Near-Surface Geochemical Investigations In The Las Hornillas Fumarolic Area, Miravalles Volcano, Costa Rica

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ABSTRACT

Preliminary investigations of out-gassing patterns associated with surface hydrothermal manifestations in the Las Hornillas area are here reported. These patterns have been resolved by using measurements of near surface concentrations of radon in ground gas, total mercury in soils, and pH of these soils obtained from sample locations systematically distributed within an area of approximately 2.5 km X 1.5 km.

Results from these investigations indicate the existance of two distinct fracture/fault systems through which gases separated from a deep thermal aquifer circualte. At the point on the surface where these systems intersect, the greatest amount of out-gassing is seen to occur. Soil mercury concentrations correlate well with shallow ground temperatures, yet appear to be more effected by near surface influences (e.g. degree of hydrothermal alteration) than do radon concentrations.

INTRODUCTION

Characteristics of out-gassing in the Las Hornillas fumarolic area have been resolved by using near surface geochemical mapping. The particular techniques employed in these investigations utilized the measurement of the inert alpha particle emitting radioactive gas radon (Rn) within shallow ground gas, the concentration of mercury (Hg), and the pH and temperature of soil at a depth of approximately 0.5 m below the surface. Sample locations were sytematically distributed within an approximate area of 2.5 km X 1.5 km, with an average sample spacing of 350 meters.

In general, Las Hornillas is situated within a broad zone designated by the Instituto Costarricense De Electricidad (ICE) as "an important geothermal anomaly," and is one of two areas where significant geochemical anomalies exist associated with surface hydrothermal manifestations (Gardner and Corrales, 1977). In addition, an intense geothermal gradient anomaly exists here that closely corresponds to a low resistivity zone (Corrales, et. al., 1977).

The results of investigations presented here are believed to be demonstative of the applicability of such geochemical techniques to the study of hydrothermal systems in Costa Rica.

GENERAL DESCRIPTION OF SURVEY AREA

Las Hornillas ("The Stoves") de Miravalles is located approximately 0.5 kilometers east of the town of Guayabo on the southwestern flank of Miravalles Volcano at an elevation of approximately 700 m above sea level, within the volcanic Cordillera del Guanacaste of northwestern Costa Rica (Fig. 1). Fumarolic activity at Las Hornillas occurs within an area of about 300 square meters, and is believed to constitute the only activity of Miravalles since the Spanish Conquest in the early 16th century (McBirney, 1958). Within the immediate vicinity of the principle fumarolic zone vegetation is sparce, and numerous boiling mud pots are accompanied by copius emissions of steam and gas. The highest measured spring temperatures (≈99°C) and highest steam and gas discharge rates occur here as well. Surface rocks in this area have been thoroughly altered to kaolinite, montmorillonite and chalcedony. White, yellow, and orange sulfate minerals also occur in several isolated pockets. Several other areas of bleached ground and associated springs exist just south and southeast of this principle zone. In general, spring discharge is more gassy in these areas and temperatires are lower (ranging from 86-94°C).

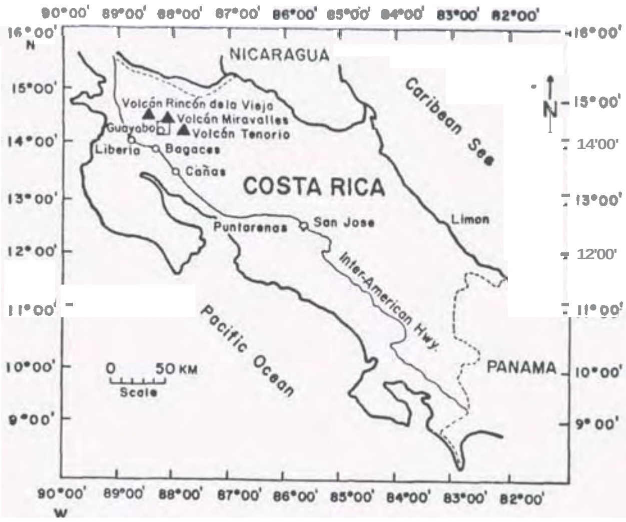

Fig. 1 General location map of Costa Rica. The Las Hornillas area is shown as an open square.

Deposition of native sulfur is seen to occur in some of these areas, whereas it is nonexistant in the principle zone.

Much of the remaining survey area north, south, and west of the principle fumarolic zone is cattle grazing land densely covered with tall grass, Geologic exposures in streambeds at various locations indicate development of a fairly mature soil profile, primarily derived from tuffs and blocky andesite lava flows.

Two exploratory geothermal wells are located within the survey area. One, PGM-1, is located approximately 700 meters south of Las Hornillas, This well, drilled to a depth of 1300 meters in July of 1979, has a maximum bottomhole liquid temperature of 244°C. The other well, PGM-2, drilled to a depth of 1208 meters in January of 1980, is located approximately 600 meters southeast of Las Hornillas and has a maximum bottom-hole liquid temperature of 219°C (ICE, 1980).

METHODS

Radon - Measurement of the concentration of the radioactive gas radon (Rn) in shallow ground gas has now become established as a viable geothermal exploration technique. Studies by various authors (Nielson, 1978; Cox, 1980a; Cox and Cuff, 1980) have shown that due to its unique chemical nature, inert Rn in ground gas can be used to delineate zones of increased permeability that are in communication at depth with areas of elevated subsurface temperatures. In a more recent test of Rn ground gas measurements as a geothermal exploration technique carried out at Wairakei, Mokai, and Broadlands geothermal fields in New Zealand, Whitehead (1981) found that there is definately a correlation of Rn alpha activity with fault structure. In a study carried out in Masaya Caldera, Nicaraqua, Crenshaw (1982) was successfully able to predict the location of faults within 80 meters of their known positions on 70% of the traverses made using this technique. He also concluded that the usefulness of this technique increased when used in conjunction with the mercury combustion method described below,

The two isotopes of radon, ^{222}Rn ($t_{½}$=3.8d) and ^{220}Rn ($t_{½}$=54.5s), are derived from decay of ^{226}Radium and ^{224}Radium respectively, accompanied by release of an alpha particle, Due to its longer half life, and thus its ability to remain mobile over greater distances, ^{222}Rn is assumed to be a greater contributor to the total radon signal measured at the surface.

The measurement of Rn was made by using commercially available alpha particle sensitive Kodak LR115, type II film. Sheets of this film were cut into 3 X 2cm squares which were affixed to the surface of cardboard strips reinforced with small, flat, wooden sticks. These strips were then fastened in verticle orientation to plastic clips at the bottom of 250 ml polypropylene cups, then burried inverted to a depth of ~0.5m at the bottom of holes dug out with a geologic rock hammer and machete. A generous amount of soil was collected and sealed in plastic sample bags, and that remaining was used to partially burry the detector cups, on top of which were placed available boulders. To facilitate ease of relocation, sample locations were marked with plastic surveyor flagging. Each detector cup was left exposed in the field for approximately 12 days to help overcome short term variations of Rn content due to meteorological, diurnal, or surface wind fluctuations. Upon retrieval the film strips were wrapped in tissue paper to minimize scratching of their surfaces, and returned to the United States for development (in 2.5M NaOH solution for 64 minutes at a constant temperature of 60°C). After development, the alpha tracks, which appear as perforations, were manually counted under 100x magnification within an area of 1cm^2 of the film, The number of tracks per cm^2 was related to the field exposure time, then recorded as T (tracks) x 10^{-2}/cm^2/hr (or simply Radon Units),

In an attempt to remove the effects of Rn emanation from the soil layer immediately below the burried detector cup, a Rn correction value was determined in the laboratory using soil samples collected at each station, The procedure for making this correction was to place the soil at the bottom of tightly sealed cups in which the same film configuration mentioned above was used. These films were exposed for 7 days, then developed and counted using the same procedure as that used for films taken from the field.

The values obtained from this measurement were then substracted from the total field measurements, The resultant "corrected" values are believed to represent the concentration of Rn derived from sources removed from the immediate vicinity of the detector cups. No attempt was made to distinguish between ^{222}Rn and ^{220}Rn isotopes.

MERCURY

Measurement of mercury (Hg) concentrations in soils has also become a fairly common technique used in geothermal exploration (e.g. Matlick and Busek, 1976; Klusman and Laudress, 1979; Cox and Cuff, 1980; Juncal and Bell, 1981). The usefullness of this element in such exploration stems basically from its high volatility at elevated temperatures, so that in deep water aquifers it would be transported with steam by simple vaporization in proportion to the underground temperature. As it approaches the surface, Hg is most likely adsorbed due to a drop in temperature, onto soils subjected to hydrothermal alteration and/or alteration by steam. Numerous studies by various authors have lent support to these ideas, In an examination of fine-grained muds of mudpots at Yellowstone National Park, White, Hinkle, and Barnes (1970) reported very high Hg concentrations which they concluded were the result of condensation from hot vapor that streams up through these muds. Koga and Noda (1976) showed that Hg concentrations in condensates at Zunil, Guatemala, are relatively high, and are related to the high content of Hg in altered rocks around fumaroles in this geothermal area.

Although statistical analysis indicates that there are likely to be two populations of Hg concentrations, one affected by geothermal activity and the other affected by secondary controls (the most important of which is the amount of organic carbon in soils), it appears that these secondary controls on Hg concentration are overwhelmed in an area of prominent geothermal activity (Klusman and Laudress, 1979).

Soil samples collected from holes dug out for placement of Rn detector cups were air dried in the laboratory and seived to <0Ø. Analysis of Hg concentrations was performed using a Jerome Model 301 Gold Film Mercury Detector (McNerney et. al., 1972), which measures total mercury collected as Hg° on gold film, after high temperature combustion of the sample. Concentrations are reported in parts per billion (ppb).

Soil Ph

The use of pH measurements in geothermal exploration is not very common; however, such measurements are believed to be useful in terms of providing additional evidence of anomalous out-gassing of volatiles (Cox and Cuff, 1980). The pH of collected soils was determined using an Orion Research Model 801A Digital pH/MV meter with a combination electrode, Each sample was seived to <0Ø, to remove course organic material, then oven heated for approximately 24 hours at a temperature of 176°C. The seived and heated sample was then mixed into a 2:1 solution of distilled water to soil by volume, and allowed to equilibrate for another 24 hours. Measurements of selected samples were repeated numerous times throughout analysis to determine reproductivity of this technique.

In addition, the temperature of soil was measured at the bottom of each Rn monitoring Station using an Omega Model HH1 Digital Thermometer with a chrome1/Alumel thermocouple.

RESULTS

The main study area covered approximately 3.75 km2 and was centered around the principle fumarolic area at Las Hornillas (Fig. 2). Sample locations were on the average spaced approximately 350 meters apart.

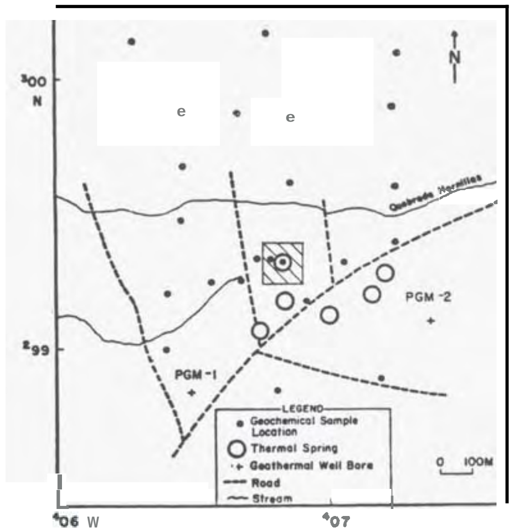

Fig. 2 Las Hornillas study area. The hatched square in the center of the figure represents the principle fumarolic zone, closed circles represent sample locations.

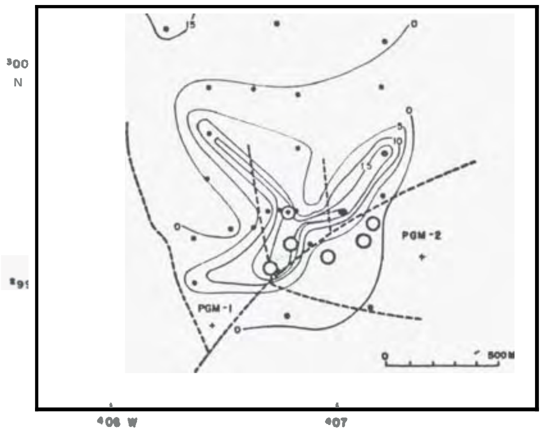

Fig. 3 Map of corrected Rn values x background at each measurement station, contoured at intervals of 5 x background.

Radon - The results of measurements of radon in shallow ground gas are presented in contoured from in Figure 3. The values used to construct this figure represent the actual corrected values times a background (soil emanation) value determined empirically for each sample location. This form of presentation was chosen because it is believed to better distinguish anomalous out-gassing zones within the general survey area as a whole. Each contour represents values that are 5 times background. The highest value recorded was 28.6 and the lowest was -1.1. Areas in which low positive and/or negative values exist are believed to represent zones where ground gas movement is either downward or static. This phenomenon is likely to be due to the presence of low permeability zones which deter the surfaceward movement of inert Rn. Replicate field measurements yielded an average standard deviation of 14%.

Mercury - Values of mercury concentration measured with the Gold Film Detector have been contoured geometrically and are presented in Figure 4. Because of the relative uniformity of soil type within this study area, no attempt was made to determine background values such as has been suggested by some authors to overcome variability in soil types (e.g. Klusman et. al., 1977; Cox, 1981). Although examination of the distribution of Hg values shows there to be two distinct populations, the major difference between them is undoubtedly related closely to the degree of hydrothermal alteration the soils have experienced in areas from which they were obtained. This belief is supported by the apparent good correlation between Hg concentration and both soil pH and temperature (r^2 = -0.6160 and r^2 = 0.9583, respectively).

The highest soil mercury concentration measured was 3051 ppb in a sample obtained from a location ≈50 meters west of the principle fumarolic zone. In this area vegetation was seen to have been recently destroyed and the recorded ground temperature (53°C) was the highest in this study other than for thermal springs. The lowest value obtained was 44.47 ppb in a sample from a location at which the lowest ground temperature was recorded (22°C). The highest values of Hg concentration were measured in samples of altered rock 20 meters west (20,000 ppb) and 200 meters northeast (17,000 ppb) of the principle fumarolic zone. Measurement of the concentration of dried fine-grained mud from boiling mudpots yielded a maximum of 9430 ppb. From repeat measurements of numerous soils an average standard deviation of 10% was obtained.

<u>Soil pH</u> - A contour map of soil pH values is presented in Figure 5. Immediately apparent upon inspection of this figure is the striking homogenity of values outside of the outlined anomalous zone on all sides. This is generally seen as being indicative of the uniformity of soil type within the study area.

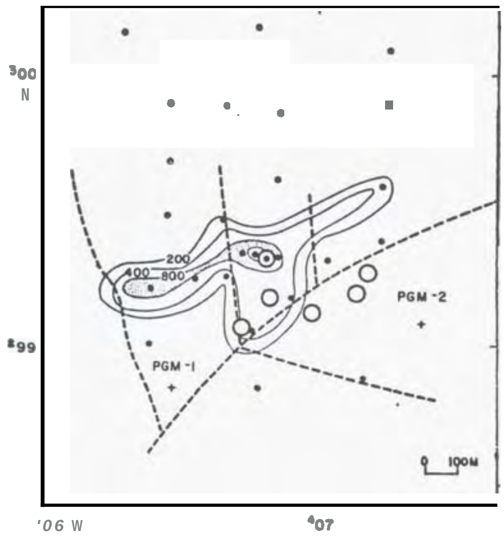

Fig. 4 Concentration of soil Hg, contoured geometrically. Concentrations are in parts per billion (ppb).

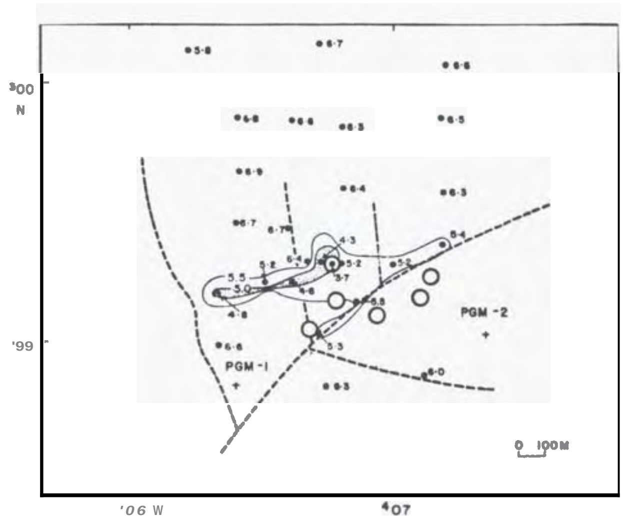

Fig. 5 Map of soil pH values, contoured at intervals of 0.5 pH units.

The lowest pH value (3.7 pH units) was obtained from a soil collected from a location directly above the most vigorous mudpot in the principle fumarolic zone, and not from a spot 50 meters west where visible steam was seen escaping the ground once the detector hole was dug, and where the highest ground temperature was measured (53°C). It should also be noted that the highest radon concentration (216.4 R.U.) was obtained at this very spot. The highest measured soil pH was 6.8 pH units. The lowest overall pH value (2.75) was obtained from a sample of fine-grained mud from a boiling mudpot, Repeat measurements of the pH of various soil samples yielded an average standard deviation of 0.07 pH units.

DISCUSSION

The chemistry of spring waters from within the principle fumarolic zone at Las Hornillas suggests that a deep, chlorinated aquifer characterized by strong SiO_2, K, B, Cl and Mg anomalies exists at depth below this area, Alkali and SiO_2 geothermometers suggest reservoir base temperatures of as much as 240°C (Gardner and Corrales, 1977). Steam separated from this saline aquifer is believed to heat shallow groundwater to sustain the fumaroles of Las Hornillas (Corrales, et. al., 1977). If this situation does indeed exist, and there are separate, deep and shallow fluid circulation systems, it is more than likely that they are in communication at depth through a highly permeable, fractured or faulted zone,

The results shown in Figures 3-5 strongly suggest that there are at least two such zones located within the study area. A remarkable similarity exists between patterns derived from contouring Hg and pH data, which corresponds to the fairly good inverse statistical correlation between them (r^2 = -0.6160). Examination of these patterns indicates the existance of two major features: an elongate zone with a northeast-southwest orientation; and an elongate zone which first trends off in the northwest direction, then broadens southwest of the principle fumarolic area. The lowest measured pH and highest Hg values observed in this study are of samples which lie within the southwestern portion of this first zone (indicated by stippling in Figures 4 and 5).

The pattern obtained from contouring corrected Rn values x background is somewhat different than those of pH and Hg. One significant difference is the pronounced definition of an elongate northwest trending zone. In addition to this, a southwest trending zone indicated by stippling in the figure, is evident within which significantly high values exist. A well defined southwest-northeast anomalous zone such as is evident in figures 4 and 5 does not exist.

Differences in the fundamental behavior of Rn and Hg as they approach the surface in the ground-gas system are likely to lead to a certain absence of correlation between their respective measured concentrations. Numerous field studies have shown that this is in fact the case (e.g. Cox and Cuff, 1980; Crenshaw, 1982), although various explanations have been offered to explain it. Excellent statistical correlation (r^2 = 0.9584) between Hg values and temperatures measured at a depth of 0.5m in this study, suggests that vaporous Hg is much more sensitive to temperature changes than Rn, Thus it is believed that the patterns obtained by contouring Hg data are probably more indicative of near surface interaction between gases derived at depth and those of shallow ground systems, than those obtained by contouring values of Rn concentration. With this in mind, the Rn x background contour map can be viewed as being representative of the deep irculation pattern of gases through high permeability zones towards the surface. The outlined anomaly west of Las Hornillas is most likely the surface signiture of a deep arcuate fault system which makes up part of the burried eastern rim of the Guyabo Caldera located further west.

Intrusion of magma into this zone probably produced associated fractures which are more superficial in nature. It is through these fractures that gases separated from the deep aquifer interact with shallow groundwater to sustain the fumaroles,

This idea is supported by the fact that no Rn anomaly exists in the area of the strong, southwest trending pH and Hg anomalies (most likely representing more superficial fractures).

The decrease in temperature of aquifer fluids and gases which may be circulating through these fractures, caused by interaction with cooler near surface groundwater, would lead to the deposition of Hg and possibly precipitation of silica minerals which might lead to non-transmittance of Rn. Where these two different fracture/fault systems intersect, however, the highest measured concentrations of Rn and lowest measured values of pH exist (directly above the most active fumaroles). A similar case has been reported by Whitehead (1981), where the highest Rn values obtained were from the intersection of two faults at Wairakei.

In general, the data presented here also show very strong indications of the existance of a ground-gas convection system in which upwelling occurs through permeable structures (faults/fractures), and downflow or static flow occurs relative to "cold" impermeable zones.

CONCLUSIONS

The results presented above indicate that at Las Hornillas the near surface Rn signature is closely related to circulation through associated, extensive fractures of gases separated from a deep thermal aquifer. This is partially supported by the fact that the highest measured Rn concentrations correspond with the lowest measured soil pH. Although good correlation between Hg concentration and shallow ground temperature exists, when compared to Rn concentration data, this occurance appears to be greatly influenced by near surface conditions (e.g. degree of hydrothermal alteration).

Recently it has been suggested that within high temperature regions measurement of soil pH concentrations can be effective in identifying drilling targets, based on close correspondence between high geothermal gradient zones and high Hg concentration anomalies (Matlick and Shiraki, 1981). This study, however has shown that only when used in conjunction with other near surface geochemical techniques is the measurement of Hg concentration truly effective as an aid to deciphering subsurface fluid and gas circulation patterns (knowledge of which is essential to drilling site selection).

This study also demonstrates the applicability of such geochemical investigations to the study of hydrothermal systems in Costa Rica, including those that may be closely related to active volcanoes where large scale convective systems may have developed.

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REFERENCES

Corrales, M.F., Koenig, J.B., and Kuwada, J.T., 1977, Exploration of the Guanacaste, Costa Rica, geothermal system: Geotherm. Resour, Counc., Trans., v. 1, p. 57-58.

cox, M.E., 1980, Ground radon survey of a geothermal area in Hawaii: Geophys. Res. Lett., v. 7, no. 4, p.283-286.

cox, M.E. and Cuff, K.E., 1980, Rn and Hg Surveys: Geothermal exploration in N.E. Maui, Hawaii: Geotherm. Resour. Counc., Trans., v. 4, p. 451-454.

Cox, M.E., 1981, An approach to problems of a geothermal mercury survey, Puna, Hawaii: Geotherm, Resour. Counc., Trans., v. 5, p. 67-70, Hawaii Institute of Geophysics, Contribution no. 1294,

Crenshaw, W.B., 1982, Ground radon and mercury surveys for location of fault systems, Masaya Caldera, Nicaragua: Senior Honors Thesis, Dartmouth College.

Gardner, M.C., Corrales, Rodrigo, 1977, Geochemical and hydrothermal investigations of the Guauacaste geothermal project, Costa Rica: Geotherm. Resour. Counc., Trans,, v, 1, p,101-102.

Institute Constarricense de Electricidad, 1980, Proyecto Geotermico de Miravalles, antecedentes y situación actual, 24pp.

Juncal, R.W., and Bell, E.J., 1981, Solid-sample geochemistry study of western Dixey Valley, Churchill County, Nevada - part II, soil geochemistry: Geotherm. Resour. Counc., Trans., v.5, p.51-54.

Klusman, R.W., and Landress, R.A., 1979, Mercury in soils of the Long Valley, California, Geothermal System: Jour, Volc. Geotherm. Res., p. 49-65.

Koga, Akito, and Noda, Tetsuro, 1976, Geachemical prospecting in vapor-dominated fields for geothermal exploration: Second U.N. Symp, Devel. Use. Geotherm. Resour. v. 1, p. 761-766.

Matlick, J.S., and Buseck, P.R., 1976, Exploration for geothermal areas using mercury; a new geochemical technique: Second U.N. Symp. Devel. Use. Geotherm, Resour., v, 1, p. 785-792.

Matlick, J.S., and Shiraki, M., 1981 Evaluation of the mercury soil mapping geothermal exploration techniques: Geotherm. Resour. Counc., Trans., v. 5, p. 95-98.

McBirney, A.R., 1958, Catalogue of active volcanoes of the world including solfatara fields: Part VI Central America, p, 137-138.

McNerney, J.J., Buseck, P.R., 1972, Mercury detection by means of thin gold films: Science, v. 178, p. 611-612.

Nielson, D.L., 1978, Radon emanometry as a geothermal exploration technique; theory and an example from Roosevelt hot springs, KGRA, Utah: Earth Sci. Lab., Univ. Utah Res. Inst., ESL-14, 31pp.

White, D.E., Hinkle, M.E. and Barnes, I., 1970, Mercury contents of natural thermal and minerals fluids: U.S. Geol. Survey Prof. Paper 713, p. 25-28.

Whitehead, N.E., 1981, A test of radon ground measurements as a geothermal prospecting tool in New Zealand: New Zealand Jour. Sci., v. 29, p. 59-64.