The Formation of Surficial Geochemical Patterns Over Buried Epithermal Gold Deposits in Desert Environments: Results of a Test of Partial Extraction Techniques

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ABSTRACT

A challenge for the geochemist is to develop and test transport theories and near surface sampling techniques for use in areas overlain by cover of exotic origin, i.e., where the surficial cover is not in any way related to the underlying bedrock.

Selective extraction methods that dissolve certain minerals or attack specific binding sites in soil suppose that some form of upward migration of ions must be taking place. Chemical components related to mineralization must travel from the bedrock-overburden interface to the surface, where they are immobilized, or change the surface chemistry in some detectable fashion. Upward migration is likely caused by a combination of diffusion down a concentration gradient, capillary action or "wicking" from the water table to the dry surface, osmotic action carrying ionic species, vegetation roots carrying elements to the surface portions of the plant, then back to the soil, or electrical fields transporting ions through the soil by cation exchange.

A geochemical orientation survey over two buried epithermal gold deposits at Marigold, Nevada was completed during 1994–95 in an attempt to determine the effectiveness of various analytical extractions, and develop a theory to explain observed geochemical responses. The 5 North deposit is covered by 25–40 m of alluvial fill, and the 8 North deposit is covered by about 100 m of fill. Soil gas, CHIM, vegetation, lag, caliche, and soil samples were included in the survey. The soil samples were subjected to a variety of chemical attacks and analyses. This report will present some of the results from the soil samples and propose a theory for the formation of surface geochemical responses.

The pH of the soil in the Marigold area was extremely alkaline, but still produced nearly a 100-fold difference in hydrogen ion concentration over the deposits. The alkaline condition suggests that iron and manganese should be stable, but that calcium may move in response to a shift in soil pH conditions. Aqua regia soluble calcium, hydroxylamine hydrochloride soluble calcium and strontium, sodium acetate soluble calcium and strontium and enzyme leach soluble strontium produced clear double-peak responses to mineralization regardless of overburden thickness. In fact, the type of analytical attack used did not really affect results. Low detection limit gold in soil was significantly correlated with calcium and strontium.

The proposed geochemical model suggests that the release of H^+ during the oxidation of buried sulphide mineralization may migrate directly to the surface, or may react with surrounding carbonate, thus producing CO_2 which migrates to the surface. In either case, a disequilibrium in pH sensitive compounds or elements such as $CaCO_3$, $MgCO_3$, Fe and Mn will occur at the soil surface in places of accumulation of H^+ or CO_2. This disequilibrium will correct itself over time by the migration of these compounds or elements away from the stimuli toward the ambient pH condition. A precipitation of these pH sensitive components will occur at the positions where chemical stability is re-established—at the margin of the stimuli—thus producing double-peak patterns over the margins of the underlying mineralization. Co-precipitation of ambient ions in the soil will produce element patterns that may appear to have moved through the overburden column, but have not. Calcium and magnesium may be the controlling ions in alkaline soils such as are found in desert environments, whereas iron and manganese may control anomaly patterns in acid to neutral soil conditions found in temperate climates.

The use of calcium in closely spaced soil samples in alkaline environments and selected element ratios, together with low detection limit gold, arsenic and antimony, is recommended as an exploration method for buried or blind mineral deposits.

INTRODUCTION

Mineral exploration is extending into geologically prospective areas which are overlain by surficial cover. Geochemical methods have been developed for use where this cover has been locally dislocated from its source, such as down-ice dispersion in areas of glacial till veneer. A far more challenging problem for the geochemist is to develop and test transport theories and near surface sampling techniques for use in areas overlain by cover of exotic origin, i.e., where the surficial cover is not in any way related to the underlying bedrock.

The past ten year period has seen the introduction of several geochemical techniques that may detect mineralization through exotic cover. The U.S. Geological Survey (USGS) and others have developed instrumentation to detect hydrocarbon, sulphur gases, CO_2 and O_2 in soil which could be related to underlying mineralization (McCarthy et al., 1986; Lovell et al., 1983). These soil gas methods have been used with success by the oil exploration industry for some time, but the relationship of soil gas components to sulphide or precious metal deposits has not been widely accepted by mineral explorationists.

The use of chemical reagents or procedures that selectively dissolve certain minerals or attack specific ion binding sites in soil has been used for more than 20 years to enhance the geochemical response from mineralization (Bradshaw et al., 1974; Chao, 1984). These techniques invariably attempt to separate ionic transportation components from the *total* geochemical noise. Recent applications of this simple concept include a physical collection of the ionic component with an electric field (CHIM) (Shmukin, 1985; Leinz and Hoover, 1993), the use of chemical extractions for various soil absorption sites (enzyme leach for MnO, hydroxylamine hydrochloride for Fe_xO_y, acetic acid for carbonates) (Clark, 1992; Hall et al., 1996; Smee, 1983) and the use of vegetation as an overall natural ion collector (Brooks et al., 1995).

All of these selective extraction methods suppose that some form of upward migration of ions must be taking place. Chemical components related to mineralization must travel from the bedrock-overburden interface to the surface, where they are immobilized or change the surface chemistry in some detectable fashion. Upward migration has been suggested to be caused by diffusion down a concentration gradient (Smee, 1983), capillary action or *wicking* from the water table to the dry surface, osmotic action carrying ionic species (Gray and Lintern, 1994), vegetation roots carrying elements to the surface portions of the plant, then back to the soil, or electrical fields transporting ions through the soil by cation exchange (Govett, 1972; Bolviken and Logn, 1975). Most likely, a combination of mechanisms occur, depending upon overburden type and depth, and upon the style of mineralization.

The search for the magic bullet to solve all exploration problems must be based on some solid theoretical and observational foundations. To date, no study has been published which addresses these geochemical methods or theories in a comprehensive fashion under controlled conditions. There are no data that compare methods directly and that recommend field and laboratory techniques. Finally, there are no studies that show data to support a particular form of transport through the overburden. This is especially surprising considering the amount of exploration funds that have been allotted to methods such as CHIM or the advertised selective extraction techniques. The use of these unsubstantiated methods by otherwise conservative companies and explorationists confirms the increasing pressure to find new deposits in difficult environments. It also highlights the sparsity of basic applied geochemical research in universities and governments, particularly in North America.

An orientation program over two buried Au deposits in Nevada, was undertaken by the author in 1994 to begin to evaluate various geochemical sampling and analytical techniques under controlled and comparative conditions. The orientation survey consisted of soil, vegetation and soil gas sampling as well as self potential (SP) geophysical and a CHIM survey. The soil samples comprised mineral horizon, pedogenic carbonate, and lag, which were analyzed using various extractions. The CHIM, SP and soil gas surveys were undertaken by members of the USGS. This research was funded by a number of mineral exploration companies which had a 12-month proprietary use of the resulting information.

This report presents some of the data concerning the mineral soil sampling and analytical extractions. Space restrictions here permit only a summary of the observed results. A more complete reporting will be published in the near future, however a working hypothesis is given which attempts to explain the observed patterns.

SELECTION OF THE STUDY AREA

Many of the world's active Au exploration areas occur in arid to semiarid environments. One of the most prolific Au producing areas is the Basin and Range geological province in the western United States, and Nevada in particular, which contains volcanic- and sediment-hosted epithermal Au bodies of multimillion ounce size. Most of the deposits found to date in Nevada have had some surficial indication of either hydrothermal alteration or Au mineralization directly. However, as the ranges become thoroughly explored, the focus is shifting toward the alluvial-filled basins. A similar situation exists in Australia and the Middle East. Some type of reliable geochemical tool is needed to augment geological extrapolation and geophysical techniques in these covered areas. The search for an orientation target was therefore restricted to the alluvial-filled basins of Nevada.

Ideally, an orientation area for this study had to possess most of the following characteristics: the geology must be reasonably well known; the mineralogy of the buried mineralization must include sulphides, Au of a nearly economic grade and Au-pathfinder elements such as As, Sb, Hg and Ba; the deposit must be at least partially oxidized; the pediment cover must comprise alluvial, fluvial or lacustrine material unrelated to the surrounding rocks; the depth of overburden must be between 15–120 m so as to form a valid but not impossible test; the present-day surface is undisturbed, or disturbance must be avoidable; the three-dimensional extent of the mineralization must be outlined by drilling.

The two buried deposits near the Marigold Mine, operated by the Marigold Mining Company in northern Nevada were eventually selected as the targets for this study.

MARIGOLD MINE AREA, GEOLOGICAL DESCRIPTION

The Marigold Mine area is located in Nevada, 20 km southeast of the town of Battle Mountain and 8 km south of the I-80 Valmy exit (Figure 1). The 8 North and 5 North deposits lie beneath alluvial cover north and west of the Marigold 8 South pit. These mineralized zones do not outcrop, and are defined entirely by drilling.

The geological description of the Marigold area is given in detail by Graney and McGibbon (1991) from which this summary is taken. Gold has been produced from the old Marigold Mine since the 1930s. A drill program was started by Cordex Exploration in 1986 on nearby mineralization, which led to the discovery of the 8 South, 8 North and 5 North mineral zones.

The Marigold deposits, which roughly line up in a north-south direction, are hosted by clastic rocks of the Valmy and Antler sequences (Figure 2). The Antler sequence, host to the 8 North and 5 North deposits, is composed of coarse conglomerates and sandstone which grade upward into limy mudstone, shales, siltstone and sandstones. Mineralization is controlled by north-south–trending basin and range faulting and northwest-striking zones of fracturing.

The 8 North mineralization extends to 300 m in a north-south direction and 170 m east-west. Gold occurs with abundant barite and is anomalous in As, Sb and Hg. The host clastic rocks are calcite-rich, with only minor silicification noticed in the drill cuttings. Overburden consisting of alluvial and fluvial outwash, and interlayered lacustrine clay, covers the 8 North deposit to a depth of 100 m.

The 5 North zone is covered by between 20 m and 50 m of alluvium and is hosted by debris flows and siltstones, with minor limestone encountered in a few drill holes. The geochemical signature of 5 North includes As, Sb and Hg with the Au, but baritization is minor. Iron-oxide staining is pronounced in the mineralized drill cuttings.

The deposits have been drilled off at 30 m centres. Surficial disturbance is minimal on the 5 North deposit, but consists of rutted tire tracks and drill fluid run off over portions of the 8 North deposit. Sample lines were positioned to avoid this disturbance. Both deposits are oxidized where drilled.
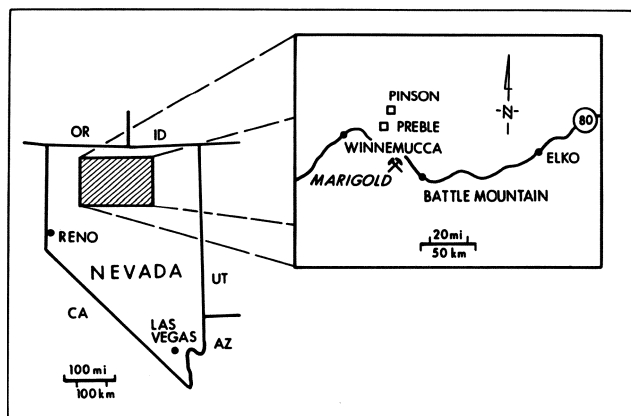

Figure 2: *Marigold Mine area, property geology and Au deposits (from Graney and McGibbon, 1991).*

Sample lines were centred over the surface projection of the mineralization with 11 sample stations spaced at 50-foot centres over mineralization, 100-foot centres for 300 feet on either side of the 50-foot centres, and then 200-foot centres for an additional 400 feet on each side, producing a total of 21 stations per line. The lines were tied into drill hole locations, then tight chained between stations. A 1-inch × 2-inch picket with sample location marked in pencil and a scribed aluminum tag was placed at each station. Hopefully these lines will be semi-permanent and will form a long-term test site for new geochemical or geophysical techniques.

A pit was dug to a depth of approximately 60 cm at each sample site. A boulder layer was usually found below 50 cm, which prevented further hand-sampling. A distinct colour and texture change was noticed at about 40 cm depth at most sites which usually coincided with a positive reaction to 10% HCl. This layer was undoubtedly the top of a pedogenic carbonate and was the selected sample medium. A Hubco sand bag was filled with about 3 kg of material and allowed to air dry.

Figure 1: *Location map, Marigold Au deposits.*

SOIL SAMPLING METHOD

The drill plan and drill sections for the 5 North and 8 North deposits were examined in detail. Sample lines were chosen so as to overlie drill sections which showed subcropping mineralization of significant grade, and minimal surface disturbance. Two sample lines were positioned over each deposit: lines 1 and 2 over 5 North, and lines 3 and 4 over 8 North. All sample spacings and distance measurements are in Imperial units, matching the mine grid and geological maps. The overburden is between 50–110 feet thick over the mineralization on line 1 and 100 feet on line 2. Line 3 is positioned near the north end of the 8 North deposit, where the mineralization subcrops beneath about 300 feet of overburden. Line 4 was also positioned over subcropping mineralization with 280–300 feet of cover. All lines over mineralization are 1900 feet in length.
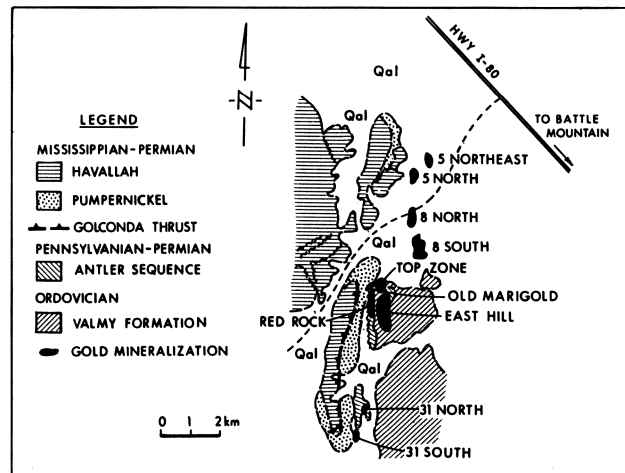
QUALITY CONTROL AND ANALYTICAL METHODS

A quality control program designed to estimate sampling and analytical errors and determine possible biases or shifts in background during analysis was implemented at the start of the sampling program. Twelve sites were selected at random at which duplicate samples were taken in the field. These duplicates, together with the regular samples, generated a total of 96 samples for the survey. Prior to field work, the samples were numbered sequentially from 1 to 96, then randomized and placed with the line and station. Once a sample was taken, the true position of the sample could not be determined without the sampling key.

Samples were sorted in numerical order before being prepared and sent for analysis. The laboratories analyzed the samples in numerical order. Upon receiving the analytical results, the data were first plotted in numerical order to determine baseline shifts, analytical batch errors, or biases in analysis. Duplicates were then removed from the analytical

stream, and bias and precision plots made using the method of Thompson and Howarth (1978). Finally, the data was sorted into line and station sequence prior to plotting profiles.

Analysis of the mineral soils was performed at a number of commercial laboratories, each selected for their expertise or equipment. All mineral soils were hand-screened to –80 mesh and split into the necessary number of bags using a riffle splitter. The excess sample pulp was placed into storage so that new analytical techniques proposed in the years to come can be tested under the same controlled conditions.

The analysis of water-soluble anions in "B" soils followed the method developed by the USGS (R. Leinz, pers. comm., 1995) using a Dionex Anion Chromatograph. This analysis included F^-, Cl^-, NO_3^{2-}, SO_4^{2-}, Br^- and PO_4^{3-}. Chemex Laboratories of Vancouver donated the analysis to this study. Bondar Clegg Laboratories of Vancouver analyzed the mineral soils for pH and conductivity using a high solids pH probe and conductivity cell. One gram of soil was slurried with 5 ml of distilled, deionized water for a constant time. Separate samples were used for pH and conductivity. Bondar Clegg donated these analyses. The enzyme leach analytical technique was provided by ACTLABS of Ancaster, Ontario at half the normal cost. Part of this orientation was to ascertain the effectiveness and specificity of the enzyme leach technique, and therefore the elements Fe and B were added to the normal element readout produced by ACTLABS. Iron, which is not normally reported by ACTLABS because of an apparent inter-element interference, was necessary to determine if the enzyme leach was indeed specific to amorphous Mn. Boron was added to ascertain if the borosilicate test tubes used in the analysis were exchanging cations with the solution or if the borate anion was mobile under the arid conditions found in Nevada. XRAL Laboratories of Toronto was responsible for providing As and Sb using hydride generation; Au analysis, with 1 ppb detection limit; plus the aqua regia (AR) soluble elements, the acetic acid (HOAc) carbonate specific selective extraction elements and the Fe/Mn specific hydroxylamine hydrochloride (HYDHCl) extraction, following the methods of Hall *et al.* (1996). XRAL donated $5,000 toward the cost of these analyses. Unfortunately, few elements were analyzed by XRAL using the ICP-MS analyzer because of inter-element interferences created by a high dissolved solids content in many of the leach solutions. Consequently, many elements do not have sufficiently low detection limits to be useful. This shortcoming will hopefully be resolved in the near future.

Table 1: *Anion correlation table* [1]

	COND	ECL	EBR	EI	DCL	DNO3	DSO4
ECL	0.67						
EBR	0.75	0.82					
EI	0.41	0.35	0.53				
DCL	0.60	0.95	0.76	0.31			
DNO3	0.36	0.39	0.44	0.38	0.43		
DSO4	0.75	0.71	0.81	0.52	0.70	0.50	
DP2O5	0.41	0.13	0.26	0.23	0.12	0.37	0.40

1.   E= Enzyme Leach; D = Dionex Anions; COND = Soil Conductivity

RESULTS

A geochemical exploration technique must be cost-effective and simple to use, produce reproducible results and form predictable and interpretable patterns. The first step in determining the validity of a geochemical method is to measure the precision of the sampling and analytical system, and the validity of the analysis. Should the precision be poor, i.e., the patterns not be reproducible, the technique is of little use to the explorationist.

Each element of each technique was initially examined using the Quality Control (QC) data. If the data were free of analytical baseline shifts and bias and the precision shown by the blind field duplicates was acceptable, the element was included in the interpretation.

Water extractable and enzyme leach anions

The use of ion chromatography for anions in soil as an exploration method is in its infancy, even though the method has been available for nearly 20 years (Smee *et al.*, 1978). Consequently, the technique is still being developed and is not as precise as it could be. The Dionex technique reported water-soluble F^-, Cl^-, NO_3^{-2}, SO_4^{-2}, Br^- and $P_2O_5^{-3}$.

A correlation calculation incorporating soil conductivity and both analytical techniques is shown in Table 1. The only directly comparable element, Cl^-, is almost perfectly correlated between the two methods; however, the enzyme leach Cl^- and Br^- are also highly correlated with Dionex SO_4^{-2}. This suggests that samples may be exhibiting an accumulation of all anions in general, rather than one specific element or compound. This is confirmed by the high correlation between soil conductivity and most of the anions. It would appear that a simple soil conductivity measurement is all that is required to track soil anions, regardless of the analytical method used. This conductivity measurement could easily be adapted to a field technique.

For the sake of brevity, no profiles will be shown here, for there was no single anion, by either of the analytical methods, that showed a consistent or interpretable response over mineralization.

Soil pH and conductivity

The measurement of pH is perhaps the most important variable a geochemist can use when attempting to understand the processes that control the distribution of other cations in soil. H^+ is extremely reactive and can mobilize other cations, such as Fe, Mn, Ca and Mg, which are sensitive to changes in pH. It is known that both the 5 North and 8 North bodies are oxidized, and would have released H^+ to the surrounding environment during the breakdown of sulphides. H^+ diffuses through cover up to 10,000 times faster than many other cations (Farr *et al.*, 1970). It is therefore prudent to measure H^+ concentration in each sample.

The measurement of soil conductivity gives an indirect indication of the concentration of soluble anions and cations. A spatial relationship between H^+ and conductivity may occur where ions have been mobilized and reprecipitated in response to a change in pH (Govett and Chork, 1977; Smee, 1983).

The pH range in the B horizon soils was 7.7 to 9.6, almost a 100-fold difference in H^+ concentration. This large spread is surprising in that the surface soils appear to be highly alkaline and should be well buffered. The only explanation for this wide range of H^+ concentration on a

Table 2: *AR, HOAC, and HYDHCL Leach correlations*[1]

	AU	AS	SB	H+	COND	CA1	CA2	CA3	FE1	FE3	MN1	MN3	SR1	SR2	SR3	RB1	RB2	RB3	BA1	BA2
AS	0.61																			
SB	0.62	0.63																		
H+	0.03	0.04	0.00																	
COND	0.13	0.29	0.26	-0.47																
CA1	0.55	0.32	0.43	-0.15	0.37															
CA2	0.54	0.32	0.44	-0.16	0.38	1.00														
CA3	0.56	0.33	0.44	-0.15	0.36	1.00	1.00													
FE1	0.43	0.37	0.64	0.14	0.00	0.25	0.26	0.25												
FE3	0.18	0.25	0.25	0.23	-0.25	-0.37	-0.38	-0.36	0.35											
MN1	0.05	0.09	0.04	0.23	-0.21	-0.05	-0.09	-0.05	0.05	0.36										
MN3	0.05	0.14	0.03	0.19	-0.16	-0.07	-0.10	-0.06	-0.08	0.37	0.97									
SR1	0.57	0.30	0.45	-0.12	0.35	0.94	0.95	0.94	0.38	-0.28	-0.15	-0.19								
SR2	0.52	0.32	0.46	-0.15	0.41	0.95	0.96	0.95	0.36	-0.32	-0.18	-0.21	0.98							
SR3	0.56	0.34	0.46	-0.13	0.37	0.95	0.96	0.95	0.37	-0.28	-0.15	-0.17	0.99	0.99						
RB1	-0.13	-0.21	0.06	0.08	-0.17	-0.13	-0.12	-0.14	0.35	0.10	-0.24	-0.34	0.00	-0.02	-0.02					
RB2	-0.03	-0.17	-0.09	0.15	-0.28	-0.02	-0.02	-0.03	0.12	-0.20	0.03	-0.03	-0.02	-0.02	-0.02	0.14				
RB3	-0.33	-0.26	-0.23	0.16	-0.50	-0.59	-0.59	-0.58	0.04	0.50	0.34	0.30	-0.59	-0.62	-0.59	0.20	0.12			
BA1	0.66	0.72	0.58	0.02	0.27	0.51	0.51	0.52	0.38	0.23	0.22	0.25	0.52	0.53	0.55	-0.18	-0.17	-0.31		
BA2	0.52	0.64	0.51	-0.05	0.34	0.46	0.47	0.47	0.38	0.14	0.11	0.14	0.48	0.52	0.52	-0.16	-0.15	-0.36	0.95	
BA3	0.59	0.68	0.52	0.00	0.26	0.45	0.45	0.47	0.35	0.24	0.25	0.29	0.46	0.48	0.50	-0.21	-0.15	-0.28	0.98	0.97

1. 1=Aqua Regia; 2=Sodium Acetate/Acetic Acid; 3= Hydroxylamine Hydrochloride

featureless gravel-covered pediment is an introduction of hydrogen from the substrate below the soil horizon. Although the H$^+$ concentration range is large, no clear interpretable pattern exists on all lines. Similarly, the soil conductivity is not a helpful tool by itself, although clear responses above mineralization occur on line 3. These profiles are not shown here because of this lack of a predictable and interpretable pattern on each line.

Aqua regia, acetic acid/sodium acetate, and hydroxylamine hydrochloride extractions

XRAL of Toronto undertook the analysis of mineral soils for Au and its pathfinder elements, and three selective leaches using a combination of AAS, ICP and ICP-MS instruments. The leaches were aqua regia (AR), acetic acid/sodium acetate (NaOAc) for carbonate-bound elements and hydroxylamine hydrochloride (HYDHCl) for Fe and Mn-bound elements (Hall, 1996; Hall, pers. comm., 1995). These are listed as attack 1, 2 and 3, respectively, on the statistical printouts. Space does not permit inclusion of all analytical results; however, these can be provided to interested parties by contacting the author.

Correlation coefficients between elements that had sufficient analytical detection limits for the majority of sample sites were calculated and are shown in Table 2. Gold is significantly correlated with As, Sb, Hg and Ba, which seems to indicate that the mineralizing elements are responding together in the mineral soils. Gold is also significantly correlated with Ca and Sr in all extractions, as is AR Ba. These correlations are strong evidence that Ca is playing a controlling role in the distribution of these elements in the near surface environment. A negative correlation exists between all types of extractions of Ca, and specifically the HYDHCl Rb. The HYDHCl Rb is, in turn, positively correlated with HYDHCl Fe. An argument can therefore be made that a selective extraction for Fe and Mn
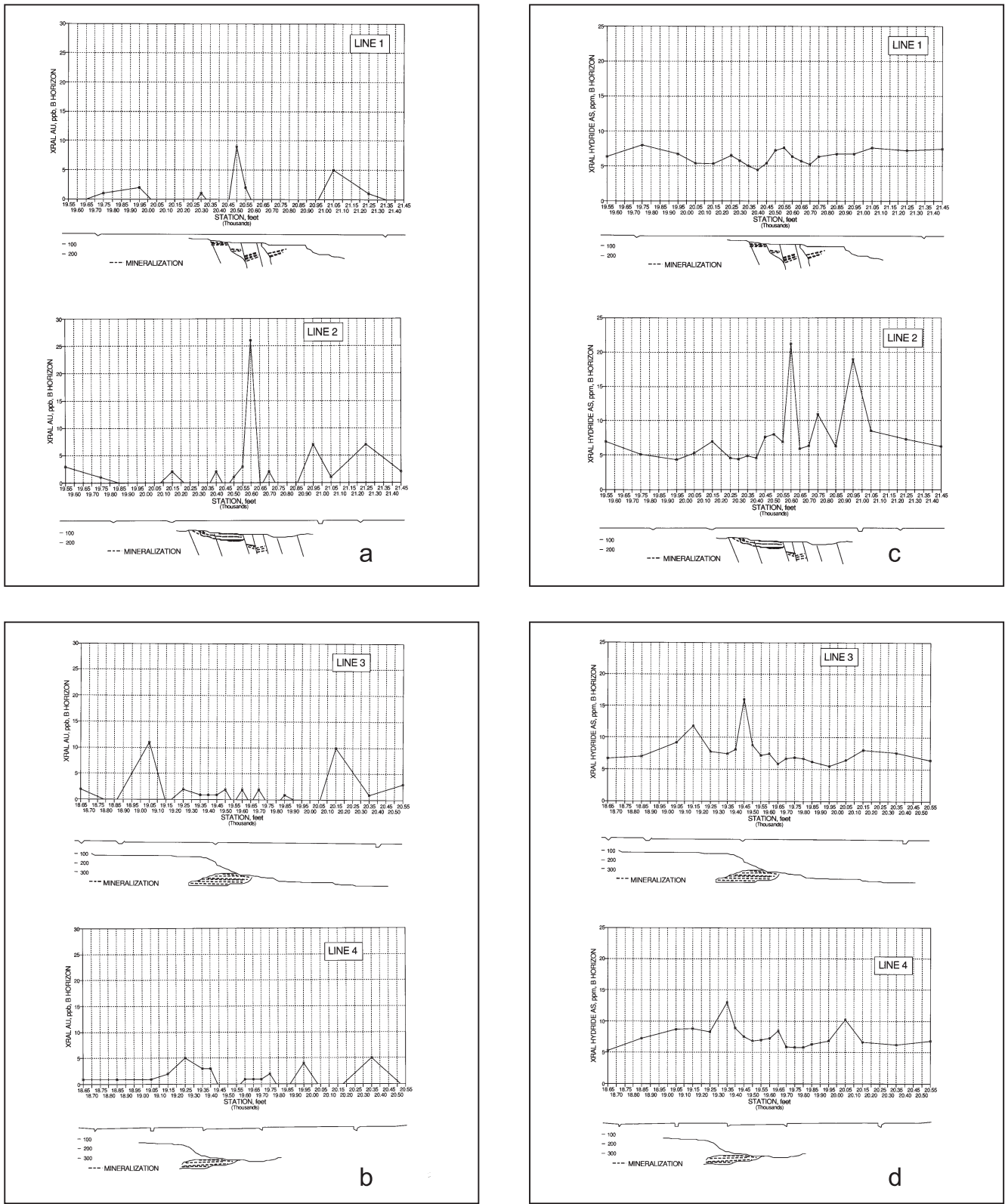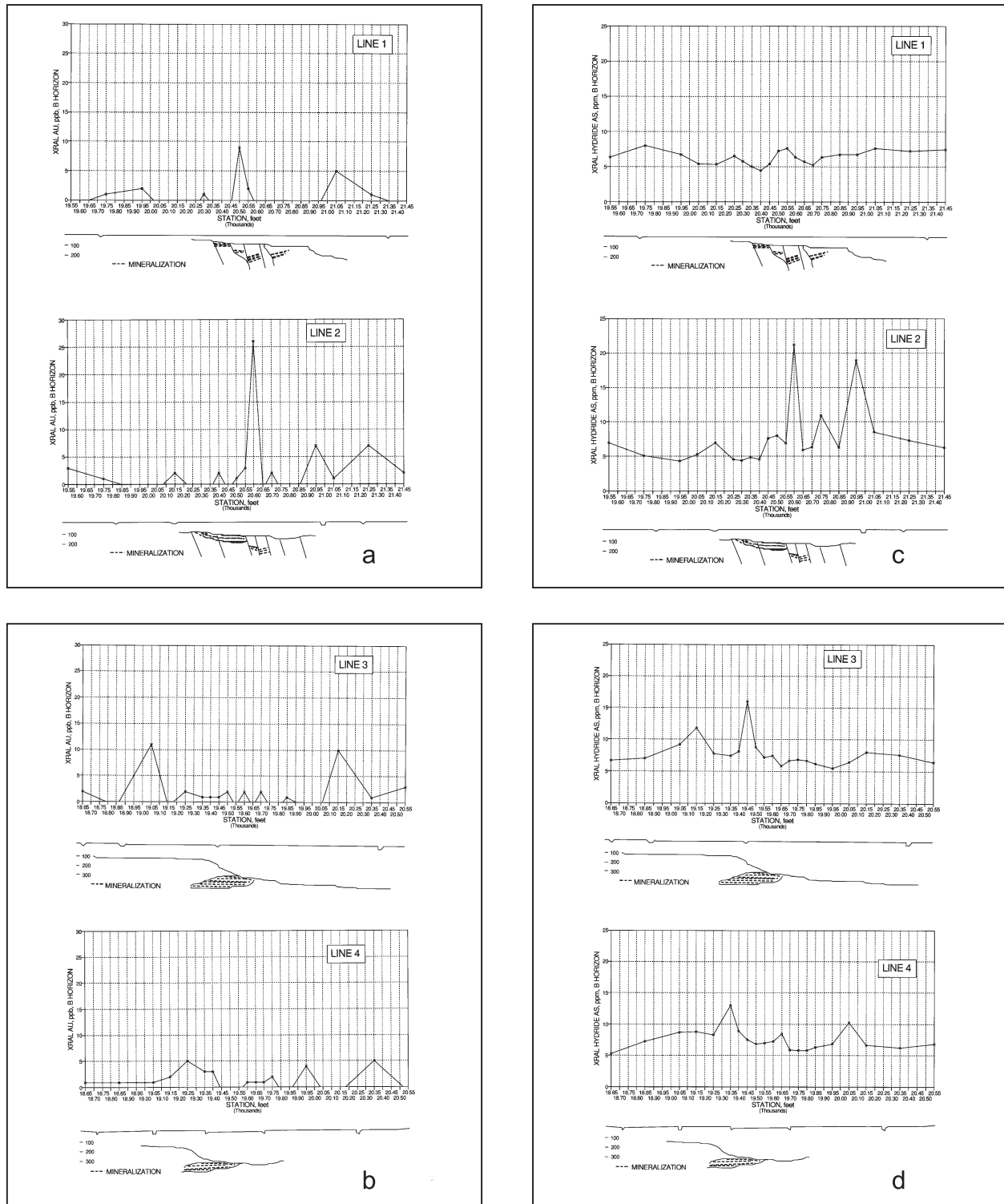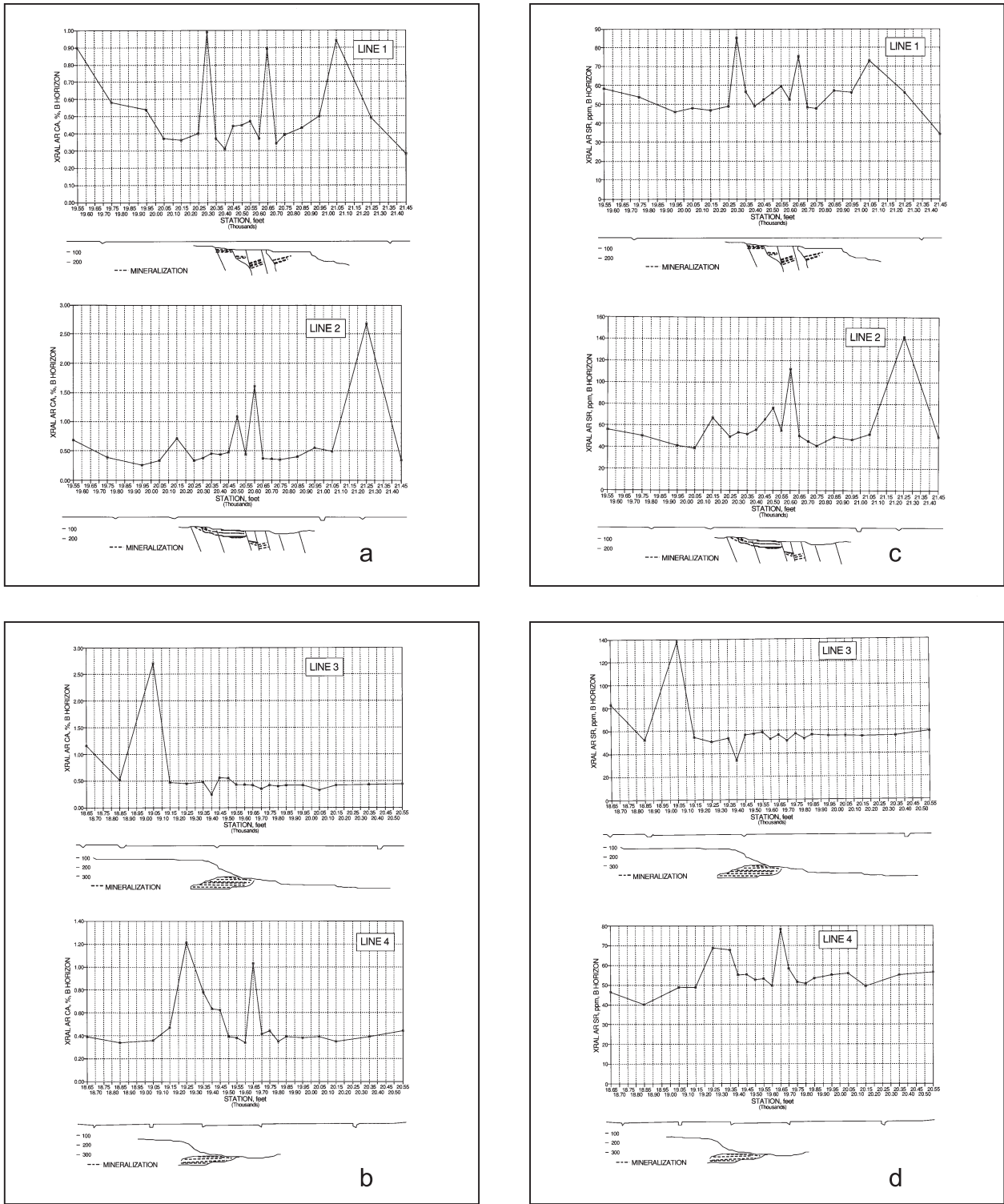
Figure 3: *Au and As profiles from mineral soils over lines 1 to 4: (a) 5 North deposit Au; (b) 8 North deposit Au; (c) 5 North deposit As; (d) 8 North deposit As.*
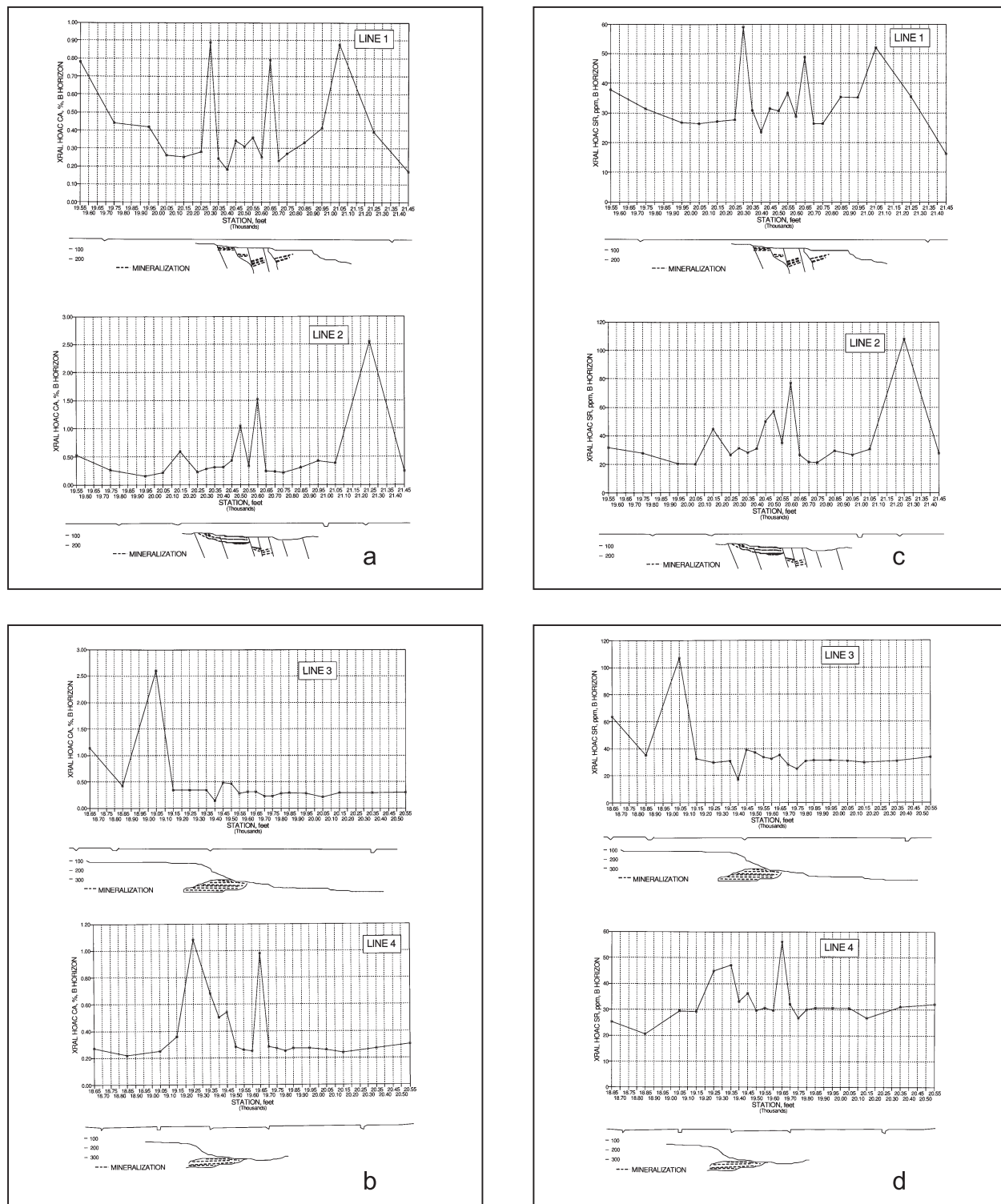
Figure 4: *Aqua regia (AR) soluble Ca and Sr from mineral soils over lines 1 to 4: (**a**) 5 North deposit Ca; (**b**) 8 North deposit Ca; (**c**) 5 North deposit Sr; (**d**) 8 North deposit Sr.*

Figure 5:   *Sodium acetate/acetic acid (HOAc) soluble Ca and Sr from mineral soils over lines 1 to 4: (**a**) 5 North deposit Ca; (**b**) 8 North deposit Ca; (**c**) 5 North deposit Sr; (**d**) 8 North deposit Sr.*

Figure 6: *Hydroxylamine hydrochloride (HYDHCl) soluble Sr, and HOAc acid soluble Ca/AR soluble Ca ratio from mineral soils over lines 1 to 4: (a) 5 North deposit HYDHCl Sr; (b) 8 North deposit HYDHCl Sr; (c) 5 North deposit HOAc/AR Ca; (d) 8 North deposit HOAc/AR calcium. This ratio shows residual Ca responses which indicate a difference in calcium solubility, thus a calcium source over the mineral deposits.*

in arid or alkaline environments could actually suppress responses from Au mineralization, and selectively eliminate the anomalous areas.

Gold and As over the 5 North deposit (Figures 3**a** and **c**) show weak positive responses over mineralization, with Au on line 1 reaching a peak value of 8 ppb, and on line 2, 26 ppb. Arsenic reaches 21 ppm on line 2, but does not respond to mineralization on line 1. Lines 3 and 4 over the 8 North deposit do not show any interpretable responses in the mineralizing elements (Figures 3**b** and **d**).

The elements that produce a consistent, interpretable response to mineralization over both deposits, regardless of chemical extraction used, are Ca and its substitute Sr. AR soluble Ca on all but line 3 (Figures 4**a** and **b**) shows a clear double-peak response over or on the margins of mineralization. Similar patterns are produced by Sr (Figures 4**c** and **d**). HOAc Ca and Sr (Figures 5**a** to **d**) produce identical patterns, as does HYDHCl Sr (Figures 6**a** and **b**). The ratios of the weak extraction HOAc Ca to AR Ca show positive residuals above the mineralization on all

lines, regardless of depth of burial, which indicates that extra Ca has been mobilized into these areas (Figures 6**c** and **d**). Both lines 1 and 2 exhibit a strong Ca response at the east end of the lines, where sample spacing was between 100 and 200 feet. Tighter sample spacing may indicate a valid anomaly exists to the east of the 5 North mineralization.

Enzyme leach

The use of a carbon-based solution to selectively leach soil of amorphous Mn-oxide and adsorbed elements has been widely used recently by a number of exploration organizations in their search for buried base and precious metal deposits. This weak extraction, known as *enzyme leach,* is claimed to be specific to amorphous Mn and to be self-limiting so that other compounds will not go into solution over time (Clark, 1992). These claims were to be tested in this study, as it is difficult to

Table 3: *Enzyme leach correlations, 5 North Deposit*

	H+	COND	CL	TI	V	MN	CO	NI	CU	ZN	AS	BR	RB	SR	ZR	MO	SB	BI	BA	PB	B
COND	-0.31																				
CL	-0.11	0.68																			
TI	0.22	-0.17	-0.18																		
V	0.37	0.08	-0.02	0.56																	
MN	0.54	-0.22	-0.06	0.09	0.42																
CO	0.44	0.01	0.00	0.62	0.81	0.70															
NI	0.36	0.14	0.04	0.73	0.83	0.48	0.91														
CU	0.17	0.41	0.15	0.74	0.71	0.14	0.71	0.85													
ZN	0.21	-0.20	-0.20	0.99	0.56	0.12	0.63	0.73	0.73												
AS	0.41	0.09	0.02	0.02	0.54	0.67	0.56	0.46	0.32	0.05											
BR	0.00	0.86	0.83	-0.03	0.25	0.02	0.25	0.34	0.50	-0.06	0.22										
RB	0.20	-0.24	-0.23	0.99	0.52	0.09	0.59	0.70	0.68	0.99	0.00	-0.10									
SR	0.06	0.21	0.26	-0.56	0.03	0.09	-0.16	-0.19	-0.26	-0.59	0.19	0.22	-0.58								
ZR	0.19	-0.16	-0.20	0.99	0.55	0.07	0.61	0.74	0.74	0.99	0.02	-0.03	0.99	-0.58							
MO	0.32	0.33	0.27	0.05	0.36	0.61	0.57	0.50	0.43	0.07	0.68	0.52	0.01	-0.06	0.05						
SB	0.09	0.07	-0.04	-0.07	0.54	0.22	0.36	0.26	0.14	-0.08	0.25	0.07	-0.08	0.30	-0.07	0.11					
I	0.36	0.40	0.26	-0.22	0.41	0.41	0.37	0.29	0.24	-0.22	0.69	0.49	-0.27	0.42	-0.22	0.60	0.36				
BA	0.10	0.42	0.26	0.31	0.75	0.20	0.59	0.66	0.69	0.29	0.34	0.53	0.25	0.19	0.30	0.32	0.52	0.41			
PB	0.26	-0.19	-0.20	0.99	0.57	0.16	0.65	0.75	0.75	0.99	0.09	-0.03	0.98	-0.58	0.98	0.11	-0.06	-0.18	0.32		
B	-0.19	0.59	0.23	-0.01	0.16	-0.18	0.05	0.17	0.34	-0.05	0.09	0.46	-0.03	0.09	0.01	0.19	0.19	0.26	0.29	-0.03	
FE	0.22	-0.19	-0.21	1.00	0.54	0.09	0.61	0.72	0.73	0.99	0.02	-0.05	0.99	-0.60	0.99	0.05	-0.09	-0.23	0.29	0.99	-0.02

understand how a chemical attack that produces weak hydrogen peroxide could dissolve Mn compounds and not Fe compounds.

The Fe concentration reported by enzyme leach ranges up to 105,000 ppb, or 105 ppm. This is 20 times higher in concentration than the highest Mn concentration reported. The enzyme leach technique can therefore be said to dissolve sesquioxides, with the overwhelming influence being Fe.

Inter-element correlations for the enzyme leach data were calculated (Tables 3 and 4) for each of the deposits prior to profile plotting. It is immediately apparent that Fe is controlling the concentration and distribution of Ti, Ni, Cu, Zn, Rb, Zr and Pb. In fact, plotting Fe is virtually the same as plotting these other elements. Enzyme leachable Mn is positively correlated with H^+, Ni, As and Mo on the 5 North area, and with V, Co and Ni on 8 North. H^+ appears to be playing a role in the availability of Mn and Fe, which may indicate that the enzyme leach analysis is sensitive to conditions where the pH may change, such as breaks in slope, seepages, varying groundwater conditions, and rock type changes.

Profile plots (not shown here) for the enzyme leach elements directly related to epithermal mineralization, As and Sb, do not show a response to mineralization on any line, nor does Fe and the correlated elements Cu, Pb, Zn and Ni. The only element to consistently respond to mineralization was Sr, as Ca is not reported by the enzyme leach method. The Sr patterns found by an enzyme leach extraction were almost identical to the previously described methods; i.e., a double-peak or "rabbit ear" response.

DISCUSSION

The results from the Marigold orientation suggest that a transport mechanism of some type is influencing the distribution of Ca and, in turn,

Table 4: *Enzyme leach correlations, 8 North Deposit*

	H+	COND	CL	TI	V	MN	CO	NI	CU	ZN	AS	BR	RB	SR	ZR	MO	SB	BI	BA	PB	B
COND	-0.62																				
CL	-0.38	0.71																			
TI	0.51	-0.51	-0.33																		
V	0.50	-0.41	-0.29	0.81																	
MN	0.47	-0.47	-0.30	0.45	0.58																
CO	0.46	-0.36	-0.21	0.76	0.79	0.80															
NI	0.45	-0.38	-0.23	0.84	0.85	0.68	0.94														
CU	0.39	-0.34	-0.17	0.94	0.87	0.43	0.80	0.89													
ZN	0.55	-0.52	-0.32	0.99	0.83	0.49	0.79	0.86	0.94												
AS	0.16	0.00	0.09	0.36	0.60	0.48	0.53	0.51	0.49	0.39											
BR	-0.32	0.64	0.80	-0.54	-0.35	-0.32	-0.31	-0.33	-0.35	-0.52	0.13										
RB	0.54	-0.52	-0.35	0.99	0.81	0.50	0.79	0.85	0.92	0.99	0.37	-0.56									
SR	0.05	-0.22	-0.15	-0.27	-0.22	-0.01	-0.21	-0.22	-0.28	-0.27	-0.10	0.09	-0.26								
ZR	0.49	-0.49	-0.33	0.99	0.82	0.45	0.78	0.85	0.95	0.99	0.35	-0.55	0.99	-0.29							
MO	-0.26	0.56	0.53	-0.37	-0.07	0.20	0.13	0.01	-0.16	-0.33	0.24	0.57	-0.35	-0.25	-0.34						
SB	0.08	-0.15	-0.13	0.14	0.28	0.34	0.45	0.41	0.20	0.15	0.21	-0.03	0.19	0.04	0.15	0.11					
I	-0.10	0.50	0.60	-0.46	-0.14	-0.17	-0.24	-0.26	-0.28	-0.43	0.16	0.76	-0.46	0.16	-0.45	0.55	-0.01				
BA	-0.02	0.10	0.13	0.09	0.11	-0.05	0.15	0.13	0.17	0.08	0.07	0.17	0.08	0.12	0.09	0.10	0.24	0.05			
PB	0.52	-0.50	-0.31	0.99	0.81	0.49	0.79	0.86	0.95	0.99	0.39	-0.53	0.99	-0.29	0.99	-0.32	0.17	-0.45	0.08		
B	-0.28	0.53	0.44	-0.30	-0.07	-0.33	-0.29	-0.28	-0.18	-0.30	0.07	0.42	-0.29	0.02	-0.29	0.32	-0.01	0.43	-0.02	-0.30	
FE	0.53	-0.50	-0.32	1.00	0.81	0.47	0.78	0.85	0.93	0.99	0.36	-0.54	1.00	-0.28	0.99	-0.35	0.16	-0.45	0.07	0.99	-0.31

Sr over mineralization. This mechanism probably involves several steps, and affects nearly all elements to some degree. In addition, Au forms a detectable anomaly and appears to be influenced by Ca over the 5 North deposit, but not the 8 North deposit. The former is overlain by about 100 feet of alluvium and the latter by over 300 feet. The typical response to mineralization appears to be double-peak or rabbit-ear shaped anomalies, with peaks over the margins of mineralization. This was seen in all analytical extractions. The peaks were sharply defined and of limited extent over the margins of the 5 North deposit, but broader over the margins of 8 North. The ratio of HOAc (carbonate specific) soluble Ca to AR soluble Ca showed clear residual anomalies over the deposit margins. This is hard evidence that two forms of Ca exist in the soil, one of which is easily dissolved and occurs near mineralization. The soil conditions are alkaline, with a pH above 8.0 in almost all locations. What type of transport processes could fit these disparate observations?

First of all, transport processes that cannot possibly be involved should be discarded. Obviously, clastic transport from mineralization through to surface is not a factor. Nor is electrogeochemical transport, as described by Bolviken and Logn (1975) and Govett (1972). There are no electrical conductors; no conductor grain-to-grain contact traversing a large Eh field; therefore, no self potential (SP) field. Without an

established electrical field (battery) no net movement of ions can occur in response to the battery. If there were natural electrical fields over the Basin and Range precious metal deposits, the best exploration technique would be SP, looking for sharp negative electrical potentials. These do not exist over the Marigold study area (D. Hoover, USGS, pers. comm., 1995), or probably any of the other sulphide-poor epithermal deposits. The movement of ions, and their adsorption by Fe or Mn, supposes both the target ions and adsorption compounds are mobile under the environmental conditions in and above the deposit. The alkaline nature of the desert environment precludes the movement of many cations. The stability diagrams for Fe and Mn at STP and a pH above 8 as shown by Garrels and Christ (1965) preclude the ionic movement of either of these elements in the Marigold environment (Figure 7). The formation of anomalies in Fe or Mn is unlikely. In fact, results in this study suggest that analyzing the sesquioxide component of soil may actually suppress valid geochemical responses.

What mechanisms support the element patterns observed at Marigold? Recent work by Lintern and Butt (1993) has shown that the sampling of a pedogenic carbonate horizon and its analysis for Au has been successful in defining Au mineralization through 40 m of overburden in South Australia. However, the origins of the anomalies are not clear. The Australians point out that the formation of calcrete is the result of the interaction of Ca^{2+} with bicarbonate (HCO_3^-). In turn, HCO_3^- is formed by the reaction of water and CO_2 gas; the latter could originate from the atmosphere, from microbial and root action, or from CO_2 released by the oxidation of mineralization. This correlation of Au and Ca also indicates that Au may be transported as an anion, perhaps a bicarbonate complex. Gray and Lintern (1994) suggest that the Au distribution in carbonate soils may be partially controlled by evapotranspirative processes and be aided by biologically generated ligands. If this is in fact the case, there may be a depth of burial limit beyond the influence of surface plants which will prevent the movement of Au to the surface.

This work over the Marigold deposit has shown that, in areas of thick recent alluvial fill, Ca anomalies can form over mineralization either with or without Au, depending on the depth of overburden. This is strong evidence that the transport mechanism does not depend on Au at all, but some other factor related to the mineralization. The large variation in H^+ concentration observed in the Marigold soils may offer a clue to the formation of Ca anomalies.

Smee (1983) proposed a mechanism for the formation of soil anomalies through lacustrine clay overburden over massive sulphide deposits in the Canadian Shield. Laboratory experiments using radioisotope doping showed that ion migration through lacustrine clay was taking place by a process of cation exchange on soil particle surfaces. The exchanged and released cation was H^+. The resulting change in pH in the soil mobilized ambient Fe, Mn, Ca and Mg which was then redistributed and precipitated in the soil column. Precipitation of the sesquioxides scavenged other ambient cations which produced pseudo-anomalies in a variety of elements. Thus, surficial responses in elements not associated with mineralization were possible. The pseudo-anomalous elements appeared as though they travelled through the overburden, but they did not. This role of H^+ and Fe was confirmed by field studies in northern Québec.

The soil pH in the temperate forest was between 5.5 and 7.0, which crosses the stability field of Fe, depending on the Eh (Figure 7). The ratio of weakly bound Fe to total Fe, when corrected for organic carbon, produced rabbit ear patterns through more than 20 m of glaciolacustrine varved clay over a massive sulphide Cu/Zn body.
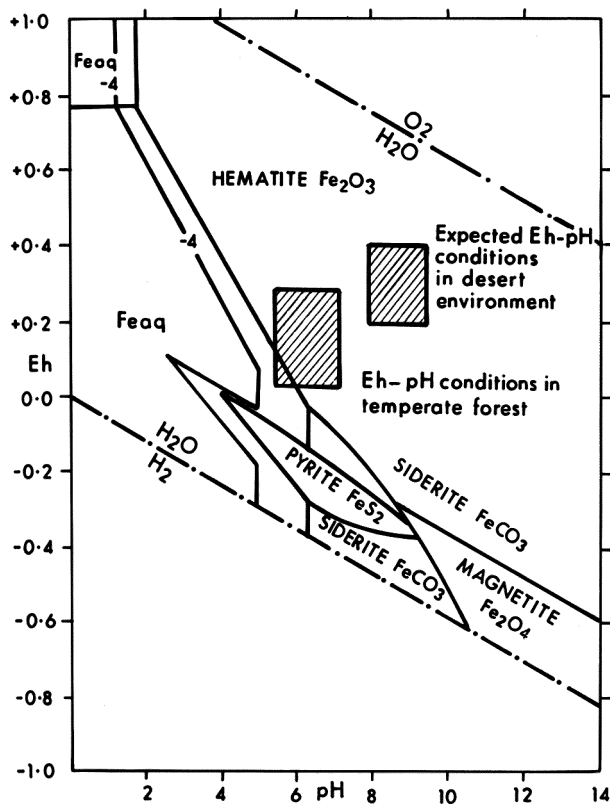
Figure 7: *Eh-pH diagram for Fe at STP conditions showing conditions found in boggy soil in temperate forest in Canada (Smee, 1993) and extrapolated conditions based on pH measurements at Marigold. Note that the temperate forest conditions cross the stability boundary for hematite, but the desert conditions do not (adapted from Garrels and Christ, 1965).*

MODEL FOR FORMATION OF SURFACE RESPONSES TO MINERALIZATION

The proposed model which attempts to tie these observations together is shown in Figures 8**a** and **b**. A mineral deposit contains at least some sulphides and is undergoing oxidation. Over time, an oxide cap will form at the top of the body, which will slow the rate of oxidation directly affecting the bedrock-overburden interface. The greatest rate of oxidation should therefore be taking place at the margins of the mineralization. The breakdown of sulphides during oxidation will release H^+ and ionic species of the elements making up the mineralization. Both H^+ and the other elements will diffuse around the deposit and form a concentration front within the overburden. The release of H^+ can result in two subsequent actions: it can react with surrounding limy rocks, in either the wall rock or overburden, and produce CO_2, or it can set up an ion exchange-based diffusion front in the overburden, and diffuse upward toward surface.

The occurrence of CO_2 in soil gas above and on the margins of ore deposits is well documented, particularly in arid environments (Lovell *et al.*, 1983; McCarthy *et al.*, 1986). The mechanism for the formation of CO_2 in these references is as explained above. Both CO_2 and H^+ will diffuse to the surface along the path of least resistance, which for both gaseous and ionic diffusion, should be straight up, above their source.

The gradual buildup over time of H^+ at the soil-alluvium interface should cause a reaction with ambient $CaCO_3$ in the soil, and the redistribution of Ca. The addition of extra CO_2 from below will, in turn, react with near surface moisture forming HCO_3^-. This should then react with the loose Ca^{2+} to reform $CaCO_3$. Given sufficient time, an excess of nearly pure $CaCO_3$ should form first above, then on the margins of mineralization. This $CaCO_3$ will be most easily dissolved by HOAc, producing a positive Ca anomaly when ratioed against AR Ca. Strontium will mimic Ca.

A change in response pattern should be caused by differing overburden thicknesses, or possibly regolith type. Figure 8**a** shows a hypothetical distribution of Ca, Sr, Au and As where bedrock cover is relatively thin. Gold and As may diffuse directly to the surface or may be taken up by plants, then redeposited to the surface (Lintern and Butt, 1993). This superimposition of transport processes could result in a one-, two-, or three-peak anomaly pattern as originally suggested by Govett (1976). The Ca and Sr anomalies should form very sharp peaks on either side of the mineral body; the short transport distance above mineralization will not permit any significant lateral dispersion.

The schematic in Figure 8**b**, where overburden thickness prevents the direct migration of the ore-forming elements to surface, shows that only Ca and Sr should produce a response to mineralization. Plant roots do not penetrate to the aureole of elements released by oxidation, thus no detectable Au or As is found in the surface soils. Broad double peaks should be found for Ca and Sr.

CONCLUSIONS

These geochemical orientation results over the two Marigold Au deposits have suggested that an element transport mechanism is active through overburden thickness exceeding 100 m.

The soils over the Marigold study area are alkaline, the pH ranging from 7.8 to 9.5. This is nearly a 100-fold difference in H^+ concentration, a surprising fact given the flat topography, high buffering capacity and

thick outwash sequence that comprises the alluvial fill. The only mechanism that could produce these sharp variations in surface H^+ is an introduction of H^+ from the subsurface by oxidation of mineralization. pH alone, however, does not produce interpretable patterns over mineralization. Some other mechanism, perhaps dependent on pH, is influencing the near surface soil chemistry.

There is no repeatable and interpretable pattern developed from anions measured with a water leach and the Dionex Ion Chromatograph, or enzyme leach ICP-MS. However, a simple soil conductivity measurement produces similar patterns in soil samples, is very much less expensive and is field portable. The enzyme leach technique is dissolving up to 20 times more Fe than Mn; it is really an extraction for sesquioxides rather than Mn alone. The Fe is controlling the distribution of most other cations, and as a result, is of little use to exploration in the alkaline environment of the desert. It may be useful in more acidic conditions where Fe would be mobile.

Those who invoke an electrogeochemical transport mechanism to explain surface anomalies should first detect the presence of a natural battery by completing an SP survey: no SP anomaly—no electrogeochemical transport. Gold, As and Sb, at very low levels, can show
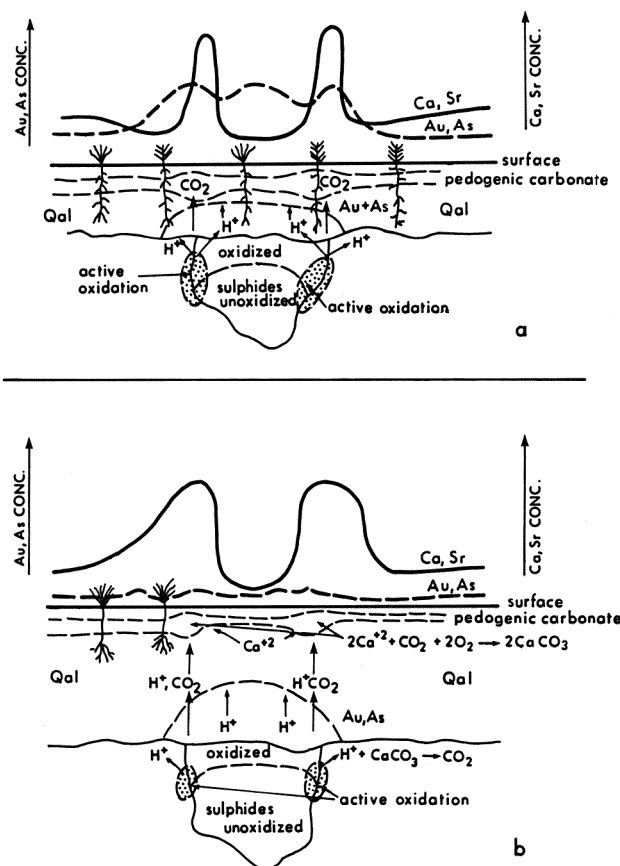
Figure 8: *Conceptual model for the formation of Ca, Sr and ore-forming element patterns in desert soils: (**a**) shallow overburden; (**b**) deep overburden. See text for explanation.*

anomalies related to mineralization through 60-70 feet of overburden. The "true" background for Au is less than 1 ppb, and is less than 0.1 ppm for As and Sb. It is therefore imperative to use analytical methods that can produce these low levels of detection for all soil sampling surveys in the Basin and Range Province.

Gold is strongly correlated with Ca. Calcium, and its accompanying element Sr, are the only elements that show a consistent, interpretable response to mineralization, regardless of depth of burial or chemical extraction used. The positive Ca residuals, when AR soluble Ca is ratioed to the weak extraction Ca, show that Ca has been mobilized or added to the soil by some mechanism.

The double-peak responses are close together where overburden is relatively thin, or the mineralization only partially subcrops, and are farther apart where the overburden is thick.

Responses to mineralization from this study indicate that migrating elements are moving vertically; little lateral transport is evident. Analysis of closely spaced soils should include pH, ultra low level Au (1 ppb or better), As and Sb (0.1 ppm or better) and AR soluble elements including Ca and Sr. All data should be plotted in profile format so that they can be easily interpreted.

Conclusions reached in this study are restricted to the pH-Eh environment found at Marigold, i.e., very alkaline and oxidizing. It is likely that the controlling element, Ca, would be replaced by Fe in more acidic environments, as found in the Canadian Shield by the author. The organizations who use the techniques or hypotheses from this study should understand the geochemical landscape prior to starting a survey. In short, there is no magic bullet.

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