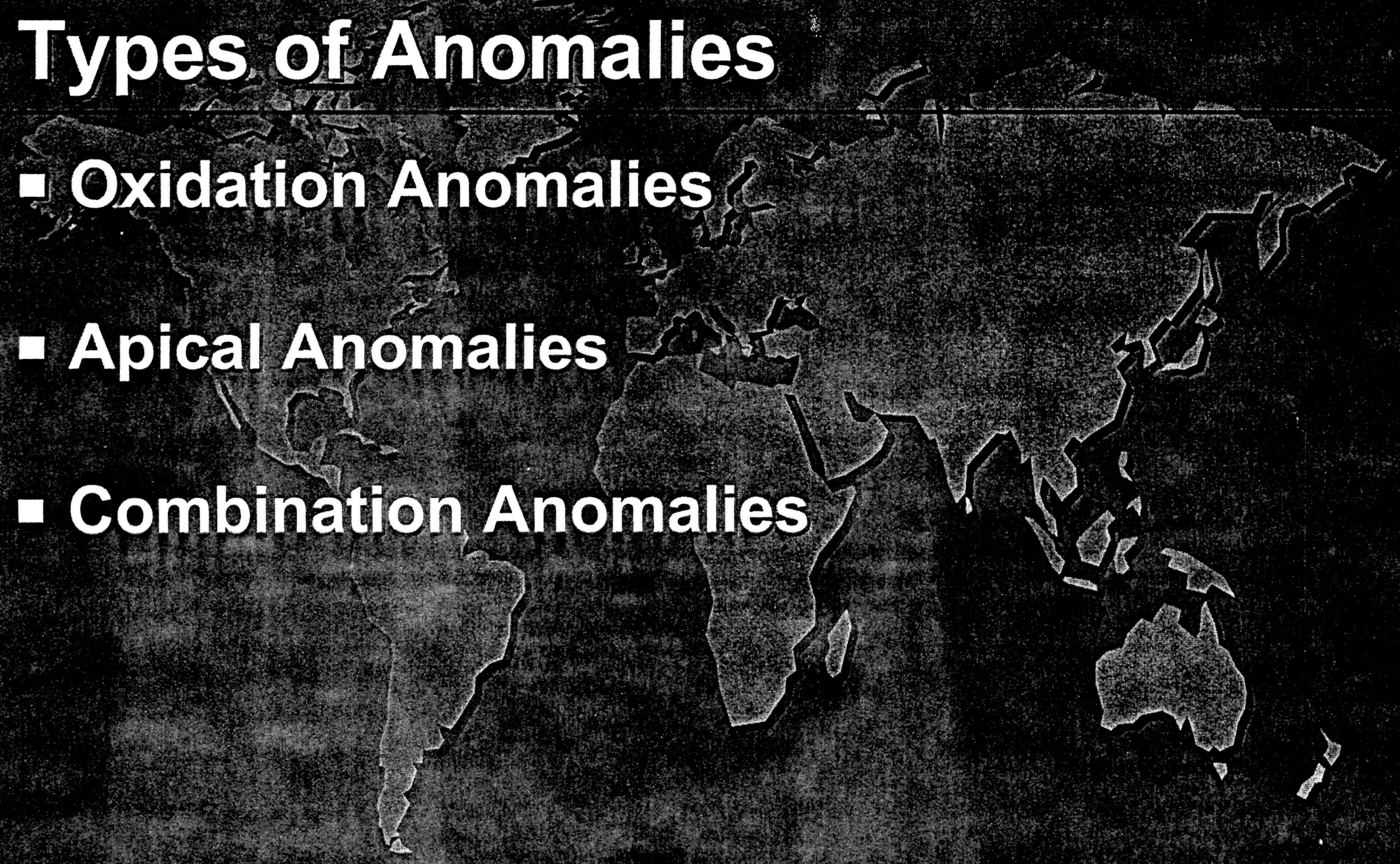
Central Tennessee MVT Deposit
Line 1000 Cl/Mn, I/Mn, Br/Mn



Assean Lake-NE Manitoba

- Manitoba Open File Report OF98-3 by Mark Fedikow and Dan Ziehlke
- mineralized zone 12 m thick with higher grade zones of 0.2-0.8 m of 7.1% Zn, 2.2% Pb, 715 g/t Ag
- capped with 11 m of wet peat, lacustrine clay and 25 m of non mineralized bedrock
- 50 m sample stations

Types of Anomalies



- Oxidation Anomalies
- Apical Anomalies
- Combination Anomalies

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Enzyme Leach $^{(SM)}$ Instrumentation

Halogens	Cl	Br	I									
Oxidation Suite	As	Mo	Sb	Re	Se	Te	V	Th	U			
Metals	Cu	Pb	Zn	Co	Ni	Cd	Ge	Bi	Ga	In	Hg	Tl
Precious Metals	Au	Ag	Pt	Pd	Os	Ru						
Rare Earth Elements	La	Ce	Pr	Nd	Sm	Eu	Gd	Yb	Lu			
High Field Strength	Zr	Yt	Nb	Hf	Ta	Ti						
Lithophile Elements	Ba	Cs	Rb	Sr	Sc	Mg	Li	Be				

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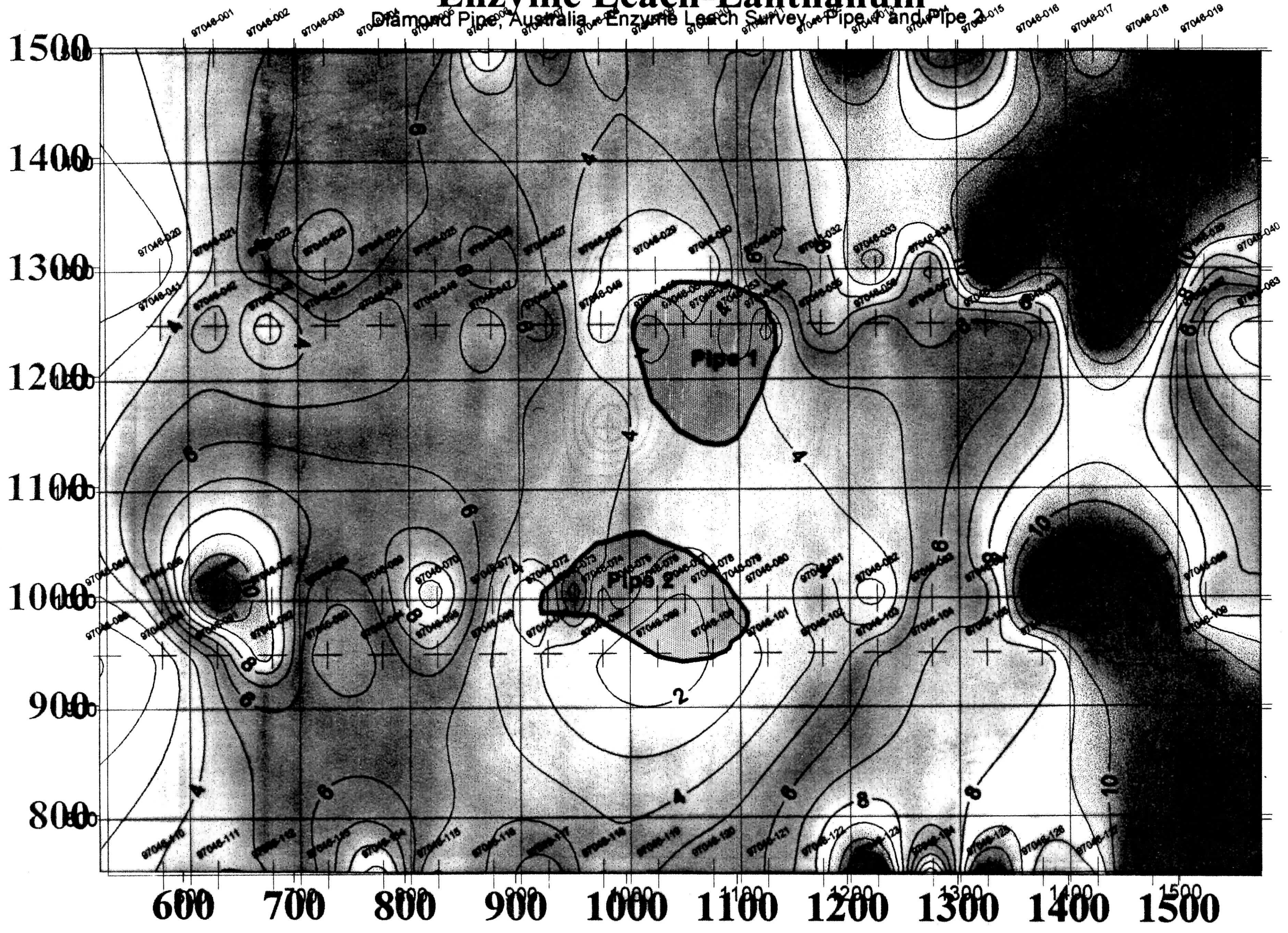
Enzyme Leach-Lanthanum

Diamond Pipe, Australia - Enzyme Leach Survey - Pipe 1 and Pipe 2



Enzyme Actlabs LLC

Camp Cooley Gas Field - Enzyme Leach Data

Element Group: Base Metals **Element: Lead**

Drawn by: Greg Hill Date: May 7, 1998