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### POTENTIAL FOR USE OF GAS FLUX MEASUREMENTS IN SURFACE EXPLORATION FOR GEOTHERMAL RESOURCES

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### ABSTRACT

Soil gas fluxes to/from the atmosphere have been measured at Roosevelt Hot Springs, Utah, Beowawe and Steamboat Springs, Nevada. Methane was measured in all three areas during the summer of 1995. Methane, CO, and stable carbon isotopes were measured at Roosevelt Hot Springs in the winter of 1996. A subtle relationship between CH4 fluxes and the geothermal anomalies was found and seasonal contrast exists because of methanotrophic oxidation in soils. The existence of methanotrophic oxidation was confirmed by stable carbon isotopic evidence. A strong positive CO<sub>2</sub> flux existed over the entire KGRA at Roosevelt, and stable carbon isotopic data supported the existence of geothermal CO<sub>2</sub> in the shallow soil gas. This geothermal CO2 was diffusing to the atmosphere where it was detected as a positive flux. The use of gas flux measurements has potential for reconnaissance geothermal exploration.

### INTRODUCTION

Soil gas geochemistry has been applied to the exploration for petroleum and gas reservoirs, mineral deposits, and geothermal reservoirs. Frequently, gases or volatiles adsorbed on soil materials have been applied to geothermal exploration, with the presumption the soil anomaly has a vertical expression of the reservoir below. Many of these techniques are indirect, for example, the measurement of mercury adsorbed onto soil materials as an indirect indicator of subsurface heat flow. Generally, soil gas techniques measure the concentration of a component in free soil gas, or adsorbed onto soil particulate. Rarely, if ever, is the direct measurement of gas transport rates through the soil into the atmosphere attempted.

This research reports on initial results of measurement of gas fluxes from the soil to/from the atmosphere above geothermal areas. The gases measured were  $CH_4$  and  $CO_2$  in the Roosevelt Hot Springs area of Utah, and  $CH_4$  fluxes at Beowawe and Steamboat Springs, Nevada. These flux measurements are based in part on the Fischer-Tropsch reaction:

The equilibrium position of this reaction is determined by temperature in the reservoir, and the components may leak upward where they can be detected. Most soils are also net producers of  $CO_2$ , which slowly leaks to the atmosphere, which can potentially produce a noisy signal.

### SAMPLING AND ANALYTICAL PROCEDURES

The Roosevelt Hot Springs area was sampled for CH<sub>4</sub> flux measurements in June, 1995, and the Beowawe and Steamboat Springs areas in July, 1995. Sixty-six locations were sampled at Roosevelt, and 33 locations each were sampled at Beowawe and Steamboat Springs. The Roosevelt Hot Springs area was sampled again for CH<sub>4</sub> and CO<sub>2</sub> measurements and flux calculations in January, 1996.

Sampling was done using flux chambers with cross-sectional areas of  $1.00 \text{ m}^2$ . A collar constructed of aluminum bar was sealed against the ground by pushing the sharp edges into the ground and sealing uneven edges with soil. The flux chamber fits into deep slots in the collar, and water is squirted into the slots to improve the seal. The chambers were covered with plastic tarps to reduce solar heating under the chambers. The air under the chamber was mixed by small, low rpm fans operated by externally-mounted motors powered by a 12 v battery.

The sampling locations were sampled in triplicate. Three independent

chambers were set up 10 m apart. Stakes were placed at one of the triplicate locations so the location could be accurately recovered, and the other two were then recovered by measurement. Gas samples were taken at timed intervals from under the chambers through a septum and a sample of the ambient atmosphere was also taken at each location. There were a total of 10 individual gas samples at each location. The gas samples were sealed in 10 mL vials which had a special "HyCar" stopper, a teflon sheet to seal the needle hole, and an aluminum crimp top cap to hold the seal in place.

The samples from a sampling trip were analyzed for CH<sub>4</sub> in random order by column gas chromatography using a Hewlett-Packard Model 5730A gas chromatograph. The column was 1/8" by 6 ft, packed with alumina, operated isothermally at 100°C, using high purity N<sub>2</sub> as a carrier gas, with flame ionization detection. The CO<sub>2</sub> was determined on the samples by gas chromatography using thermal conductivity detection. Separation of CO<sub>2</sub> from other components was accomplished using a "Hayesep D" column operated at 40°C with helium as the carrier gas. A 1.00 mL sample was injected using a gas-tight syringe with a Chaney adapter to improve precision in the volume of sample being injected. Secondary standards were made by mixing measured amounts using synthesized standards from Scott Specialty Gases in gas dilution bottles. These secondary standards were used to construct calibration curves for determination of  $CH_4$  or  $CO_2$  concentration.

If there is a positive flux of a gas from the soil to the atmosphere, the concentration of the gas will increase under the chamber with time, relative to the atmospheric concentration. If there is a negative flux, the concentration will decrease under the chamber with time. The flux for an individual chamber at a location is calculated using the atmospheric concentration at that location as the "zero time" sample. The change of concentration with time (dc/dt) was used, along with the volume under the flux chamber, to calculate flux.

In addition, samples for stable carbon isotopic analysis were taken at selected locations. The three selected locations were in the "anomalous" area, which is a north-south band east of the Opal Mound Fault where a temperature anomaly was observed at 1.0 meter depth. The  $\delta^{13}$ C of CH<sub>4</sub> and  $\delta^{13}$ C of CO<sub>2</sub> were measured for the final flux sample in each triplicate flux measurement. The same isotopic ratios were measured in soil gas at depths of 30 cm, 60 cm, and 100 cm at each of the three selected locations. An air sample was collected at each of the three locations for isotopic analysis. Gas samples were taken from the steaming ground in Negro Mag Wash north of the power plant, and from steaming ground at the old Roosevelt Hot Spring.

The stable carbon isotope ratios were determined by a new technique that allows determination of isotopic ratios on small samples, rather than 1-10 liter samples. This technique is gas chromatography-micro-combustionisotope ratio mass spectrometry (irmGCMS; Merritt et al. 1995; Sansone et al. 1996). The isotopic ratios were determined in the lsotope Biogeochemistry Laboratory at the University of Hawaii on a Finnigan MAT 252 isotope ratio mass spectrometer.

## RESULTS OF SUMMER MEASUREMENTS OF METHANE FLUXES

The results of the  $CH_4$  flux measurements at Roosevelt, Beowawe, and Steamboat Springs areas indicated upon average, negative  $CH_4$  fluxes over the sampled areas. Table 1 lists the mean, standard deviation, minimum and maximum flux values for sampled locations. Each of the locations, in turn, represents the average of triplicate flux measurements. Most of the triplicate measurements were not all of the same sign, suggesting small scale variability on the 10 m level. Similar small scale variance was found in the sedimentary basin studies of Jakel and Klusman (research in progress).

The results suggested a small negative flux in all three sampled areas, although the standard deviation allowed for a possible overlap with zero flux, particularly for Beowawe and Steamboat Springs. The most probable cause for a negative flux is consumption of  $CH_4$  by methanotrophic bacteria in the soil. If there is a flux of  $CH_4$  from the geothermal reservoir, it was not apparent at the surface. High summer temperatures in the soil would

potentially enhance the methanotrophic consumption of  $CH_4$ , whether from the reservoir or from the atmosphere.

A contour map of the measured fluxes at Roosevelt Hot Springs is shown as Figure 1. The distribution of areas of positive and negative fluxes seemed to be random, and did not reflect the surface expression of the geothermal areas. The known area of geochemical anomalies in soil gas and in adsorbed species at Roosevelt lies within the central part of the KGRA. It appears that if there is a CH<sub>4</sub> flux from the reservoir, it was not measurable at the soil-atmosphere interface. Similar distributions of CH<sub>4</sub> fluxes for Beowawe and Steamboat Springs showed an apparent random distribution of positive and negative CH<sub>4</sub> fluxes. There was possibly an equilibrium between fluxes and consumption by methanotrophic bacteria:

## MODIFICATION OF RESEARCH BASED ON INITIAL RESULTS

An adjustment of the research was made as a result of finding negative  $CH_4$  fluxes over all three geothermal areas where measurements were made and a pattern that was not obviously related to the known anomalous area at Roosevelt. The revised plan was to repeat the flux sampling for  $CH_4$  at Roosevelt in early January, 1996. The possibility of lower methanotrophic activity in the soils may allow for a signal to reach the surface. In addition, measurements of  $CO_2$  fluxes at the same locations as the  $CH_4$  fluxes would be made. Carbon dioxide is the other major constituent in the Fischer-Tropsch reaction shown in Equation (1). If there is geothermal production of  $CO_2$ , it may be more likely to appear in the winter, due to lower biological activity in the soils.

# RESULTS OF WINTER SAMPLING OF GAS FLUXES AT ROOSEVELT HOT SPRINGS

The results of winter CH<sub>4</sub> flux measurements at Roosevelt Hot Springs area initially appeared similar to that of the sampling in June, 1995. A random distribution of small magnitude positive and negative fluxes were observed (Figure 2). The average CH<sub>4</sub> flux, standard deviation, and range for the winter sampling at Roosevelt Hot Springs is shown in Table 1. The mean flux for the 66 locations was slightly higher, but still essentially zero, and the standard deviation and range were much greater, which was an important clue in the understanding of the processes occurring with CH, in the soil gas. Seasonal differences in mean flux value have been observed in other sedimentary basins, which seem to be related to soil moisture status (Jakel and Klusman, Research in Progress). This data suggested that methanotrophic bacterial oxidation was occurring in the soils of the Roosevelt area in the winter as well as the summer, but at different rates.

The CH<sub>4</sub> concentrations and stable carbon isotopic analysis of CH<sub>4</sub> from the atmosphere, steaming ground, soil gas, and flux samples are shown in Table 2. The average CH<sub>4</sub> concentration in air at Roosevelt was  $1.69\pm0.078$  ppmv and the  $\delta^{13}$ C for air averaged - $47.51\pm0.47$ %. The CH<sub>4</sub> concentration was typical for North American continental air in the winter, and not Table 1. Summary Results of Gas Flux Measurements Over Known Geothermal Resource Areas.

	Nn	Mean ng CH₄m⁻²day⁻¹	Standard Deviation	Range mg CH₄m <sup>-2</sup> day <sup>-1</sup>
Methane: Summer, 1995 Roosevelt Hot	5			
Springs, UT	66	-1.55	1.38	-5.25 to +1.48
Beowawe, NV	33	-0.64	1.44	-4.49 to +2.45
Steamboat				
Springs, NV	33	-0.04	1.51	-3.05 to +2.55
Methane: Winter, 1996 Roosevelt Hot				
Springs, UT	66	0.02	5.55	-11.2 to +20.8
	N	Mean	Standard	Range
	IN N	ng CO <sub>2</sub> m "day "	Deviation	
Carbon Dioxide: Winter, "	1996			
Springs, UT	66	1243.4	1227	0.0 to +8036.

being downwind from any sources of methanogenesis. The global atmospheric CH<sub>4</sub>  $\delta^{13}$ C is between -47 and -48‰ (Schoell, 1988). The steaming ground averaged 1.73±0.24 ppmv and the  $\delta^{13}$ C was -47.57±0.60‰, which is obviously similar in CH<sub>4</sub> concentration and  $\delta^{13}$ C to that of atmospheric air. Literature data on the carbon isotopic composition of geothermal CH<sub>4</sub> has a relatively wide range, overlapping the small range for atmospheric air. If the CH<sub>4</sub> collected from the steaming ground had a significantly different isotopic composition, a geothermal source may have been recognizable. This suggests that stable carbon isotopes do not allow one to distinguish geothermal CH<sub>4</sub> from atmospheric CH<sub>4</sub> at Roosevelt.

The stable carbon isotopic data on soil gas CH4 does allow for some conclusions to be drawn. A small temperature anomaly occurs at 1.0 meter depth at the Opal Mound and Main Road sampling site, and the old Roosevelt Hot Springs site was substantially warmer at depth probably due to the proximity of steaming ground. During the January, 1996 sampling, the deeper samples had even more temperature contrast. If methanotrophic oxidation of CH<sub>4</sub> were occurring, the residual CH<sub>4</sub> will be isotopically heavier than the starting CH4 (Whiticar and Faber, 1986). An increasingly negative  $\delta^{13}$ C value suggests a higher proportion of the CH4 has been oxidized. Since warmer temperatures favor biogenic activity, the degree of methanotrophic oxidation of CH<sub>4</sub> should increase with soil depth in the winter. The Opal Mound and Main Road locations show less negative  $\delta^{13}C$ values with increasing depth, consistent with an increasing degree of microbial oxidation with increasing depth. The old Roosevelt Hot Springs location had the greatest soil temperature anomaly, which could potentially allow significant methanotrophic oxidation even in the 30 cm sample. There was also more uniformity of  $\delta^{13}$ C values between the three different depths at the old Roosevelt Hot Springs location.

All soil gas samples, except one, were isotopically heavier than air or steaming ground samples. The one exception has essentially the same  $\delta^{13}$ C value as air or steaming ground. From this one can conclude that significant methanotrophic oxidation of CH<sub>4</sub> was occurring in the soil. The nine flux chamber samples, taken after 150 minutes in place had an average  $\delta^{13}$ C value of -46.12 ± 0.70‰. This was slightly heavier than air, but overlapped with the isotopic composition of CH4 in air. When the chambers were placed in the collars, there was atmospheric air under the chamber. Upward diffusion of isotopically heavier CH4 from the soil into the chamber will change the  $\delta^{13}$ C to a less negative value. Downward diffusion of atmospheric CH4 into the soil to supply methanotrophic bacteria favors the lighter isotope, leaving a heavier residual CH4 in the chamber. Either process should tend to cause the residual CH4 to become isotopically heavier.

The average CH<sub>4</sub> concentration in the nine chambers at the three selected locations at the end of the flux integration was  $1.66\pm0.17$  ppmv. This is slightly less, but overlapping with the average air concentration of  $1.69\pm0.078$  ppmv. The average flux for the nine chambers was  $-0.58\pm1.23$  mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>. The slightly lower average CH<sub>4</sub> concentration in the flux chambers is consistent with a small negative flux and consistent with methanotrophic oxidation of atmospheric CH<sub>4</sub>, not oxidation of geothermal CH<sub>4</sub>.

A Spearman Rank correlation was computed for the flux measurements at the 66 locations (Table 3). Of particular interest is the negative correlation of  $CH_{4(summer)}$ vs.  $CH_{4(winter)}$ . If only one process were operating continuously to control  $CH_4$  fluxes, these two sets of measurements taken six months apart should have a positive correlation coefficient. Instead, there was a significant negative correlation. Furthermore, neither

	<b>Opal Mound</b>	Main Road	Old Roosevelt	Steami	ning Ground	
	•		Hot Springs	RHS	Negro Mag	
CH <sub>4</sub> Conc.			·			
in air or	1.78	1.64	1.65	1.50	1.68	
steaming grou	nd			1.55	2.18	
(ppmv)				1.75	1.71	
δ <sup>13</sup> C for						
CH₄ in air	а	-47.18	-47.84	-47.04	-47.88	
or steaming				-47.39	-47.74	
ground (‰)				-46.85	-48.50	
Soil gas						
30 cm (ppmv	) 1.07	1.73	0.89			
δ <sup>13</sup> C <sub>CH4</sub> (‰} –	43.83	-47.62	-32.84			
60 cm (ppmv	) 0.54	1.38	1.14			
δ <sup>13</sup> C <sub>CH4</sub> (‰)	-39.44	-33.09	-33.12			
100 cm (ppm)	/) 1.25	2.54	1.47			
δ <sup>13</sup> C <sub>CH4</sub> (‰)	-31.76	а	-34.37			
CH₄ Flux						
(mg m <sup>-2</sup> d <sup>-1</sup> )						
Ā	-0.88	-3.57	· -0.46			
в	-0.41	0.35	0.02			
С	0.73	-0.33	-0.69			

Table 2. Methane Concentrations and Stable Carbon Isotopic Ratios at Selected Locations in the Roosevelt Known Geothermal Resource Area (Winter, 1995-96).

<sup>a</sup> Data lost due to machine or operator error.

seasonal measurement of CH4 flux correlated significantly with  $CO_2$  flux. Therefore, the process operating on  $CH_4$ was different from the process controlling CO<sub>2</sub> flux. If the difference in CH<sub>4</sub> flux calculated as [CH<sub>4(summer</sub>] - [CH<sub>4(winter</sub>]] is compared with the CH4 flux in the two seasons, there was a significant positive correlation with CH4(summer) and a significant negative correlation with CH4(winter). This data suggests that methanotrophic oxidation of CH4 in the soil operated over the entire sampled area in the summer, but only over areas of higher heat flow in the winter. This is also consistent with the stable carbon isotope data in Table 2. It is also consistent with a higher mean CH<sub>4</sub> flux in the winter, and a greater standard deviation in  $\mathsf{CH}_{\mathtt{A}}$ fluxes. Czepial et al. (1995) has measured the depth where CH4 oxidation takes place in soils and found the highest rate in the 3-6 cm range. During the winter measurements at Roosevelt, the soils at this depth were generally frozen, except possibly in those areas where there was thermal leakage.

Figure 3 shows a contour map of the differences in  $CH_4$  fluxes in the two seasons for the 66 locations where flux measurements were made. Areas of positive values are areas where the methanotrophic oxidation of  $CH_4$  in soils continued during winter months. This difference map outlines the areas of extensive faulting and the known subsurface reservoir rather well. An important conclusion, is that in the case of the Roosevelt Hot Springs area, measurement of  $CH_4$  in the atmosphere or measurement of soil fluxes of  $CH_4$  will not be effective as an above ground exploration tool, in either summer or winter conditions. The contour map of differences shown in Figure 3 demonstrated the  $CH_4$  measurements were not random values representing noise in the sampling and analytical process, but was a subtle, indirect indication of thermal leakage (heat flow).

### Carbon Dioxide Fluxes at Roosevelt Hot Springs

The results of  $CO_2$  flux measurements at Roosevelt Hot Springs are shown in Figure 4 and Table 1. A cumulative frequency plot clearly indicated two populations of CO, flux values, with a break in slope at approximately 250 mg CO<sub>2</sub> m<sup>-2</sup>d<sup>-1</sup>. The lower flux samples were primarily from areas in the southern portion of the sampled area, which may be the result of silica sealing faults, inhibiting the amount of CO<sub>2</sub> that was escaping to the atmosphere. A number of these corresponded to the location of the Opal Mound Fault, the Negro Mag Fault, and inferred fault locations. The CO<sub>2</sub> fluxes of Figure 4 shows areas of high and low flux with some degree of parallel orientation to the main trends of faulting in the area. Whether this flux adequately outlines the geothermal area is questionable because true background may be outside the sampled area. It is possible that a very large area of anomalous CO2 flux exists, which covers the

	CO <sub>4(summer)</sub>	CO <sub>4(winter)</sub>	Difference	CO <sub>2(winter</sub>
	1.000	-0.349	0.526	-0.006
	-	(0.005)	(0.000)	(0.959)
CH <sub>4(winter)</sub>	-0.349	1.000	-0.971	0.014
-(()()())	(0.005)	-	(0.000)	(0.907)
Difference	0.526	-0.971	1.000	-0.019
	(0.000)	(0.000)	-	(0.878)
CO <sub>2(winter)</sub>	-0.006	0.014	-0.019	1.000
E(*********/	(0.959)	(0.907)	(0.878)	-

 Table 3.
 Spearman Rank Correlations of Soil Gas Fluxes at Roosevelt Hot Springs (Significance in Parentheses).

entire KGRA at Roosevelt Hot Springs. This suggest potentially favorable opportunities for reconnaissance exploration in the Basin and Range.

The CO<sub>2</sub> concentrations and stable carbon isotopic analyses of CO<sub>2</sub> from the atmosphere, steaming ground, soil gas, and flux samples are shown in Table 4. The average CO<sub>2</sub> concentration in air was 350 ppmv and the  $\delta^{13}$ C for CO<sub>2</sub> in air at the three locations averaged -11.20  $\pm$  0.19‰. The average  $\delta^{13}$ C for CO<sub>2</sub> in air is approximately -7.5‰ as a global average. The difference between -7.5‰ and -11.2‰ might be explained as a shift toward lighter values caused by aerobic decay and soil respiration involving isotopically light organic matter in the soil. Since the sampling was in the winter, no active photosynthesis was occurring in the region, which would selectively remove isotopically lighter CO<sub>2</sub>, causing a shift in remaining CO2 to heavier values. On a global basis, atmospheric CO<sub>2</sub> would be expected to be isotopically heavier than observed in the atmosphere at Roosevelt in the winter.

The CO<sub>2</sub> from the steaming ground averaged -6.79  $\pm$  0.23‰, excluding sample 4002, which had an isotopic concentration similar to air. The low CO<sub>2</sub> concentration in sample 4002, relative to the other five steaming ground samples also suggested significant air dilution. Literature data for geothermal systems around the world suggest a typical range for  $\delta^{13}$ C of -1 to -9‰ for CO<sub>2</sub> in geothermal systems (Giggenbach, 1982).

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Some observations about the soil gas samples include increasing  $CO_2$  concentration with depth, suggesting a source from below. Eight of the nine soil gas samples contained  $CO_2$  which was isotopically heavier than the average samples being isotopically heavier than geothermal  $CO_2$ . With the exception of one of nine samples from the three locations, the isotopic composition becomes heavier with depth, which is also consistent diffusive loss of geothermal  $CO_2$  to the atmosphere.

A fractionation factor for relative diffusive loss, a can be calculated as the square root of the ratio of masses of the lighter molecule ( ${}^{12}CO_2$ ) to the heavier molecule ( ${}^{13}CO_2$ ). This gave an a value of 0.9888, which can be used in the Rayleigh equation to estimate the fraction, f, of geothermal CO<sub>2</sub> remaining in the soil gas:

$$R/R_0 = f^{(\alpha-1)} \tag{2}$$

where R and R<sub>o</sub> are the isotopic ratios of CO<sub>2</sub> at the depth in the soil of interest, and of the geothermal source CO2, respectively. We have assumed the 100 cm soil gas samples have the highest proportion of geothermal CO<sub>2</sub> and the least possible amount of CO2 from either the atmosphere, or from soil respiration of organic matter, diluting the soil gas. Samples from this depth were then the most appropriate to use in a calculation of the amount of geothermal CO2 remaining in the soil gas. This calculation yielded f values of 0.71 for the Opal Mound location, 0.87 for the Main Road location, and 0.72 for the old Roosevelt Hot Spring location. Alternatively, one can express the diffusive loss of geothermal CO<sub>2</sub> from the 100 cm depth in the soil gas to range from 13-29% for the three locations. The important conclusion is that there is loss of geothermal CO<sub>2</sub> to the atmosphere in the Roosevelt Hot Springs area. This is also recognized as positive CO<sub>2</sub> fluxes shown in Figure 4. An important caution is necessary. During the summer, there is potential interference by photosynthesis and possible increased soil respiration of CO<sub>2</sub>, which could possibly reduce the contrast shown in Figure 4.

The isotopic composition for the flux chamber samples at the three locations gave a less clear picture of the geothermal contribution to the atmosphere. If the flux chamber gas sample was isotopically heavier than  $CO_2$  in air, it was being diluted with geothermal  $CO_2$ . Four of the nine chamber measurements were isotopically heavier than air. If the flux chamber sample is isotopically lighter than air, it is being diluted with  $CO_2$  derived from soil respiration operating on vegetative material in the soil, or on the soil surface. Four of the nine chamber measurements were isotopically lighter than air. There was one tie value.

### Table 4.

Carbon Dioxide Concentrations and Stable Carbon Isotopic Ratios at Selected Locations in the Roosevelt Known Geothermal Resource Area (Winter, 1995-96).

	Opal Ma Mound Roa	in Old Roosevelt ad Hot Springs	Steaming Ground RHS Negro Mag
CO <sub>2</sub> Conc. in air or steaming ground	365 277	409	15680 4340 9650 5970
(ppmv) <sup>613</sup> C for			2890* 5900
CO <sub>2</sub> in air or steaming ground (‰)	-11.15 -11	.05 -11.41	-6.73 -6.47 -6.46 -6.96 -11.83ª -7.33
Soil gas			
30 cm (ppmv) ð <sup>13</sup> C <sub>co2</sub> (‰)	6060 1580 -4.58 -10	2380 .02 -3.74	
60 cm (ppmv) <i>6</i> <sup>13</sup> C <sub>co2</sub> (‰)	3780 2520 -3.34 -4	4050 .48 -3.54	
100 cm (ppmv)	13160 5030	5590	
δ <sup>13</sup> C <sub>CO2</sub> (‰)	-2.90 -5	.16 -2.96	
Final flux chamber sample			
A (ppmv)	1280 415	687	
δ' <sup>3</sup> C <sub>co2</sub> (‰)	-10.18 -11	.07 -13.15	
B (ppmv)	-9 68 -11	65 -12.03	
	929 421	905	
δ <sup>13</sup> C <sub>CO2</sub> (‰)	-11.26 -11	.20 -10.52	
CO <sub>2</sub> Flux			
A A	1178 685	244	
В	1096 194	255	
С	1999 381	3400	

Isotopic data suggest this sample is heavily diluted by air. The sample is rejected from mean and standard deviation calculations.

When the flux chamber was placed in the collars, atmospheric air with a CO2 isotopic composition of -11.20‰ was enclosed. Partially fractionated geothermal CO, then begins to seep into the chamber. Due to the fractionation caused by the diffusion process, it will be somewhat lighter than -6.79‰, but its actual isotopic ratio is unknown. The fractionation is a function of the diffusion rate through the entire rock and soil column above the reservoir. Only if the seepage rate is high, or the chamber is left in place for a long time will the isotopic ratio be shifted sufficiently from -11.20‰ to reliably detect the isotopic shift. In the case of chambers being diluted with CO2 isotopically lighter than atmospheric air, it is likely derived from vegetative decay. Shrub-dominated areas, which at Roosevelt is Big sagebrush (Artemesia tridentata), is a C3 plant utilizing the Calvin-Benson photosynthetic pathway. C3 plants produce organic materials with a range of -22 to -33‰. Decay of these organic materials will produce CO2 which is similar to slightly lighter in isotopic composition.

Therefore, a shift to  $\delta^{13}$ C values for CO<sub>2</sub> which are lighter than -11.20‰ suggests seepage of biological CO<sub>2</sub> into the flux chambers.

Another conclusion can be drawn from these observations. Geothermal CO2 can be recognized at a depth of 100 cm from isotopic composition. The rate of diffusive transport into the atmosphere was not rapid enough to recognize geothermal CO<sub>2</sub> in the flux chambers by use of stable carbon isotopes alone. The positive flux of CO<sub>2</sub>, augmented by the presence of geothermal CO<sub>2</sub> in the soil gas at shallow depth does document seepage and is potentially useful in exploration. This opens the way for measurement of CO2 concentrations in the field by infrared techniques for samples from under flux chambers, or in the air from gradient methods such as the modified Bowen ratio method. Long-path measurement of CO2 by Fourier transform infrared (FTIR) may also be possible, which will allow for rapid reconnaissance to be done using above ground measurements.



Figure 1. Methane flux contour map of the Roosevelt Hot Springs known geothermal resource area, June, 1995 (mg CH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>).





Figure 3. Seasonal methane flux difference calculated as June, 1995 minus January, 1996 flux (mg CH<sub>4</sub> m<sup>-2</sup>d<sup>-1</sup>).





Figure 2. Methane flux contour map of the Roosevelt Hot Springs known geothermal resource area, January, 1996 (mg CH<sub>4</sub> m<sup>2</sup>d<sup>-1</sup>).





Figure 4. Carbon dioxide flux contour map of the Roosevelt Hot Springs known geothermal resource area, January, 1996 (mg  $CO_2 \ m^2 d^{-1}$ ).

### SUMMARY AND CONCLUSIONS

Soil gas flux measurements of CH<sub>4</sub> and CO<sub>2</sub> were carried out at three geothermal areas in the summer of 1995 and winter of 1996. The areas sampled included; Roosevelt Hot Springs Utah; Beowawe, Nevada; and Steamboat Springs, Nevada. The results of measurement of CH, fluxes for all three areas initially appeared negative. A random distribution of small positive and negative fluxes suggested no surface expression by measurement of CH4 leakage. It was hypothesized that methanotrophic oxidation of CH<sub>4</sub> was occurring in the soils, masking any geothermal leakage, if present. Follow-up experiments were carried out at Roosevelt Hot Springs to verify the hypothesized reason for a lack of an observable CH<sub>4</sub> flux anomaly. A repeat of the CH4 flux measurements were made in the winter season to determine if methanotrophic activity may have decreased, or only shifted deeper in the soil column. In addition, measurement of CO<sub>2</sub> fluxes at all locations and stable carbon isotopic ratios were made at selected locations.

The winter flux measurements for CH<sub>4</sub> at Roosevelt seemed to yield similar results as the summer measurements; a poorly discernible flux anomaly, but did exhibit higher fluxes, and a greater range of flux values. There was also a negative correlation between CH<sub>4</sub> fluxes in the two seasons. This suggested that methanotrophic oxidation of CH<sub>4</sub> was occurring in the soil during the summer over the entire area. During the winter, methanotrophic oxidation of CH<sub>4</sub> was occurring only in those areas of significant heat flux. The CO<sub>2</sub> flux measurements exhibited a significant anomaly over the Roosevelt Hot Spring area, and offers the promise of the use of CO<sub>2</sub> measurements at the soil-atmosphere interface in exploration for geothermal areas.

Stable carbon isotopic measurements confirmed that methanotrophic oxidation of  $CH_4$  was occurring in the soil column. Similar measurements on the carbon isotopic composition of  $CO_2$  demonstrated the presence of geothermal  $CO_2$  in shallow soils and a partial leakage to the atmosphere due to diffusion. The flux data from the 66 locations where triplicate flux measurements were made suggested the entire Roosevelt Hot Springs KGRA may be anomalous with respect to  $CO_2$  flux.

These results demonstrate the potential for ground level measurement of gas fluxes in geothermal exploration, fault definition, and subsurface structure elucidation. The next logical step is to carry out measurements using some newer technology, followed by above the ground measurements, as well as at ground level. If successful, the potential for above-ground, longpath, open-path measurements by Fourier transform infrared spectroscopy (FTIR) can be achieved.

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