BACA PROJECT

DATA AND REPORTS

GEOLOGY

No.	Transfer Date	Release Date	Title
1.	B	B	Hydrothermal Geology of the Valles Caldera, New Mexico by R.F. Dondanville - 1971.
2.	B	B	Airborne Infrared Geothermal Exploration--Valles Caldera, New Mexico Earth Resources Operations, North American Rockwell Corp.-1972.
3.	B	B	Electrical Resistivity Survey in Valles Caldera, New Mexico by Group Seven, Inc. - 1972.
4.	B	B	Additional Data--Electrical Resistivity Survey in the Valles Caldera, New Mexico by Group Seven, Inc. - 1972.
5.	B	B	Reconnaissance Resistivity Survey Baca Property, McPhar - 1973.
6.	B	B	Supplemental Report--Reconnaissance Resistivity and Schlumberger Depth Sounding Surveys Baca Property - McPhar - 1973.
7.	B	B	Quantitative Gravity Interpretation Valles Caldera Area, New Mexico by R.L. Segar - 1974.
8.	B	B	Mercury Soil Gas Survey Baca Prospect by Allied Geophysics Inc. - 1974.
9.	A	A	Mercury analysis - 1974 gradient holes.
10.	B	B	Geothermal Geology of the Redondo Creek Area Baca Location by T.R. Slodowski - 1976.
11.	B	B	Magnetotelluric--Telluric Profile Survey, Valles Caldera Prospect by Geonomics - 1976 as reprocessed by QEB Inc. - 1978.
12.	B	B	Geological Resume of the Valles Caldera by T.R. Slodowski - 1977.

MERCURY SOIL GAS SURVEY
BACA PROSPECT
SANDOVAL COUNTY, NEW MEXICO

AUGUST 1974

Pool # 5

for

UNION OIL COMPANY
GEOTHERMAL DIVISION
P.O. BOX 7600
LOS ANGELES, CA. 90051

CONTENTS

ILLUSTRATIONS

I INTRODUCTION

Mercury is the only metal that exists as a liquid at ordinary temperatures. As such, it is a highly mobile element having sufficient vapor pressure to cause it to move great distances, even when confined by low permeability barriers as exist in the subsurface of the earth. When activated by high temperatures, however, its capability to migrate is increased many fold. This is illustrated by the table of vapor pressure shown below.

TABLE I

Vapor pressure of Hg expressed in mm of Hg.

Temp. °C	P_{mm}	Temp. °C	P_{mm}
0	0.00018	100	0.273
10	0.00049	200	17.29
20	0.00120	300	246.80
		358	760 =1 atmosphere
30	0.00278	400	1574.10
40	0.00608		
50	0.01267		

The Hg soil gas method for prospecting for geothermal cells is thus based on three premises: 1) the ability of heat to mobilize mercury in pre-existing subsurface rocks, and 2) the contribution of juvenile mercury accompanying

juvenile hydrothermal fluids, and 3) the lower pressure existing at the surface of the earth which causes the mercury to move toward that surface. The mercury soil gas method should therefore be an ideal prospecting tool for outlining potential areas of geothermal energy.

II   PROCEDURE

With the use of the mercury soil gas collectors operating in numerous environs, measureable amounts of Hg have always been collected, the only exception noted to date is in heavily frozen ground, which appears to form an unpenetrable barrier to the passage of all gases. A photograph of the collector cone appears in the literature at the back of this report.

In practice, the collector cone is buried in the ground to a depth to several inches and the loose soil that is removed from the hole tamped down around the outside of the cone. A small 1" disc of 180-mesh silver screen is placed in the orifice of the aparatus, and the fan is switched on for a period of ten minutes causing the gases to move out of the soil under the cone and through the screen. After collecting, each screen is then placed in a sealed glass vial and refrigerated until it reaches the assayer. The cold environment of storage is

a precaution to prevent vaporization of the Hg from the silver amalgam. This procedure is not absolutely necessary, as the vapor pressure of Hg (Table I) at room temperature or field temperatures is less than 0.005 mm of Hg pressure, but it does guard against inadvertant exposure to high temperatures while in transit. Blank silver screens exposed to air for 30 seconds or so before being placed in the vial usually pick up about 10 to 15 ppb of Hg. This forms part of the background level measured in the course of surveying.
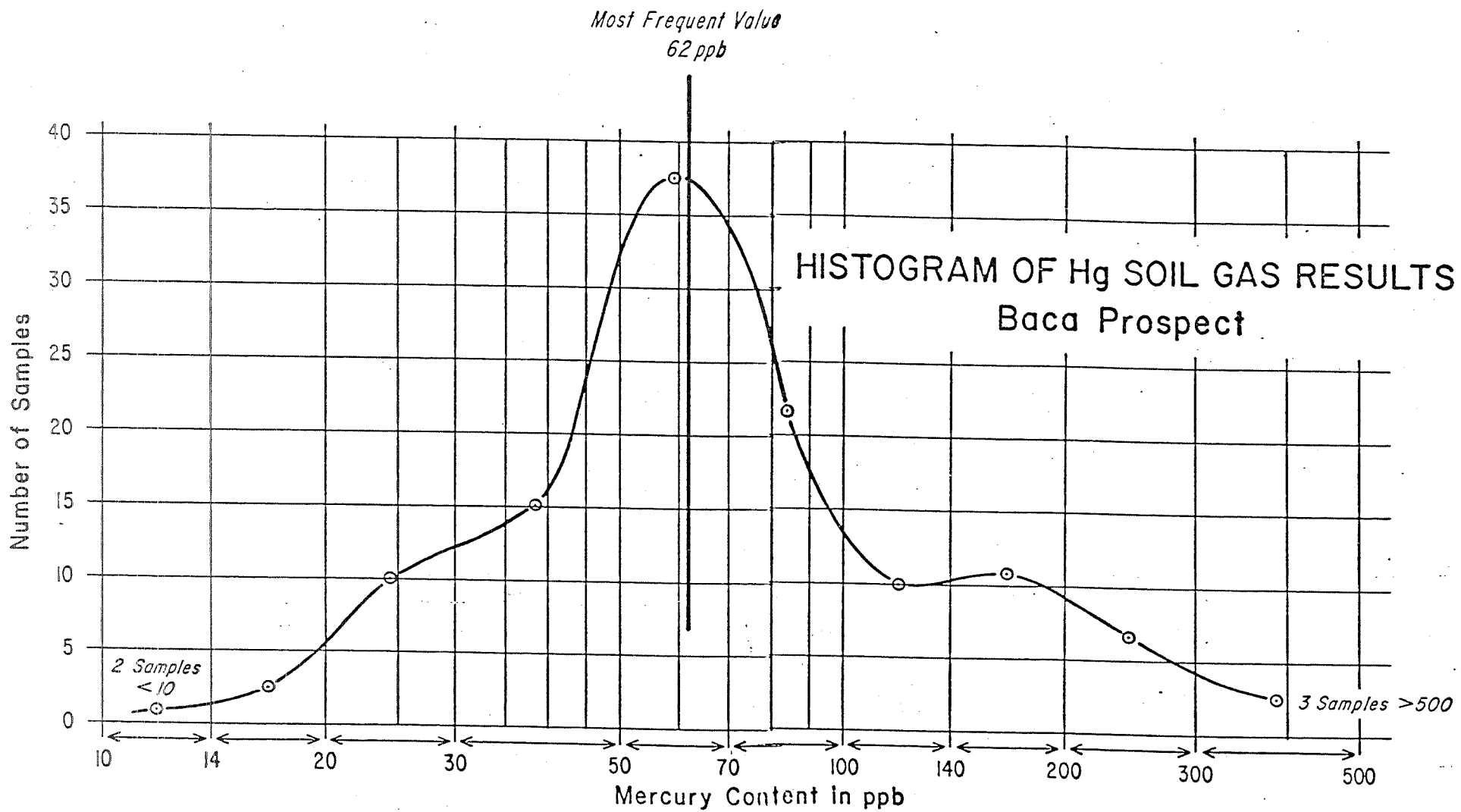
The mercury present on the screens is assayed by the atomic absorption method to concentrations of approximately two parts per billion (although they can easily be assayed to a precision of a fraction of this amount) and the results are plotted against sample locations in plan or profile form. In some cases, averaging techniques are employed to smooth the scatter inherent in the method. This scatter is typical of most geochemical surveys and has given rise to many averaging techniques of both manual and computer types.

A general treatment of Hg soil gas methods has recently appeared in the literature and is referred to at the end of this report.

III RESULTS - BACA PROSPECT

The mercury soil gas grid appears in Plate 1. It
was carried out along the existent road network as
specified by the Union Oil Geothermal Division. Sample
interval was one-half mile along the roads as measured by
truck speedometer. A more uniform two-dimensional sampling
net, with scattered sampling points between roads, would
have provided a better picture of the distribution of
mercury soil gas in the area, but was not judged necessary
for this preliminary test. In Plate 1 the assay value in
parts per billion appears above each sample point, and
above the assay value appears the weighted average calcu-
lated according to the formula: $Av = (a+2b+c)/4$, where b is
the sample value being averaged and a and c are the assay
values on either side.

An even dozen anomalies were encountered by this
survey, an anomaly in this case being defined as an area
having samples with averages greater than 100 ppb. Only
two of these show averages exceeding 200 ppb, and these
occur around the two high assays at points S29 and S85.
In both of these areas adjacent samples support the high
assays of the central points.

Most Frequent Value
62 ppb

HISTOGRAM OF Hg SOIL GAS RESULTS
Baca Prospect

Number of Samples

2 Samples
< 10

3 Samples > 500

Mercury Content in ppb

-5-

The background level in the area may be judged by reference to Figure 1, where the "most frequent value" is seen to be approximately 62 ppb Hg. If the area as a whole is elevated in mercury content because of the pronounced geothermal activity, then this average value may be likewise elevated, and the true background value may be somewhat lower, perhaps 50 ppb. The above mentioned anomalous areas can therefore be considered as having Hg soil gas levels at least twice background.

Since no geological or geothermal parameters were provided for comparison with the Hg soil gas results, it is not possible in this report to evaluate the effectiveness of the Hg soil gas technique as a prospecting tool on the Baca prospect.

IV CONCLUSIONS AND RECOMMENDATIONS

1. The Hg soil gas method was tested for usefulness as a prospecting tool for geothermal cells on the Baca prospect in Sandoval County, New Mexico.

2. A background level of approximately 62 ppb of mercury was registered on silver screens in a ten-minute amalgamation test.
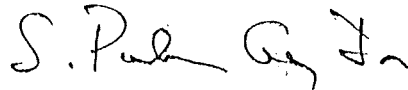
3.   A dozen anomalies exhibiting average values
greater than 100 ppb were located.   In two of these areas
the averge values exceeded 200 ppb, and samples in both
of these reached values several times the 100 ppb level.

4.   A more uniform grid, with stations spaced
every mile or half mile throughout the area, would have
provided better coverage for comparison with the geolo-
gical and geothermal results.

5.   As no geological or geothermal maps were pro-
vided for comparison with the Hg soil gas method, evalu-
ation of the usefulness of the method in this area cannot
be made a part of this report.

Respectfully submitted,

APPLIED GEOPHYSICS, INC.

S. Parker Gay, Jr.
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APPENDIX

Geochemical Exploration Using Mercury Vapor

John J. McNerney and Peter R. Buseck

Abstract

Mercury is commonly present in trace amounts in base metal sulfides. The chemical characteristics of Hg permit its release from oxidizing sulfides and, being extremely volatile, it can migrate through considerable depths of overburden. Anomalous concentrations of Hg may often be detected in soil gas overlying a deeply buried sulfide source, providing sufficiently sensitive analytical techniques are available such as the new Au thin film Hg detector.

Laboratory experiments simulating natural occurrences were used to evaluate the effects of changes in barometric pressure, temperature, and soil moisture on the migration and release of Hg from soil gas. Diurnal changes in barometric pressure affect the emission of Hg in soil gas so as to limit accurate sampling using a static collection system such as plastic hemispheres. By use of a soil pump a pressure gradient is artificially produced, overcoming short term variations in atmospheric pressure. Wet soil inhibits Hg migration in soil gas sufficiently to make accurate measurements difficult.

A variety of base and precious metal deposits were tested and in all cases Hg anomalies were detected in soil gas. The most intense and reproducible anomalies occur over high-grade vein deposits, especially those containing Zn-Pb-Ag mineralization. Anomalies over porphyry Cu deposits are less intense and are often difficult to distinguish from normal background variation. Laboratory experiments and field studies indicate that Hg vapor in soil gas is a valuable geochemical prospecting tool.

Introduction

THE continually increasing demand for base and precious metals has led to vigorous exploration programs to locate new ore bodies. Geochemical techniques play an increasingly prominent role in this search. Laboratory research combined with field studies have firmly established the value of geochemical indicators in exploration to the extent that routine geochemical sampling has become an integral part of comprehensive exploration programs.

The most commonly used geochemical sampling techniques depend heavily on the occurrence of rock outcrops, stream sediments, residual soils, or derivative waters spatially related to an ore occurrence. Additionally, the correlation between the observed anomalies and the associated ore bodies is not a simple one. We feel that the use of Hg has great advantages over conventional geochemical techniques because of the simplicity and low cost of sampling, and because of the relative ease of relating anomalies to the underlying sulfide source. Furthermore post-mineral overburden does not limit the validity and usefulness of the technique. This follows from the assumption that Hg degassing is continuous. Once the Hg vapor gradient to the surface has been established, the thickness of overburden or its character, providing it is porous, is not of importance.

Mercury is a trace element in many sulfide minerals and is also commonly associated with the noble metals, Au and Ag. Additionally, Hg in its native state or in volatile compounds is generated when the host minerals are oxidized, as by weathering. The resulting Hg vapor tends to migrate readily in the natural environment; indeed, the high mobility of Hg makes it unique among the heavy metals. If anomalous Hg can be detected at the surface it can serve as a pathfinder for locating the sources that released the Hg.

Mercury aureoles are known to extend, with diminishing intensity, for considerable distances from a primary source. Ozerova (1962) showed that anomalous Hg concentrations in soils could be detected as far as two kilometers from the source area. Additionally, we have found pronounced local anomalies directly above ore deposits, suggesting that Hg vapor can delimit specific ore bodies as well as general target areas.

The use of Hg in soils for geochemical prospecting is now well established (Saukov, 1946; James, 1962; Friedrich and Hawkes, 1966; Warren et al., 1966), but up to the present, published results using Hg vapor as a geochemical indicator of buried ores have been limited. The method was initially proposed by Sergeev (1961) and shortly thereafter Hawkes and Williston (1962) discussed its use. McCarthy et al. (1969) and Khayretdinov (1971) have presented comprehensive studies demonstrating the practical applications of Hg vapor for locating buried deposits.

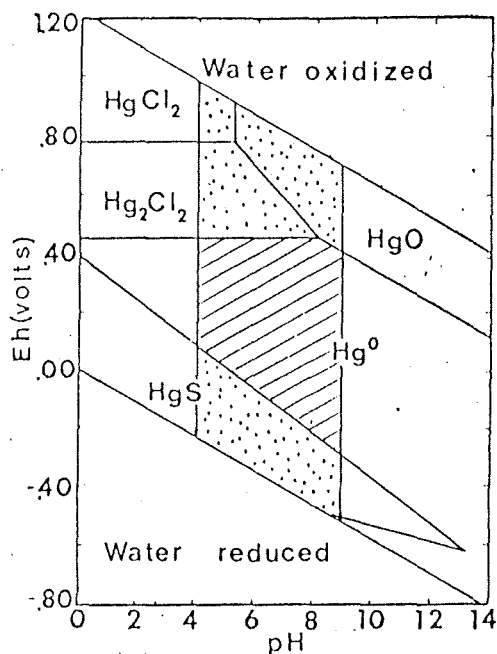The objects of this paper are (a) to evaluate the

FIG. 1. Stability fields for Hg species at 25°C and one atmosphere pressure. System includes water containing 36 ppm Cl⁻, total sulfur 96 ppm as SO_4^{-2} (Hem, 1970). The patterned area outlines the usual limits of Eh and pH in the natural environment. The striped area outlines the stability field of elemental Hg within these limits.

technique of using Hg vapor for geochemical exploration, (b) to describe laboratory experiments designed to evaluate the variables that affect the migration and detection of Hg vapor in soil gas, (c) to discuss various procedures for collecting and measuring the Hg content of soil gases, and (d) to present field data collected over several types of known ore deposits. This technique is applicable to ore deposits in arid regions, such as exist in the western United States, Australia, and Africa. This is of particular importance as large portions of these areas are covered by volcanics, lake sediments, or alluvium of postmineralization age where conventional geochemical sampling may be of limited use.

Geochemistry of Mercury

Mercury occurs in a limited number of mineral species in the natural environment. The principal Hg mineral, cinnabar (HgS), has a restricted stability field and will, in an oxidizing environment, yield native Hg. The relative instability of cinnabar is demonstrated by the fact that there are no known Precambrian ore deposits of cinnabar, although sulfide deposits of other metals are common.

Elemental Hg does not readily bond with oxygen; it has a low melting point and is highly volatile. Consideration of the Eh-pH diagram (Fig. 1) compiled from Hem (1970) shows that Hg° has a wide

field of stability under conditions that are reasonable for the natural environment. Mercury may occur in soils either in organic or inorganic compounds, or in the elemental state. Little is known about the role of organic compounds in fixing Hg in the soil. Although a great variety of such organic compounds occur, most of these are either highly volatile or unstable.

Our data confirm that Hg° is released from buried ore bodies and, once released, migrates toward the surface. A possible mechanism for Hg release from sulfides in the zone of oxidation is as follows: sulfide minerals lying within this zone release electrons upon reaction with oxygen. Using sphalerite as an example, $ZnS + 4H_2O + 4Hg^{2+} \rightarrow Zn^{2+} + SO_4^{2-} + 8H^+ + 4Hg°$. Sulfur undergoes the relevant half-reaction $S^{2-} \rightarrow S^{6+} + 8e^-$. Thus each formula weight of sulfide ion that is oxidized can release enough electrons to reduce four Hg^{2+} ions. Presumably this is far in excess of any Hg that is present as a trace constituent in the sphalerite. This reaction may also proceed in steps, so that Hg^{1+} rather than Hg° is produced initially. Elemental Hg could then be generated by the reaction $2Hg^{1+} \rightarrow Hg° + Hg^{2+}$ (Jonasson and Boyle, 1972). Similar reactions for other sulfides can account for the generation of Hg° where oxygen is available.

Mercury may also be released from below the zone of oxidation. In this case the required electron source must be internal, a more problematic situation. Polyvalent ions or non-stoichiometric phases provide possible sources. Iron commonly occurs in several oxidation states. Transfer of electrons between the ferrous and mercuric ions could release elemental Hg; $2Fe^{2+} + Hg^{2+} \rightarrow 2Fe^{+3} + Hg°$ would be a possible reaction.

Although less likely, another type of reaction that could release Hg depends on deviations from stoichiometry of sulfides. For example, work on the system Pb — S shows that the galena composition at high temperatures can, in some instances, be represented as $(Pb_{1,\delta}S)$, where (δ) is a small number (Bloem and Kroger, 1956). On cooling, galena could free electrons by changing toward stoichiometry. These electrons, small in number because of the slight change in stoichiometry, could reduce Hg^{2+}, thereby facilitating its release into the vapor state: $Pb_{1,\delta}S + \delta HgS \rightarrow 1 + \delta PbS + \delta Hg°$.

Khayretdinov (1971) has proposed another possible mechanism for the continual release of Hg from a sulfide body. He suggests that some trace Hg associated with sulfide is in the elemental state, chemisorbed on the crystal surfaces. Temperature changes and/or variance in the electrochemical potential may release this Hg°.

In the special case where the ore body is subjected

to reheating, $Hg°$ could be released by dissociation of HgS, which is enhanced by the presence of H_2O (Dickson, 1968). This could help produce the observed anomalies, but the period of Hg release would be limited and thus present a detectable target for only a restricted portion of the history of the ore body.

Abundances of Hg in selected minerals of interest are shown in Table 1. In general the sulfides are appreciably enriched in Hg relative to the gangue minerals. Sphalerite may contain large quantities of Hg, suggesting that its presence can result in strong Hg anomalies. The primary Cu sulfides found in vein and porphyry Cu deposits also may contain low but significant quantities of Hg. The Hg content of various unmineralized rock types is generally lower than that of sulfide minerals (Fleischer, 1970).

Analytical Procedures and Sampling Devices

Instrumentation

A Lemaire model 500B Mercury Vapor Detector was used to obtain most of the laboratory data reported in the Experimental section below. The instrument utilizes atomic absorption spectrometry at the 2537 Å Hg line. It has a working sensitivity of 5 nanograms of Hg per 0.2 liters of air.

During the course of this project, but after most of the experimental work was completed, a new Hg vapor detector was developed (NcNerney et al., 1972). This instrument operates by measuring the resistance increase of a thin (<300 Å) Au film when elemental Hg is adsorbed on the film surface. The instrument is field portable and has an absolute sensitivity better than 0.05 ng. It is more precise

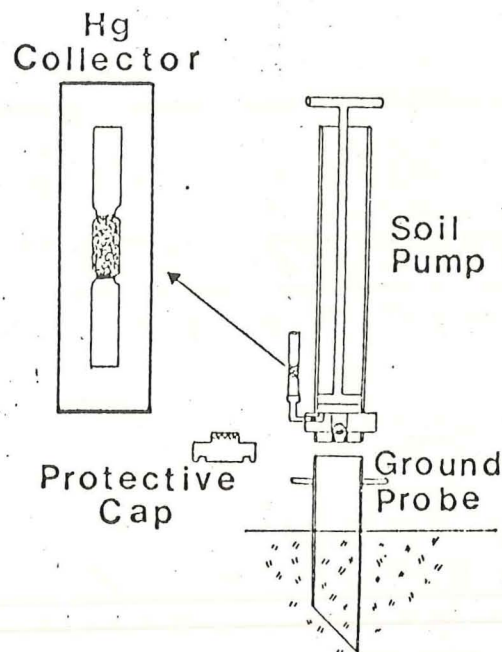
Hg Collector

Soil Pump

Protective Cap

Ground Probe

FIG. 2. Schematic diagram of soil pumping apparatus and noble metal collecting tube.

and sensitive than the Lemaire atomic absorption unit and was used for all of the field studies.

Both instruments used in this study were calibrated using known quantities of Hg vapor. The vapor is obtained by placing a drop of elemental Hg into a polyethylene bottle which is held at a controlled temperature. After equilibrium between liquid and vapor has been established, known quantities of vapor are extracted with calibrated syringes and then analyzed as standards.

Noble metal collectors

Noble metal traps were used to collect the Hg in experimental and field work. A variety of Au and Ag forms were tested, including Ag and Au wool and foil, Ag mesh, Au plated on glass shards, and Au sponge. The Ag and Au wools proved to be the most efficient, presumably because of their relatively large surface area. The Au sponge also proved highly efficient, but sintered during the heating cycle, thereby reducing its surface area and collecting efficiency.

Extreme care was taken to ensure that the Ag and Au collectors used in this project were free of Hg. Cleaning the collectors involved a number of heating cycles at temperatures above 500°C. When not being used, the collectors were stored in a muffle furnace at 500°C. In the field the collectors were heated in a portable propane furnace before use in order to assure that they were free of Hg.

TABLE 1.   Mercury Content of Selected Minerals

	No. of Analyses[1]	Range (ppm Hg)[1]		Range (ppm Hg)[2]	
Sulfides					
Galena	10	0.5 –	300	0.4 –	70
Sphalerite	11	5 –	3,400	0.1 –	200
Pyrite	3	0.5 –	10	0.1 –	100
Sulfosalts	7	0.1 –	100	0.1 –	500
Chalcopyrite	—	—		0.1 –	40
Bornite	—	—		0.1 –	30
Oxides					
Pyrolusite	—	—		1 –	1,000
"Limonites"	—	—		0.1 –	500
Gangue					
Barite	7	0.03–	2	0.2 –	200
Siderite	4	0.01–	5	0.01–	10
Calcite	18	—		0.01–	20
Quartz	—	—		0.01–	2

[1] Ozerova (1959).
[2] Jonasson and Boyle (1972).

TABLE 2.   Precision of Hg Sampling over Desert Soil
Experiments.   Measurement of Replicate Samples
Were with the Lemaire Detector.

Test Number	Number of Samples	Mean Value (ng Hg)	Range (ng Hg)	Standard Deviation (ng Hg)
1	8	12	9–16	2.3
2	8	31	26–39	4.9
3	7	36	33–42	3.2
4	7	38	30–42	4.1

For use with the soil pump, noble metal collectors, either Au or Ag wool, are placed into 10 mm I.D. Vycor tubing. The tube is necked down on either side, holding the collectors firmly in place (Fig. 2) and permitting maximum contact with the sampled air passing through the tube. It is important to analyze the Hg adsorbed on the noble metal collectors as soon as possible after collection, preferably within 48 hours, because otherwise Hg diffuses into the crystal structure of the collectors. Once such diffusion becomes appreciable, it is difficult to volatilize all the adsorbed Hg during a single heating.

Sampling devices

Several types of sampling devices were used to collect Hg from the soil gas. The initial experiments were made with a battery operated blower which forced air over the noble metal collector. This proved to be cumbersome and did not give results of high precision.

A much simpler static collecting system was also tried. This consisted of flat or curved sheets placed over the ground with Ag mesh placed over a hole cut in the center of the sheets. These were used in sunny spots so that the inside air would be heated, causing convection which forced air over the Ag. This method had the great advantage of simplicity; the collectors have no moving parts and require no continual operator monitoring. Although these domes and plastic sheets were used for our experimental work, all our included field data were obtained using the soil pump described below.

To counteract the effects of atmospheric variations a dynamic collecting system was developed. The device resembles a large hypodermic needle, consisting of a soil pump, ground probe, protective cap, and hammer with replaceable hard plastic heads (Fig. 2). The ground probe is hammered 20 cm into the ground. The soil gas is pumped out by creating a partial vacuum over a portion of soil and is then passed over the noble metal collectors. The volume of air sampled at any site can be easily controlled by the number of pump strokes. Depending on the terrain and availability of soil, 30–50 samples can be collected and analyzed in a single day.

Experimental

Introduction

The concentration of Hg in soil gas depends on a number of climatic and physical variables: these include temperature, barometric pressure, permeability of overburden, soil type, and soil moisture (McCarthy et al., 1969). Laboratory experiments were conducted to understand and evaluate these variables better. Plastic cans 1.2 m tall were filled with soil after placing a small quantity of metallic Hg at the bottom. In addition, 1.5 m deep holes were dug in the ground and a small quantity of Hg was placed at the bottom of each hole; the holes were then filled with soil. Within a matter of days substantial quantities of Hg vapor were emitted from the surface of the soil.

In order to collect Hg emitted during these experiments we used 30 cm square sheets of clear plexiglas with a 5 cm hole in the center of each sheet. The sheets were placed over the experiments, leaving 7.5 cm air space above the soil. Squares of 40 mesh Ag screen were placed over the 5 cm holes. The Hg vapor in the air that passed through these screens (mainly as the result of convection) was collected on the Ag.

Table 2 lists a series of replicate samples collected in these experiments to evaluate the reproducibility within any collection period.

Barometric pressure

During the course of a day in Arizona barometric pressure usually varies in a predictable manner; pressure rises from early morning until approximately 10 or 11 A.M., then falls steadily until 4 to 6 P.M. when a daily low is normally achieved. Samples of soil gas were collected with a static sampler from one of our plastic can experiments at one-half hour intervals from 7 A.M. to 7 P.M. in order to evaluate the magnitude of the effect of diurnal changes in barometric pressure on the emission of Hg. Figure 3 shows results obtained from a series of samples taken over the course of one day.

Mercury emission is sensitive to changes in barometric pressure. Barometric highs correspond to Hg lows and barometric lows correspond to Hg highs. The averaged amounts of Hg collected during the barometric low in late afternoon was nearly twice that obtained during the mid-morning high. The diurnal changes in pressure in Figure 3 were of average intensity according to the Phoenix Weather Bureau. The experiment was run in the shade where the air temperature varied between 15 and 25°C.

The results of any sampling program using a static collection device in which samples are ob-

tained on different days, or even at different times of the day, could be adjusted to compensate for changes in pressure by sampling from a standard sample site throughout the day and proportioning the unknown to the standard values. Such a procedure is awkward and time consuming. The problem of variance in mercury concentrations due to changes in barometric pressure can be avoided by using a dynamic sampler which would create a sufficient pressure gradient so that diurnal changes in barometric pressure are small in comparison and therefore will not greatly affect the results.

Temperature

The effects of temperature on the emission of Hg in soil gas was evaluated. Not only does the vapor pressure of elemental Hg increase exponentially with rising temperature, but convection of air above and in the uppermost layers of the soil increases substantially if the ground temperature is greater than the air temperature.

Infrared lamps were used to heat the soil in one of the plastic can experiments while the emitted vapor was collected at 2°C intervals over the range 10° to 72°C. The soil temperature was measured at a soil depth of 1.5 cm. Approximately 10 minutes elapsed for each 2°C rise in soil temperature. Figure 4 is a plot of the Hg emitted from the soil as a function of soil temperature. The air temperature at the time of this experiment was 25°C. A portion of the gradual rise in Hg emission above 25°C (Fig. 4) may, in fact, be due to increased convection, but it is likely that the rise in vapor pressure of Hg with temperature is the primary cause of the increase.

The above data suggest that short term variations in temperature have only a relatively minor effect on the emission of Hg in soil gas, unless the ground temperature exceeds approximately 40°C.
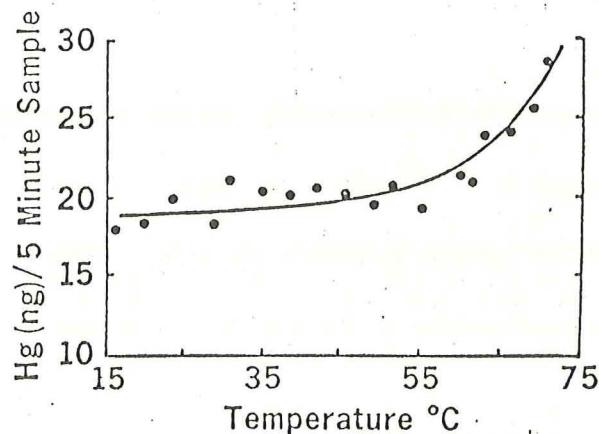
FIG. 4. Mercury emission from a desert soil experiment as a function of soil temperature.

Soil moisture and type

We have determined that wet soil temporarily inhibits the emission of Hg. Laboratory experiments and field studies have both shown that soil gas emission, at least that portion that contains Hg, ceases almost entirely after a soaking rain. This "transient" moisture is a difficult variable to evaluate quantitatively. The clogging of pore spaces in the soil is probably, in part, responsible for this effect.

Soil type must be considered together with soil moisture. Equal moisture content in two different soils can produce different effects. In field testing in northern Nevada it was found that only a slight moisture content was needed to decrease the results by a factor of two or three. Soil in this area has a high clay content. As a comparison, field testing was also carried out in southern Arizona at a time when the soil had a high moisture content. Although the results were somewhat erratic, the magnitude of mercury emission in comparison was relatively high. The soil in this area is granular and contains little clay.

Soil moisture would severely hamper the use of this technique as an exploration tool in normally dry climates after a soaking rain. Although we have obtained results in some wet soils, our results were poor and because of this our field testing was generally restricted to dry soil.

Field Studies

Introduction

Extensive field work in Arizona, Nevada, and Western Australia indicates that the measurement of Hg in soil gas is a useful prospecting technique. In this section we will point out some successes in its use as well as attendant difficulties.

Two methods of soil gas sampling were employed, both using the soil pump and collectors described
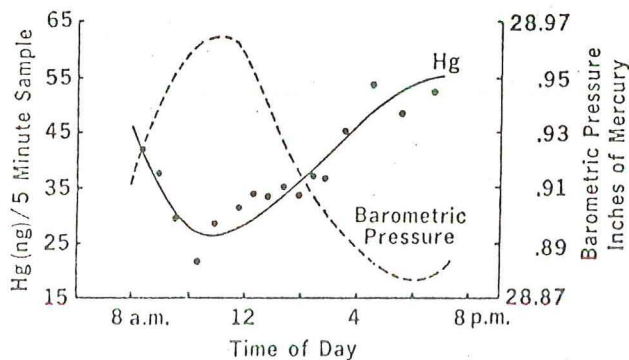

FIG. 3. Variations in Hg emission from a desert soil experiment as a function of atmospheric pressure. The dashed line indicates the barometric pressure and the solid line indicates Hg emission. Mercury was collected using a static sampler.
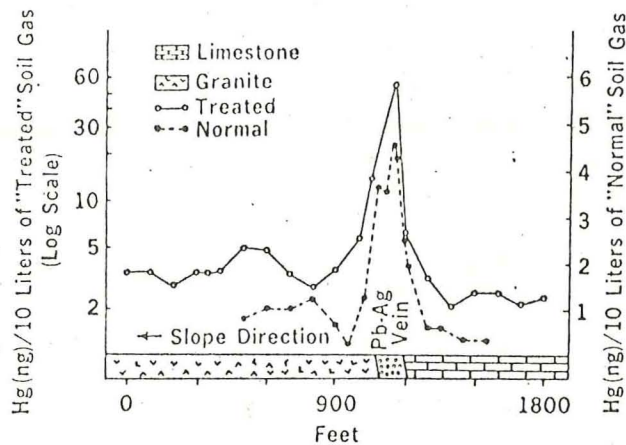
FIG. 5. Mercury in soil gas collected on traverses run over the Mowry vein. The samples referred to as "treated" were collected after the addition of 30 ml of 3% H_2O_2 to the undisturbed top layer of soil. Note that the scale for "treated" soil gas is logarithmic.

previously (Fig. 2). In the first method, called "normal," a set volume of soil gas, generally 10 liters, was pumped at each sample station. In the second method, referred to as "treated," 30 ml of 3% H_2O_2 were added to the top layer of soil before pumping the soil gas. This enhanced the Hg values considerably. In the field study at the Mowry Mine, the two techniques are compared. "Normal" sampling was done at the 4-Metals and Jarillas deposits and "treated" at the Vekol Mine.

Samples were taken over deposits ranging from low-grade porphyry Cu deposits to high-grade Cu-Pb-Ag veins. The reported studies are only a few of many carried out over the past three years.

Mowry Mine

In the early part of this study extensive work was done at the Mowry Mine. The purpose was to calibrate the sampling equipment and techniques as well as to field test the new Au film Hg detector.

The deposit, a high-grade Pb-Ag vein (Schrader and Hill, 1915), is located in the Patagonia Range in southern Arizona. This mine was a significant producer at the turn of the century but has not operated for many years. Similar vein type mineralization had showed anomalous Hg in soil gas in our sampling in the vicinity of the Magma Mine at Superior, Arizona.

Two identical traverses, one utilizing the "treated" and the other the "normal" sampling technique, were run two weeks apart across an unworked extension of the Mowry vein (Fig. 5). The anomaly peaks on both traverses correspond to the location of the vein. The principal difference between the results obtained by the two sampling techniques is the relative magnitude of Hg values. The Hg values

using the "treated" method are 5–10 times those obtained by "normal" sampling. A number of short traverses were run over other sections of this vein; in all cases the anomaly corresponded to the location of the vein.

The rather narrow Hg anomaly has very little lateral dispersion, although the traverse line approaches the vein up an approximate 20° slope. This suggests that little if any downslope movement of Hg occurred. On traverses run over the section of the vein that has been extensively stoped, the Hg in soil gas was only slightly greater than that over the adjacent barren rocks.

The work at Mowry also tested the possible influence of diurnal changes in barometric pressure and temperature on our sampling technique. The traverses recorded in Figure 5 were run a number of times both in the early morning and late afternoon and, within the limits of our sampling error, no variance in Hg values was noted.

Jarillas deposit

The Jarillas deposit, also located in the Patagonia Range, Arizona, is one of a series of small mines and prospects situated along an apparently favorable subsurface structure approximately 3 km in length. This deposit was selected to test the effectiveness of the Hg sampling technique in locating subsurface structures related to mineral occurrences. A traverse was run normal to the structure, near but not at the actual mine workings.

The ore deposits in this area occur in quartz fissure veins associated with diorite dikes cutting quartz monzonite country rock (Schrader and Hill, 1915). Although local pockets are rich in Cu, Pb,
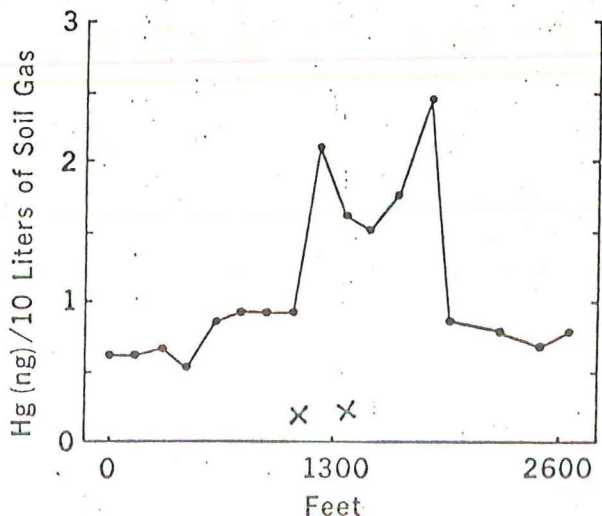

FIG. 6. "Normal" vapor sampling for Hg in soil gas on a traverse near the Jarillas deposit. X indicates prospect pits along the mineralized zone.

and Ag, the deposits are discontinuous. The Hg anomaly (Fig. 6) occurs over a broad area contain-ing numerous diorite dikes on strike with the afore-mentioned structure. No mineralization was visible on the surface in the immediate vicinity of the traverse.

4-Metals Mine

The 4-Metals Mine, also located in the Patagonia Range, is a small deposit of disseminated Cu in a quartz monzonite breccia pipe which intrudes older granite or quartz monzonite. Recent unpublished work by Norandex Exploration has shown the Cu content to be approximately 0.7 percent.

A traverse was run along the contours of a very steep slope. Extensive background sampling in the vicinity had shown average values of 0.6 to 0.8 ng Hg/10 liters of soil gas; values of 2 to 5 ng Hg/10 liters (Fig. 7) collected over the mineralized breccia pipe are highly anomalous. The rocky nature of the ground in this area made it extremely difficult to seat the soil pump firmly. This factor is partly responsible for the somewhat erratic values shown in Figure 7; they may also reflect real variations in subsurface mineralization.

Vekol Mine

The Vekol Mine, located in the Vekol Mountains, Arizona, was described by Carpenter (1947). Silver with some Pb and Cu was produced from the mine. The mineralization appears to be associated with an andesite dike cutting Cambrian limestone. The major portion of the mineralization occurs as re-placement beds in the limestone adjacent to the dike. The object of our traverses was to locate this dike
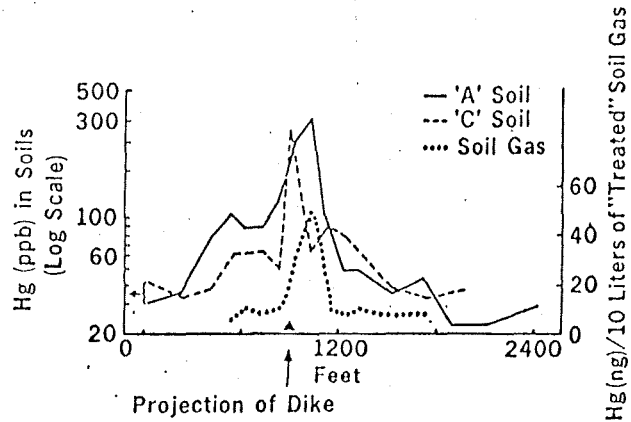

FIG. 8. Comparison of soil sampling versus "treated" vapor sampling for Hg over the Vekol dike. Note that the scale for the soil samples is logarithmic.

where it is covered by pediment south of the mine workings.

In addition to sampling soil gas after treatment with H_2O_2, soil samples were collected from both the 'A' and 'C' horizons. These soils were analyzed for Hg using the technique described by Vaughn (1967). One quarter gram of the −80 mesh fraction of the soils was heated in a Vycor bulb to red heat and the resulting vapors passed over Au wool collectors. These were heated in turn and the evolved Hg was measured using the Au film Hg detector. All repli-cate samples, some run over twenty times, gave values of ±7% of the mean (Fig. 8).

Of the methods tested, the soil analyses of the 'C' horizon and the soil gas anomaly seem to pinpoint the vein position with the greatest accuracy. The rather broad anomaly in the 'A' horizon could in part be related to dump material washed down from the old mine workings.

Porphyry copper deposits

We have sampled soil gas over four porphyry Cu deposits in Arizona, all of which are buried under alluvium and/or fanglomerate, in some cases several hundred feet thick. Primary mineralization in all these bodies consists of chalcopyrite with lesser bornite; in some cases there are presumably minor amounts of sphalerite and galena. Pyrite is abundant.

The Hg in soil gas is typically very low, resulting in poor reproducibility of data. In all cases Hg anomalies in soil gas were detected over the ore bodies, but these anomalies were irregular and averaged two to three times background, with local "highs" above this. Extended sampling to deter-mine reliable background values is required. Al-though this does not preclude Hg in soil gas as an indicator of porphyry Cu deposits, it does place
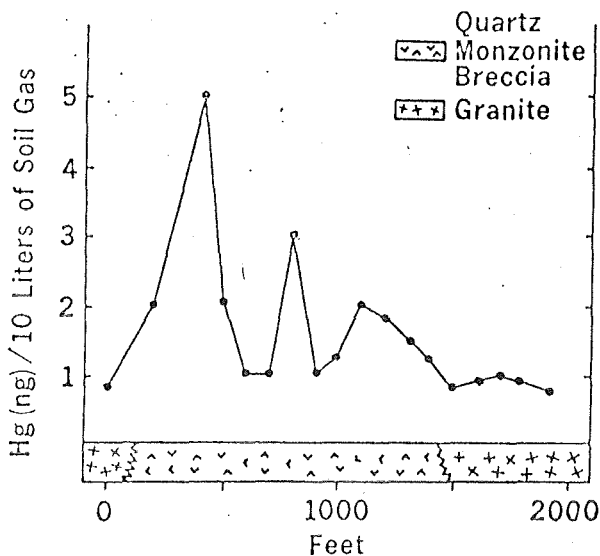

FIG. 7. "Normal" vapor sampling for Hg in soil gas over the 4-Metals deposit.

limitations on it as a definitive technique. We feel, however, that further work is needed and warranted.

Conclusions

(1) All of the deposits tested showed anomalous Hg concentrations in soil gas. High grade vein deposits, especially those containing sphalerite, gave the greatest Hg vapor anomalies.

(2) In addition to pronounced local anomalies directly over certain deposits, broad dispersion halos were detected over some, but not all, deposits.

(3) Porphyry Cu deposits provide distinct but low Hg vapor anomalies. Extensive sampling and high analytical precision will be required to outline these important deposits confidently.

(4) Mercury vapor may be used to detect buried structures.

(5) Using the soil pump and portable Au thin film Hg detector, Hg vapor can be routinely measured in the field. Such sampling is rapid, relatively inexpensive, and eliminates the analytical time lag common to most geochemical techniques.

(6) The addition of H_2O_2 solution to the soil immediately before pumping enhances Hg vapor values.

(7) Mercury emission from soil gas is, in part, dependent on atmospheric pressure. Fluctuations in pressure limit the usefulness of static sampling but may be avoided by using a dynamic sampling system.

(8) Short term temperature variations do not greatly affect Hg emission from soil gas. Seasonal changes, however, may be important, and results between winter and summer sampling may not be comparable.

(9) Soil moisture apparently disrupts the equilibrium of Hg in soil gas. Complications arise when the normal moisture content of soil is varied. In an arid climate, sampling should be discontinued after a rain until the soil is dry. In a temperate or moist climate Hg equilibrium in soil gas may be established in damp or wet soil.

## Acknowledgments

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mercury soil gas surveying
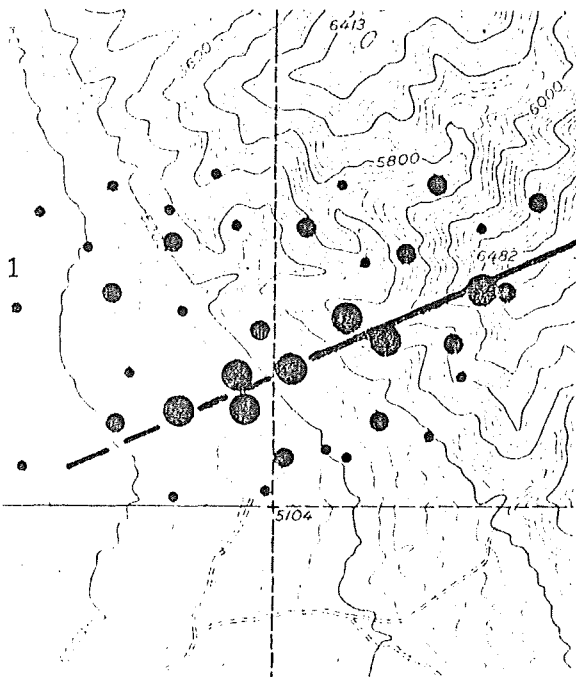
The tracing of narrow mineralized structures from exposed outcrops onto and across alluvial covered pediments is one of the mercury soil gas method's most exciting uses. Many times such confined targets are not detectable by standard geophysical methods due to their small size and/or their great depth of burial. Above, a typical example from the Basin-Range.

*Collector Cone for soil gas surveys. Mercury accumulates on the silver screens in the housing at top.*

In association with University of Utah professor Dr. M. L. Jensen, Applied Geophysics, Inc., is pleased to offer to the mining industry integrated programs of mercury soil gas surveying—from data collection in the field through sample assay and analysis to final interpretation of the results. Dr. Jensen, an internationally known scientist who has made significant contributions to the field of geochemistry and isotope geology, has been perfecting techniques of mercury soil gas analysis for over three years, and Applied Geophysics believes Dr. Jensen's methods are far more effective, as well as being more economical to run, than any other offered to industry to date (1973).

Soil gas almost invariably contains mercury in minute quantities, and the mercury soil gas method is a valuable exploration method for the following reasons:

1. Mercury is associated as a trace element with the majority of mineral deposits.
2. Mercury's high vapor pressure allows it to continually diffuse from mineralized zones, even from considerable depths.
3. It is readily collected by the Jensen apparatus where it is deposited as an amalgam on silver screens.
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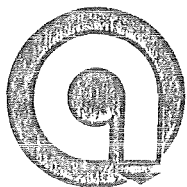
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