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Exploration for Geothermal Areas Using Mercury: a New Geochemical Technique

JOSEPH S. MATLICK, III*Department of Geology, Arizona State University, Tempe, Arizona 85281, USA***PETER R. BUSECK***Department of Chemistry, Arizona State University, Tempe, Arizona 85281, USA*

ABSTRACT

High-sensitivity measurements of mercury in soil indicate strong positive anomalies over regions of geothermal activity in three of four areas tested (Long Valley, California; Summer Lake and Klamath Falls, Oregon). All thermal springs are enclosed with the mercury anomaly areas; in distinction to other geochemical methods currently in use, this method also can be used in areas free of heated waters. We thus confirm the strong association of Hg with geothermal activity.

INTRODUCTION

Proven techniques for the exploration of geothermal areas are severely limited in both numbers and effectiveness. In this paper we document a new approach in the search for geothermal areas. The detection of trace levels of Hg can be used to supplant, or more desirably, complement existing geophysical and geochemical exploration programs.

Mercury deposits typically occur in regions containing evidence of geothermal activity, such as hot springs. Examples are summarized by White (1967). An equally strong correlation exists when areas of known geothermal activity are examined. They typically contain at least minor cinnabar and other Hg minerals. Examples include The Geysers, California; Wairakei, New Zealand; Geyser, Iceland; Larderello, Italy; and Kamchatka, USSR.

There clearly is abundant evidence for the association of unusual amounts of Hg with areas containing major geothermal activity. It is logical to project this situation to prospective geothermal areas. However, because of lower surficial geothermal activity we might predict that the Hg concentrations at the surface will be too low to produce detectable Hg mineralization. For this reason it is necessary to look for Hg concentrations that are anomalous only in regard to the nongeothermal surroundings. The project described in this paper was designed to test the hypothesis that such Hg anomalies are associated with geothermal systems and can thus be used as an exploration guide.

The great volatility of Hg adds to its usefulness for geothermal exploration. The high vapor pressure of Hg makes it extremely mobile, and the elevated temperatures near a geothermal reservoir tend to increase this mobility. Thus, Hg migrates upwards and away from the geothermal

reservoir. Added to this effect are the relatively high concentrations of Hg in thermal water (for example, White, Hinkle, and Barnes, 1970). The result is that soils overlying and adjacent to geothermal areas should be enriched in Hg, the latter having been trapped on the surfaces of clays and organic and organometallic compounds.

The techniques employed in this study are similar to those used for the geochemical exploration for base and precious metal ore deposits (McNerney and Buseck, 1973; McCarthy, et al., 1969; Hawkes and Williston, 1962). Soils, sampled along a regular grid, were measured. In order to obtain the necessary sensitivities in the parts per billion (ppb) range, a gold-film Hg detector developed in our laboratories was used (McNerney, Buseck, and Hanson, 1972).

Four field areas were studied: Long Valley and East Mesa, California, and the Summer Lake and Klamath Falls regions in Oregon. They represent a range of geological settings as well as intensity of geothermal activity. The California areas are proven geothermal areas with considerable published geological and geophysical data available. The city of Klamath Falls, a known geothermal resource area, contains many homes, businesses, and schools that are heated from the natural hot waters. Summer Lake, on the other hand, is a large prospective geothermal area. Measurements for three of the areas were made in the field; the East Mesa samples were analyzed in the laboratory.

All of the districts except East Mesa show strong positive Hg anomalies. The peak-to-background ratios extend to >550:1, with backgrounds averaging 5 ppb. Where geophysical data is available, it correlates well with the Hg anomalies. All hot springs in the four areas also fall in areas of anomalously high Hg. The results show that Hg measurements, if of sufficiently high sensitivity and precision, can be used to reliably locate areas of geothermal activity. In distinction to other geochemical exploration methods for geothermal areas, Hg measurements can also be used to locate geothermal areas free of aqueous activity.

EXPERIMENTAL TECHNIQUES

Sampling

The A soil horizon was determined to be the most useful for Hg sampling. This confirms the results of Jonasson and

Boyle (1972), who found that A-horizon soils over mineralized belts contain approximately twice the Hg concentrations of the B or C horizons. Sampling was conducted on approximately a 1.6 km (1.0 mile) grid. In view of the large anomalous area created by a geothermal reservoir, sampling on this grid should detect all significant geothermal areas.

The soil samples were sized using an 80 mesh, stainless steel sieve. The -80 fraction was immediately sealed in a clean, airtight glass vial. All samples were analyzed in the field within a few hours of their collection except at East Mesa, where the samples were stored for a week and subsequently analyzed in the laboratory.

Analytical Procedure

The Hg analyzer used in this study was developed by McNerney, Buseck, and Hanson (1972). The instrument is based on the phenomenon that a thin gold film undergoes a significant increase in resistance when Hg is absorbed. Two Au films connected into opposite arms of a simple dc bridge circuit are used, one as a sensor and the other as a reference.

Soil analysis starts by placing a measured sample into a quartz test tube and heating it to $>800^{\circ}\text{C}$ with a propane torch. In the process of soil analysis all the Hg is vaporized. It is then transported by a carrier gas (Hg-free air) through Mallcosorb, a commercially prepared material by the Mallinckrodt Co., and the magnesium perchlorate. These remove any H_2O , HCl, CO_2 , and sulfur gases which may be present. Following this the gas is split into a reference and a sensor fraction. The Hg in the former is removed by passing the gas over palladium chloride before the gas reaches the reference Au film. The Hg in the sensor fraction is collected by amalgamation with the sensor Au film. The resulting differences in composition, and thus electrical resistance, between the reference and sensing Au films are measured electronically and displayed on either a voltmeter or a strip-chart recorder.

The instrument is field portable with an absolute sensitivity better than 0.05 ppb Hg. Under field conditions, the precision of the instrument is greater than 1 ppb Hg.

All analyses are given in ppb of Hg; however, this is not completely accurate because soils were measured volumetrically rather than by mass. The data are correct if the soil density is 1.1 gm/cm^3 , a reasonable average for a -80 fraction soil.

Analytical Reproducibility

McNerney and Buseck (1973) demonstrated that temperature and barometric pressure affect the emission of elemental Hg vapor from the soil. To determine whether these variables would similarly affect Hg measurements from bulk soils, samples from fixed reference points (R.P.) were collected and analyzed continually throughout the summer of 1974. The R.P. results are summarized in Table 1.

As can be seen, daily variables, including temperature and barometric pressure, have little or no effect on Hg values when soil rather than vapor samples are analyzed. The last value for R. P. 1 was obtained on August 10, 1974, while all other values were obtained between May 27 and June 6, 1974. Thus, the Hg concentrations in these soil samples appear to be reproducible both over short periods of time and over an entire summer exploration season.

Table 1. Reference point concentrations (ppb of Hg).

R.P. 1 (Long Valley, California)	R.P. 2	R.P. 3 (Summer Lake, Oregon)	R.P. 4
60	20	12.5	18.5
57.5	22	11	17.25
57.5	20	13	17.25
60	21.5	13	17.25
58	22.5	13	16.75
58	23.25	13	16.75
56.25	22	11	17
56		13	
56		11.25	
		13.25	
		11	
		11.5	
$\bar{X} = 57.70$	21.60	12.1	17.20
$\sigma = 1.53$	1.22	1.0	0.69
Range = 58.0 ± 2.0	21.6 ± 1.7	12.1 ± 1.2	17.6 ± 0.9
Air temperature:	-2.2° to 32.2°C	$\bar{X} = \text{Mean}$	
Barometric pressure:	757.4 to 765.0 mm of Hg	$\sigma = 1 \text{ Standard Deviation}$	

LONG VALLEY CALDERA, CALIFORNIA

Long Valley is located in Mono County, California, approximately 72 km northwest of Bishop, California. Physically, Long Valley is a volcanotectonic depression formed by collapse along steeply dipping, normal faults (Pakiser, Kane, and Jackson, 1964). The collapse followed a large volcanic eruption. Volcanic activity continued after the formation of Long Valley, with the last dated volcanic eruption occurring 220 years ago (M. Sheridan, personal commun., 1975).

Geothermal activity followed the large eruption and persists today. Evidence of this thermal activity is abundant and includes hydrothermal clay deposits, hot springs, fumaroles, and mud pots. Water temperatures of the hot springs range up to 93°C , with flow rates extending up to 10 gal/min or 0.6 l/sec (Lewis, 1974).

Hg Anomalies

Long Valley was selected as the first test area because of the pervasive evidence of geothermal activity and the extensive supporting geological and geophysical data. Approximately 400 samples (Fig. 1) were analyzed. These samples covered the entire caldera and extended up to 15 km outside its boundary. The Hg values from within the caldera are significantly higher than those from outside. Thus, the entire caldera displays a variable, broad, positive Hg anomaly. This makes it difficult to determine a suitable background concentration. Consequently, it was assumed that the Hg values from the immediate vicinity of the caldera represent the "true" background of Long Valley. Forty-nine samples collected within 27 km of the caldera center produced an average of 5.5 ppb Hg. Thus, 5.5 ppb Hg was chosen as the background. One small area in the caldera exhibits Hg values ranging from 5.5 to 9.0 ppb Hg, supporting the data from outside Long Valley.

The Hg concentrations are contoured on Figure 2 as multiples of the background; for example, the 22 ppb contour has peak-to-background ratio of 4:1. The 22, 33, and 55 ppb Hg contours are arbitrarily selected for discussion

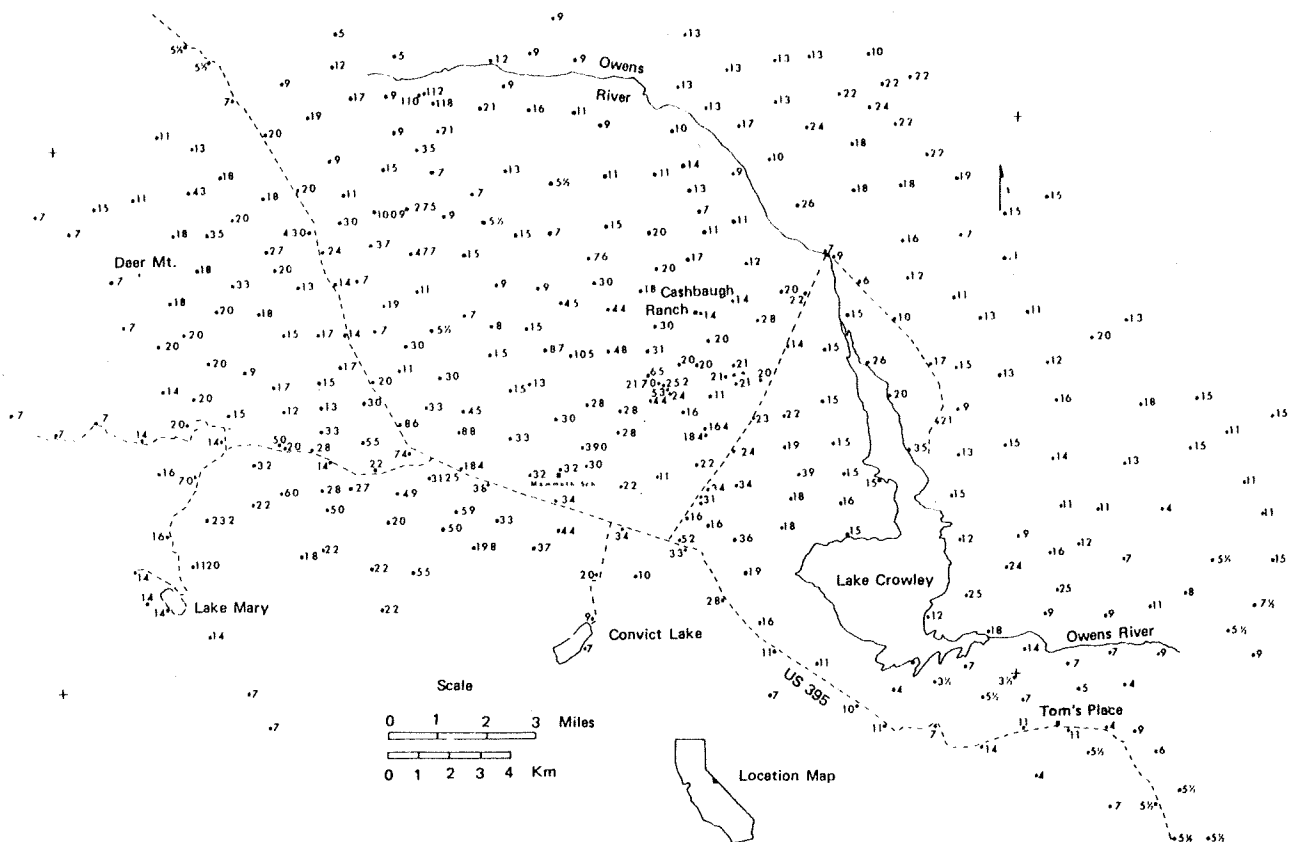


Figure 1. Mercury concentrations (in ppb) for sampling sites at Long Valley, California.

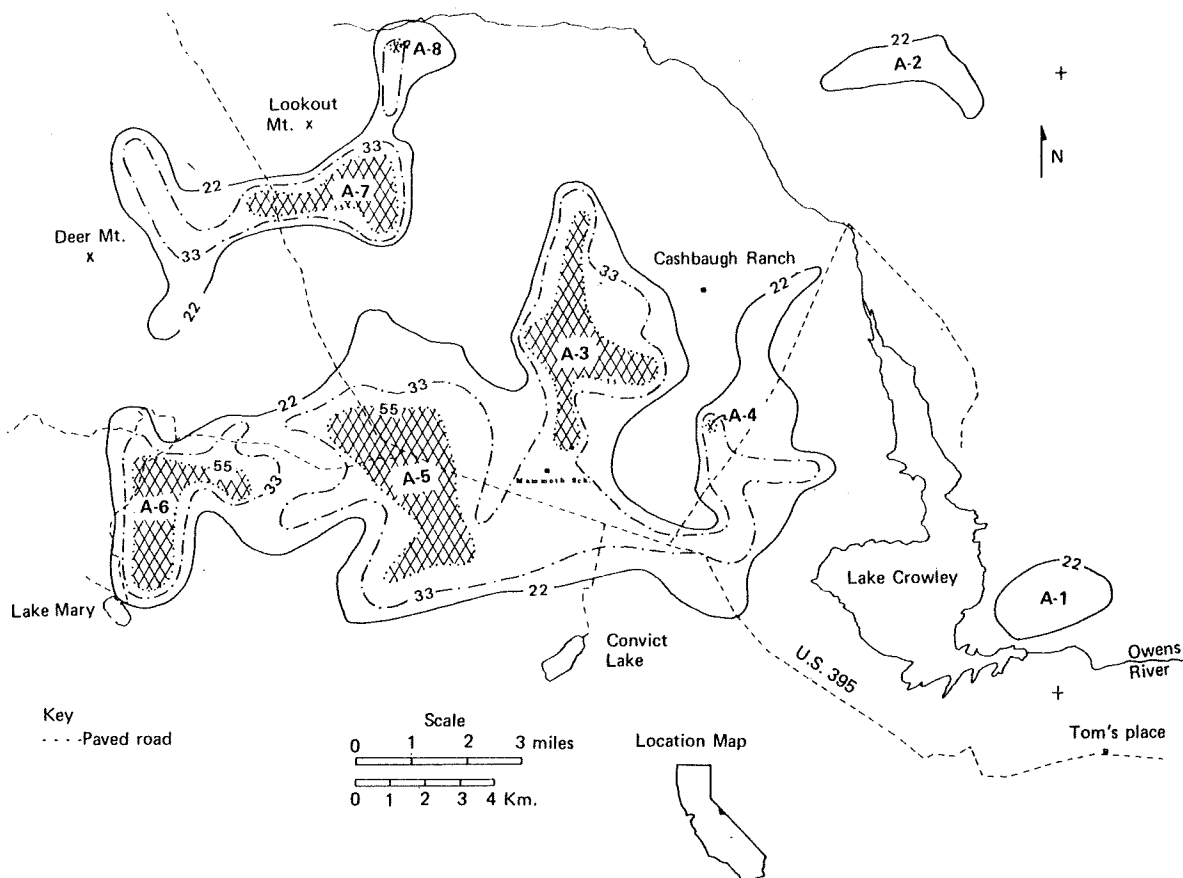


Figure 2. Mercury anomalies at Long Valley, California. The contours correspond to peak to background ratios of >4:1 (22), >6:1 (33), and >10:1 (55 ppb Hg).

Table 2. Hg anomalies in Long Valley.

Anomaly	Peak to background ratio greater than:	Size (km ²)	Major exposed geological units	Hot springs	Mineralization	Probable origin
A-1	4:1	5	Alluvium, tuff	No	Cinnabar and pyrite	Mineralization
A-2	4:1	10	Alluvium	No	None	Geothermal activity
A-3	10:1	10	Alluvium, rhyolite	Yes	None	Geothermal activity
A-4	10:1	0.1	Alluvium, rhyolite	Yes	None	Geothermal activity
A-5	10:1	15.5	Basalt, rhyolite, granite, alluvium	Yes	None	Geothermal activity
A-6	10:1	6.5	Alluvium, latite	No	Au and Ag	Mineralization
A-7	10:1	6.5	Pumice, basalt, alluvium, rhyolite	No	None	Geothermal activity
A-8	10:1	0.1	Alluvium	No	None	Geothermal activity

because they display all the essential data. If another contour interval is chosen, the size and shape of the Hg anomalies change, but the central position of the anomalies does not move. The 55 ppb contour, containing all Hg values greater than 55 ppb, includes Hg concentrations up to 3125 ppb (peak-to-background ratio, 568:1). Characteristics of the individual anomalies are summarized in Table 2.

Comparison With Other Geological Data

Differences in geological formations may generate geochemical anomalies (Hawkes and Webb, 1962). To determine whether or not geological variations could be responsible for the Hg anomalies in Long Valley, representative rock samples were collected and analyzed in duplicate for Hg. The results are tabulated in Table 3. Assuming that the samples shown in Table 3 are representative, rocks from Long Valley display a very small range of Hg concentrations (25 to 34 ppb). It is hard to imagine that such rocks alone could have been the origin of soil anomalies with peak-to-background ratios greater than 10:1. Additional support for discounting geological diversity as the cause of these Hg anomalies is that most anomalies traverse different lithological units.

Since geophysical methods have been used to outline geothermal reservoirs and locate geothermal drilling sites, a comparison between geophysical and Hg studies conducted in Long Valley is appropriate. The comparison of the specific Hg anomalies and the geophysical anomalies is listed in Table 4. The data strongly suggest that the Hg method is useful for locating geothermal reservoirs because all of the geophysical anomalies indicative of geothermal activity are coincident with Hg anomalies. No strong Hg anomalies were found in areas where geophysical techniques produced negative results. In addition, Hg anomalies were detected in areas where no geophysical data are available.

SUMMER LAKE BASIN, OREGON

Summer Lake is a large, shallow lake located in the Basin and Range province of southeastern Oregon. The structural setting, a graben bordered by normal faults, is typical of the Basin and Range region. Tectonic and volcanic activity have persisted until late Pliocene time (Peterson and McIntyre, 1970). Normal faults have down-dropped the graben approximately 2.5 km with respect to the western horst (R. Blank, Jr., 1974, written commun.). The basin is surrounded by Miocene and Pliocene volcanic rocks that range from basaltic to rhyolitic in composition.

Table 3. Hg concentration of representative rocks from Long Valley, California (ppb of Hg).

Rock type	Sample #1	Sample #2
Granite	25.7	25.3
Basalt	34.1	34.1
Rhyolite	27.7	27.0
Obsidian	27.3	27.6

Table 4. Hg and geophysical anomalies in Long Valley.

Hg anomalies	Geophysical anomalies	Reference*
A-1	None	
A-2	None	
A-3	Resistivity, AMT	2,3
A-4	Resistivity, AMT	2,3
A-5	Resistivity, AMT Aeromagnetic	2,3,4
A-6	None	
A-7	Gravity	1
A-8	None	

Note: Resistivity and AMT field studies were not done in the area of A-6, A-7, and A-8.

* (1) Pakiser, 1964 (2) Stanley et al., 1973 (3) Hoover et al., 1973 (4) Pakiser et al., 1964

Mineralization in the Summer Lake area is spotty and has not been mapped. The largest described mineralized area, the Brattain Mining District, is approximately 8 km due south of Paisley, Oregon, and contains epithermal minerals of lead, zinc, gold, mercury, copper, and silver (Peterson and McIntyre, 1970). The only other described occurrences of sulfide mineralization in the Summer Lake region are two cinnabar prospects located next to the southwestern corner of Summer Lake.

Geothermal activity evident at the surface in the Summer Lake Basin is limited to a few thermal springs and wells. With the exception of one well, the water is classified as warm. This single well has a water temperature of 47°C. Springs and wells which issue warm water are limited to two areas in the Summer Lake Basin, one about 6.5 km north of Paisley, Oregon, and the other at the northern end of Summer Lake. All of the thermal springs and wells located in the Summer Lake graben are situated near large normal faults.

Hg Anomalies

The region surrounding Summer Lake was selected as the second test area of this study. Approximately 360 sites

were sampled and analyzed in the Summer Lake Basin, using the procedures discussed above. The Hg concentrations are contoured in Figure 3 and summarized in Table 5. As in Long Valley, the Hg contours are multiples of the background concentration of Hg, 4 ppb.

Except for A-6, the origin of the Hg anomalies appears relatively straightforward. The Brattain mining district is located 1.6 km to the west and at a higher elevation than A-6. As this district is entered from the east, soil Hg concentrations change from 20 ppb to over 100 ppb. Dispersal of weathered sulfide mineralization from the "in-place"

mineralization may be responsible for the southern half of anomaly A-6. However, this explanation does not account for the northern half of the anomaly for the following reasons:

1. The northern half of A-6 is partially covered by sand dunes. These sand dunes cover sediments which could have been derived from the mineralized district.
2. The northern end of A-6 is at an elevation which would preclude the migration of sediments from the mineralized area to it.

Also, within the northern half of A-6, a few irrigation wells yield warm water (19°C). It appears, then, that geothermal activity accounts, at least, for this portion of the anomaly.

KLAMATH FALLS, OREGON

The city of Klamath Falls is located on the boundary of the Cascade and Basin and Range provinces in south-central Oregon (Figure 4). Recent major volcanic features surround the area, with Crater Lake to the north and the Medicine Lake highlands to the south. The structural setting is typical of Basin and Range regions, horsts and grabens bounded by large normal faults. The city of Klamath Falls occupies a large, northwest-trending graben. Geological cover within the region is predominately Pliocene-Pleistocene volcanic rocks with minor recent, lacustrine sediments.

A vapor-dominated geothermal reservoir exists beneath the city of Klamath Falls. Before recent water-table lowering resulting from increased residential well pumping, numerous hot springs also occurred in Klamath Falls. Business and property owners have drilled wells throughout the thermal area to obtain water for space heating.

The following reservoir characteristics are summarized from Peterson and McIntyre (1970). Hot water and/or steam (60 to 113°C) is encountered at depths between 30 and 550 m in space-heating wells. Well logs indicate that a hundred or more meters of diatomaceous tuffs and layered lacustrine sediments act as the cap rock. Fractured lava flows and zones of scoria and cinders function as the geothermal aquifer. A crystallizing igneous body is the hypothesized heat source. Thermal activity in Klamath Falls led the federal government to declare 68.8 km as a Known Geothermal Resource Area (Bowen, 1972).

Hg Anomalies

The geothermal area in Klamath Falls was sampled at the end of the summer field session (Fig. 4). The results

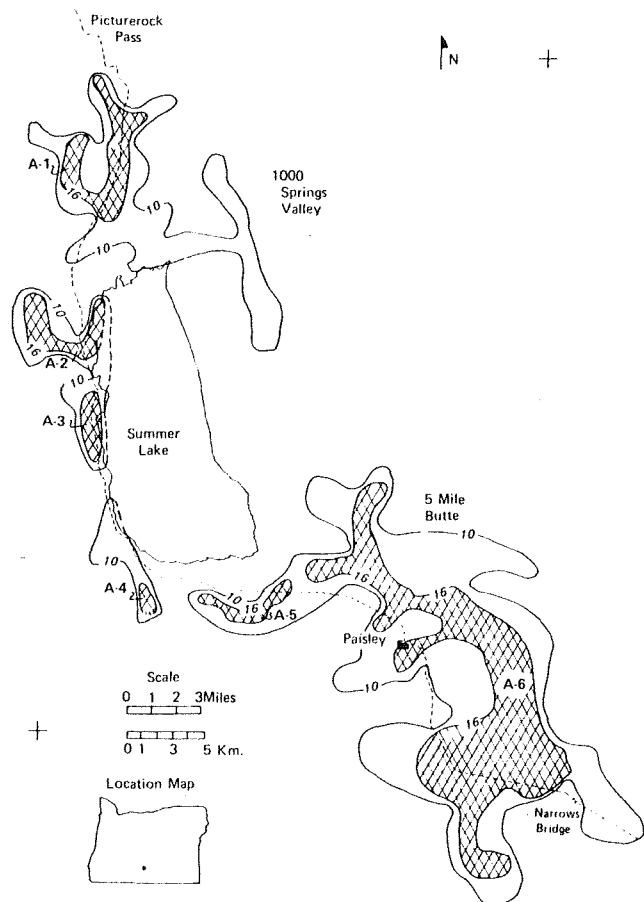


Figure 3. Mercury anomalies in Summer Lake basin, Oregon. The contours correspond to peak to background ratios of >2.5 (10) and $>4:1$ (16 ppb Hg).

Table 5. Hg anomalies in the Summer Lake Basin.

Anomaly	Peak to background concentration greater than:	Size (km ²)	Major exposed geological units	Thermal springs or wells	Mineralization	Probable origin
A-1	4:1	10	Basalt, rhyolite, alluvium	Yes	None	Geothermal activity
A-2	4:1	10	Basalt, rhyolite, alluvium	Yes	None	Geothermal activity
A-3	4:1	1.6	Alluvium	No	None	Geothermal activity
A-4	4:1	2.5	Alluvium	No	Cinnabar	Mineralization
A-5	4:1	3.3	Alluvium	Yes	None	Geothermal activity
A-6	4:1	105	Alluvium, tuff, basalt, rhyolite, dacite	Yes	Extensive evidence, the Brattain mining district	Mineralization and geothermal activity

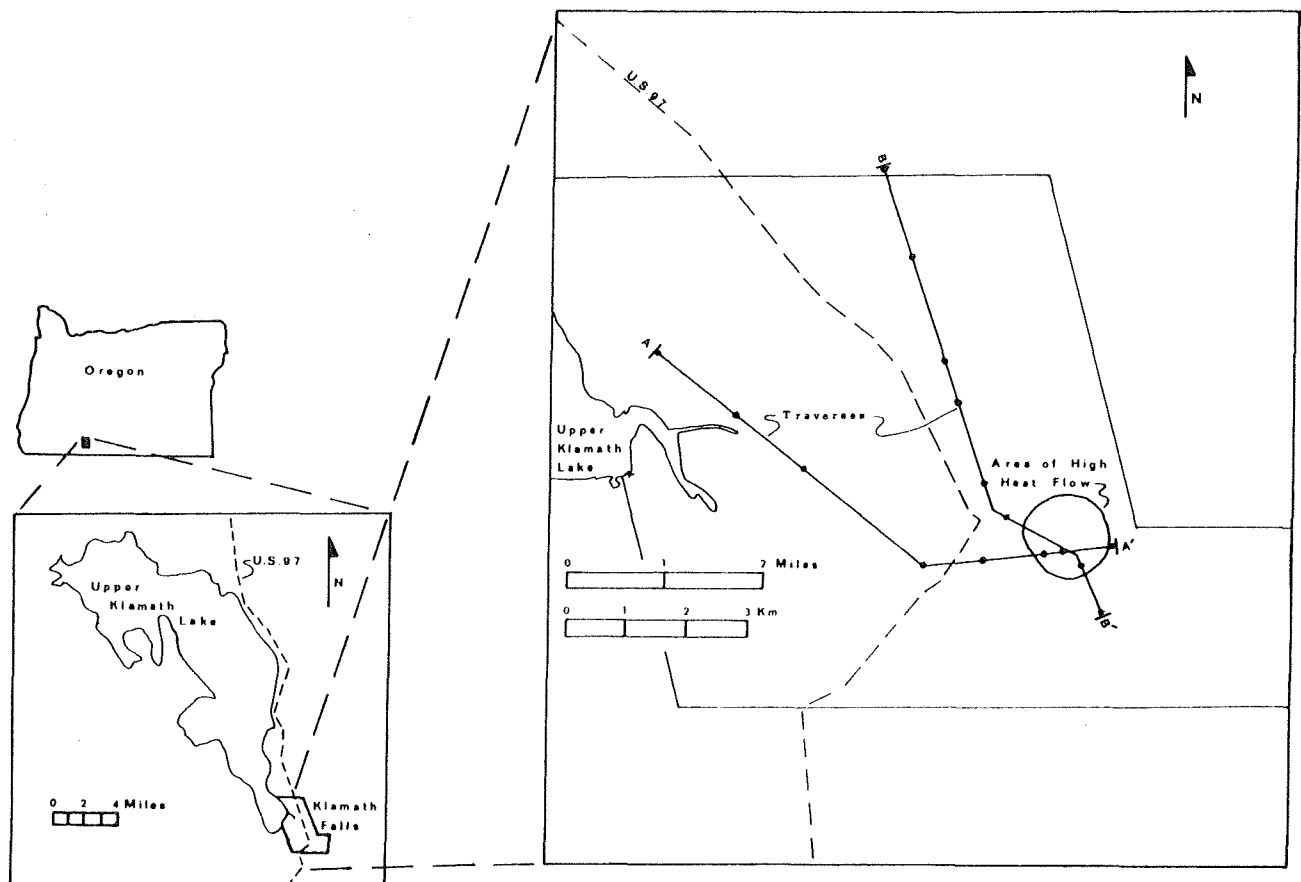


Figure 4. Klamath Falls, Oregon: Location map and position of traverses A-A' and B-B' through the area of highest heat flow.

from the 17 analyzed samples are plotted in Figure 5. The background value was not determined because time did not permit sampling outside of the known thermal area. However, a background value of 10 ppb Hg has been assigned to the area for peak-to-background determinations. This concentration of Hg is considered a normal value for soil by Williston (1964) and is larger by a factor of 2 than the measured background values at Long Valley and Summer Lake, thus providing a conservative estimate. As Figure 5 reveals, all samples have peak-to-background ratios greater than 4.8:1. Approaching the area of high heat flow, Hg concentrations increase approximately ten-fold, relative to the concentrations just outside the area of high heat flow. A sample collected in the area of high heat flow yielded 512 ppb Hg (a 51:1 anomaly).

EAST MESA IN IMPERIAL VALLEY

East Mesa is located approximately 16 km east of Holtville, California. This region is situated on the east flank of the Salton Sea structural trough, a large active rift valley. Seismic refraction data indicate that the basement is located at a depth of approximately 4 km (Biehler, Kovach and Allen, 1964). Recent deltaic sediments of the Colorado River have filled the rift valley. Soil cover today consists entirely of sand dunes.

On the basis of temperature gradient studies, Rex (1971) determined that the East Mesa region is a thermally anomalous area. A temperature gradient of 10°F per 100 feet (18.3°C/100 m) occurs here. Five wells have been drilled

in the center of this anomalous area. The data on these wells characterize the geothermal reservoir as a liquid-dominated system located in fractured sandstone.

Hg Measurements

In January, 1975, 84 soil samples were collected in and around East Mesa. These were analyzed for Hg in the laboratory at Arizona State University. Collecting samples in the field and analyzing them at a later date could present problems with obtaining accurate results. In order to minimize these potential difficulties, precautions were taken. Samples were stored in clean, airtight glass vials and left sealed until they were analyzed. Also, in order to validate delayed analysis, duplicate soil samples were collected in Tempe, Arizona, before leaving for East Mesa. The procedure for the collection and analysis of these two samples was the same as for samples taken at East Mesa. The Hg content of one sample was measured before the trip to East Mesa and the second sample was measured afterwards. The Hg concentration of both samples was 30 ± 1.1 ppb. In this case a delay of a week between sampling and analysis did not affect the results.

Based on the analytical mean of all 84 East Mesa samples, the background concentration is 5.3 ppb Hg. Using this background value, a continuous Hg anomaly was not detected at East Mesa, although isolated values were as much as four times background. The East Mesa geothermal area differs from all the other geothermal areas considered in this study in that a continuous Hg anomaly does not

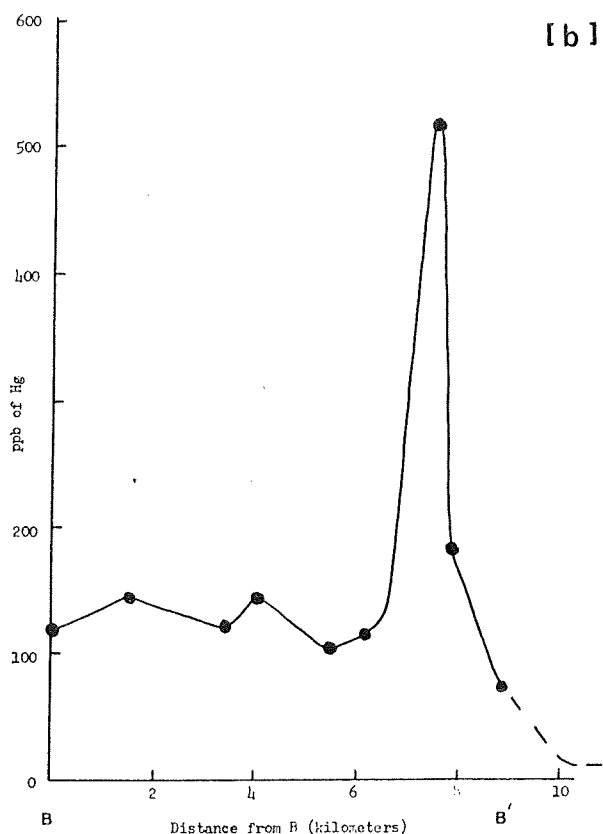
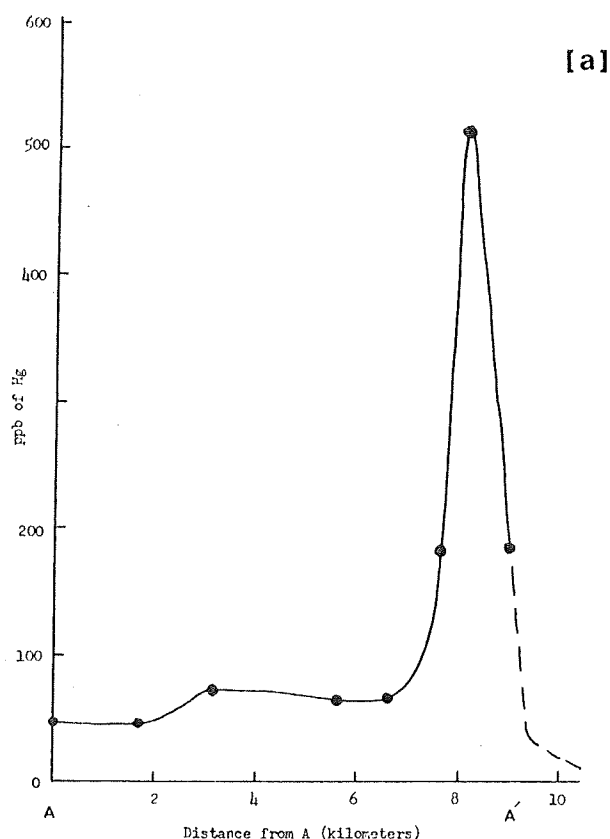


Figure 5. Mercury concentrations (in ppb) along traverses (a) A-A' (b) B-B' at Klamath Falls, Oregon.

accompany geothermal activity. Possible explanations for the lack of a Hg anomaly include the following:

1. Much of the East Mesa soil consists of quartz. Because quartz has a low collection and retention efficiency for Hg, the soil would not readily absorb Hg.
2. The overburden capping the geothermal reservoir is impermeable. Well log data from Mesa Well 6-1 indicate approximately 28 m of sediment approaching 0% porosity, with adjacent beds (130 m) having less than 2.5% porosity (U.S. Bureau of Reclamation, 1973). This low porosity may prevent the escape of Hg to the surface.
3. The large volume of clay contained in the buried deltaic sediments may absorb most of the Hg rising from the geothermal reservoir.

DISCUSSIONS AND CONCLUSIONS

Based on the observed association of geothermal activity and Hg deposits, Hg geochemistry was used as an exploration tool to locate geothermal areas. The most extensive study was conducted in and around Long Valley, California. This area has been one of the regions most thoroughly studied for geothermal activity through the use of geophysical techniques. All of the geophysical anomalies suggesting geothermal areas coincide with Hg anomalies. Further, all the hot springs also coincide with Hg anomalies. In addition, the Hg study has defined two anomalies in areas not covered by the geophysical studies, suggesting new prospective areas of geothermal activity.

The intensity of geothermal activity at Summer Lake is less than at Long Valley. Yet, here again, the Hg anomalies enclose all thermal springs and wells. An anomaly also exists over the mineralization of the Brattain Mining district, consistent with the Hg geochemical exploration method of McNerney and Buseck (1973).

The high heat flow area at Klamath Falls produces a marked Hg anomaly. Although this geothermal region is well known (its waters have long been used for space heating), it could have easily been located solely on the basis of Hg measurements.

East Mesa produced the only negative results in this series of Hg studies. Although geothermal activity occurs here, no continuous Hg anomaly was detected. There are several possible reasons for this lack of an anomaly and further work will be required in areas like East Mesa.

Several conclusions can be reached from the above studies:

1. Hg and geothermal activity are associated with one another. All thermal springs occurring in the studied areas have accompanying Hg anomalies.
2. Both broad and local Hg anomalies can be outlined, with local highs superimposed on the lower broad anomaly covering almost all of Long Valley. The Hg anomalies vary from 0.1 to 105 km² in area.
3. Hg background concentrations in the tested areas approximate 5 ppb. High peak to background ratios typically occur near hot springs; the highest detected value, near a hot spring in Long Valley, is >550:1.
4. Exploration using Hg has the advantage of being relatively rapid, inexpensive and possible in the field. Highly reproducible analytical results are available the same day samples are collected.

5. Hg exploration can be used in areas free of hot springs. In this regard it is unique among current geochemical exploration techniques.

Based on our field studies we conclude that Hg measurements, made with a suitably sensitive and precise analytical instrument, can provide an excellent exploration tool in the search for new geothermal areas.

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