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METHANE, CARBON DIOXIDE, OXYGEN, AND NITROGEN IN SOIL GAS OVERLYING  
COAL BEDS OF THE UPPER CRETACEOUS FRUITLAND FORMATION IN THE SAN  
JUAN BASIN, LA PLATA COUNTY, SOUTHWESTERN COLORADO

by

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## **Abstract**

This report presents data from sampling of near-surface soil porosity for its content of methane, carbon dioxide, nitrogen, and oxygen in an area overlying a deposit of producing coal-bed methane from the Upper Cretaceous Fruitland Formation in the San Juan Basin of southwestern Colorado. Most soil gas samples did not have detectable levels of methane. One explanation for this is that a recent, heavy rainstorm prior to sampling may have left most of the soil porosity waterlogged and reduced soil gas methane levels. However, elevated concentrations of methane occurred in two soil gas samples (several hundred to several thousand times methane in air) and two gas seep samples were about one-half methane and the balance carbon dioxide. Carbon dioxide concentrations are elevated above atmospheric concentration in all soil gas samples; however, the soil gas concentrations of this gas from plant metabolism in this area are unknown and may account for the elevated levels.

## **Introduction**

This report presents data from sampling of near-surface soil porosity for its content of methane, carbon dioxide, nitrogen, and oxygen. The focus of the study was methane, which, after carbon dioxide, is the second most important greenhouse gas. Releases of methane into the atmosphere, whether by natural or anthropogenic processes are of interest because of the ability of the gas to absorb infrared radiation and increase the release of heat to the atmosphere. Coal is known to release methane, water, and carbon dioxide (Tissot and Welte, 1984) as it matures or increases in rank. The early stages of maturation from peat and beyond release mostly water and carbon dioxide, whereas the latter stages, especially those from medium volatile bituminous coal and beyond, tend to generate methane. Higher rank coal, such as low volatile bituminous and anthracite, generates approximately 100 cm<sup>3</sup> of methane per gram of coal. For coal of less than about 30 percent organic matter, most of this generated methane cannot be stored in the coal, either in free form or in an adsorbed state, and is liberated from the coal (Tissot and Welte, 1984). The maturation of sedimentary carbon over geologic time, because of its large mass, may be a substantial contributor of methane to the atmosphere (Herring and Dean, 1987).

We examined the hypothesis of whether or not the known existence of methane, produced from maturation of sedimentary organic matter (in this case from coal beds), in subsurface rocks would produce some signature in overlying soil. If so, then the existence of methane in the soil gas would suggest that the gas generated at depth is migrating to the surface on its way to escape into the atmosphere. Soil gas levels of methane would then become important in quantifying the flux of methane release to the atmosphere. In addition, the presence of methane in soil gas might also be useful as an exploration indicator for the presence of methane in subsurface rocks.

## **Location**

The area chosen to sample was one presently under development of coal-bed methane production in coal beds; hence, methane was known to exist in underground rocks. The site chosen for examination was Valencia Canyon on the Southern Ute Indian Reservation, southern La Plata County, southwestern Colorado. Sampling at this site continues previous USGS investigations that measured soil gas, principally helium but with some hydrocarbon data, in the same region and assessed environmental and geological implications of those gases (Cunningham, 1988). We acknowledge and thank Bowen-Edwards Corporation and the Southern Ute Tribe for access to the sampling area. Location of sample sites is shown in figure 1. Methane is being produced from Upper Cretaceous Fruitland Formation coal beds, which in the sample area range from about 50 to a few hundred m in depth below the ground surface and lie within a structural monocline that dips southeast at about 30°.

Geology and stratigraphy of the area, including discussion of the coal beds is presented in Sandberg (1990). Coal resources, origin of the coal in the area, and the geology of these same rocks in nearby areas are discussed by Roberts (1991) and by Roberts and McCabe (1992). Methane resources for the coal beds are discussed and inventoried by Fassett (1991).

## **Sampling and Methods**

Soil gas samples were obtained from 23 localities in Valencia Canyon (fig. 1). In addition, two gas seeps in springs were sampled. The first, Seep A, released bubbling gas at 5.3 liters per minute. The second, Seep B, was a bubbling spring immediately next to an abandoned, broken-off gas or water well pipe.

Sampling occurred May 23 and 24, 1991, two days after heavy to moderate rain in the area. Five traverses perpendicular to regional strike were selected; two (B,E) are along stream drainages on what appears to be major fractures, two (A,C) are along minor stream drainages; one (D) is not on drainage or apparent fracture. Samples were also taken over known pipelines and in open areas about half-way between apparent fractures.

Soil gas was sampled by driving a hollow, 1-m stainless steel probe into the soil and underlying bedrock. Prior to sampling, the probe was flushed by withdrawing an amount of gas

greater than the internal volume. Gas samples were extracted by attaching a syringe to a sampling port and withdrawing a volume of about 15 cm<sup>3</sup> of gas. The syringe samples were injected into stainless steel sample cylinders of approximately 6 cm<sup>3</sup> volume that were equipped with Swagelock valves and returned to Denver for analysis approximately 2 weeks later. The gas seeps were sampled using water-filled bottles inverted over the bubbling gas. The gas was directed into the bottles using an inverted funnel held under water at the surface of the seep. Atmospheric contamination of the gas seep sample was negligible. The bottles had spring-latched, ceramic stoppers fitted with rubber gasket seals. The bottles were refrigerated immediately and kept cold until subsequent analysis.

Cylinders for the soil gas samples were not or were only partially evacuated and contained air at a maximum of 1 atmosphere pressure (Denver) prior to sampling. This was not deemed to present a difficulty to analysis of methane because atmospheric levels of methane are less than 1 part per million (ppm), whereas expected soil levels, if methane was diffusing through the soil on its way to release into the atmosphere, would be expected to be many more, perhaps several thousand times this amount. In addition, the sample cylinders were overpressured with the soil gas samples to between 3 and 4 atmospheres so that the background methane content of the cylinders would be negligible compared to any levels that were elevated well above atmospheric background.

The gas samples were analyzed using a Hewlett Packard gas chromatograph (GC) equipped with a flame ionization and a thermal conductivity detector and using helium as a carrier gas. The gases analyzed for were methane, carbon dioxide, nitrogen, and oxygen. Two gas seep samples also were analyzed for their carbon isotope ratios using standard analytical isotopic techniques.

The absence of replicated and control samples, both of the soil gas samples and of replicate analyses by GC, cannot exclude possible sampling or instrumental error, respectively. In addition, difficulties were encountered with the standards used for GC analysis. Notably, the presence of 2 to 5 percent oxygen in the two hydrocarbon standards that were used indicates contamination or air leakage into the GC line. For methane calibration, we averaged the coefficient from the hydrocarbon standard that was analyzed on the first day with the two standards analyzed on the second day and the CO<sub>2</sub> standard that contained 1.0 percent methane. The variance in these standards for methane is about plus or minus 50 percent of the peak area to concentration coefficient that was used. Nevertheless, the consistent use of this single value is sufficient to indicate trends in relative concentrations as well as the type of extreme relative differences in concentrations encountered in this study.

## **Results**

The results of the gas analyses are listed in table 1. The table includes the raw measures of the integrated peak areas as well as the conversion into concentration for the various gases. For CO<sub>2</sub>, the concentrations listed in the table are likely plus or minus a factor of 2 due to inaccuracies in the measurement of the small peak for CO<sub>2</sub> concentrations similar to air. Ratios of certain gas concentrations also are included. Table 2 lists composition of the seep samples including the stable carbon isotopic ratio ( $\delta^{13}\text{C}$ ).

Only five soil gas localities had methane levels greater than atmospheric background. Three of these, on transect C and E, indicated traces of methane, perhaps 2 to 5 ppm, as indicated by GC peaks a few times larger than for the air blanks. The other two, on Transect D, had elevated methane concentrations of 0.02 and 1.5 percent, several hundred and several thousand times, respectively, atmospheric background concentration.

## **Discussion**

In overview, there is little areal pattern to the few soil gas samples that had methane concentrations above atmospheric levels and no particular relationship to geology or topography. Samples with elevated levels tended to be those close to the principal valley axes (Valencia Canyon, Long Glade), although exceptions to this tendency also exist. The two soil gas samples

that were most elevated in methane are on transect D on each side of the ridge to the east of Valencia Canyon. Most soil gas samples did not have detectable levels of methane. One explanation for this is that the recent, heavy rainstorm prior to sampling may have left most of the surficial soil porosity waterlogged and reduced soil gas methane levels. Another possibility for the minimal methane concentrations is that the soil probes and syringe samplers contaminated the soil gas samples with atmospheric gases while sampling under vacuum. Concentrations of nitrogen and oxygen and the oxygen to nitrogen ratio are consistent with atmospheric values and could suggest atmospheric contamination. On the other hand, CO<sub>2</sub> concentrations, which are always in excess of atmospheric concentration by a factor of 10 or greater, conclusively indicate that not all of the sample resulted from atmospheric contamination.

The stable carbon isotopic ratios of the methane and carbon dioxide from the seep samples are similar to those measured elsewhere for these gases in association with Fruitland Formation coal beds (Rice, 1993). The methane is lighter by a few per mil than the typical values for gas in this coal and may reflect some admixing of biogenic methane into the seep gas as it rises from the coal beds toward the surface.

The release of nitrogen associated with maturation of sedimentary organic carbon occurs but is not well documented (Tissot and Welte, 1984). In other words, some of the nitrogen detected in soil gas in our study might result from coal maturation. However, the consistent N<sub>2</sub>/O<sub>2</sub> ratio of the soil gas samples, virtually identical to that of air, suggests that only atmospheric nitrogen is present in the soil gas samples.

Carbon dioxide concentrations are elevated for nearly all soil gas samples when corrected for the atmospheric component of CO<sub>2</sub> that would accompany the nitrogen in the samples (assuming nitrogen to be only atmospheric). This excess amount of CO<sub>2</sub> ranges from 2 to about 200 times atmospheric value, assumed here to be 350 ppm. We expect that some of the excess CO<sub>2</sub> might be associated with degassing of the underlying coal beds. However, soil zones are also reservoirs of CO<sub>2</sub> that is associated with plant metabolism, and unless this contribution is known, it is not possible to make any inference about CO<sub>2</sub> release from the coal beds. There is no particular spatial trend of CO<sub>2</sub> according to geology or topography.

### **Summary and Recommendations**

The data presented here are equivocal; they do not clearly support or contradict the hypothesis that methane egresses through the soil zone overlying gassy coal beds and escapes into the atmosphere. Most soil gas samples did not have detectable levels of methane. However, this may be due to the possibility suggested above. Nevertheless, it is recommended that some of the soil gas sampling stations be re-occupied and re-sampled. Furthermore, any subsequent analytical work should be controlled using a series of replicate samples from some of the sample sites and of replicate injections of splits of the same samples and standards into the GC. Finally, if it indeed appears that sites sampled in this study do have substantive levels of soil gas CH<sub>4</sub>, then a continual program of monitoring should be implemented to examine possible temporal variation in soil gas content and effusion fluxes. For example, these might include diurnal or seasonal variability as a function of weather conditions. Once temporal variation in the flux of methane is understood for various localities, then areal variations can be examined to identify relationships with geological stratigraphy and structure of the rocks.

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## **Bibliography**

- Cunningham, Kimberley I., 1988, Preliminary interpretation of soil-gas data and relationships to other hydrocarbon microseepage indicators, Four Corners Platform-San Juan Basin transitional area, southwest Colorado and northwest New Mexico; *in* Fassett, J.E., ed., Geology and coal-bed methane resources of the northern San Juan Basin, Colorado and New Mexico: Denver, Colo., Rocky Mountain Association of Geologists, p. 305-315
- Fassett, J.E., 1991, Oil and gas resources of the San Juan basin, New Mexico and Colorado; *in*: Gluskoter, H.J., Rice, D.D., and Taylor, R.B., eds., Economic Geology, v. P-2 of The Geology of North America: Boulder, Colo., Geological Society of America, p. 357-372.
- Herring, J.R., and Dean, W.E., 1987, Methane fluxes from coal rank increase and natural coal fires: American Chemical Society, Abstracts, National Mtg., Spring 1987, 1 p.
- Rice, D.D., 1993, Composition and origins of coal-bed gas; *in* Law, B.E., and Rice, D.D., eds., Hydrocarbons from coal: American Association of Petroleum Geologists, Studies in Geology 38, p. 159-184.
- Roberts, L.N.R., 1991, Coal resources of the Fruitland Formation in part of the Ute Mountain Ute Indian Reservation, San Juan County, New Mexico: U.S. Geological Survey Bulletin 1938, 15 p.
- Roberts, L.N.R., and McCabe, P.J., 1992, Peat accumulation in coastal-plain mires--A model for coals of the Fruitland Formation (Upper Cretaceous) of southern Colorado, USA: International Journal of Coal Geology, v. 21, p. 115-138.
- Sandberg, D.T., 1990, Coal resources of Upper Cretaceous Fruitland Formation in the Southern Ute Indian Reservation, southwestern Colorado; *in* Zech, R.S., ed., Geology and mineral resources of the Southern Ute Indian Reservation: U.S. Geological Survey Professional Paper 1505-D, 24 p.
- Tissot, B.P., and Welte, D.H., 1984, Petroleum formation and occurrence (2d ed.): New York, Springer-Verlag, 699 p.

## **Appendix**

### **Field notes: Methane in soil gas, southwestern Colorado, Southern Ute Indian Reservation, Pinkerton Mesa quadrangle, La Plata County, May 23-24, 1991**

Weather conditions, clear and dry on days of sampling; heavy to moderate rains on 5/21/91, which may mean that water contents in the soil were higher than normal and that soil porosity was reduced.

Five traverses selected; two (B,E) are along stream drainages on what appears to be major fractures, two (A,C) along minor stream drainages; one (D) not on drainage or apparent fracture. Samples were also taken over known pipelines and in open areas about half-way between apparent fractures.

Samples tubes: NE, not evacuated; PE, partially evacuated; op, overpressure

**5/23/91**

**E1 Soda Springs 317NE** add 10cc; equilibrate with atmosphere; add 15cc op  
1 m probe 3 m north of road in soil on sloping outcrop

**E2 145NE** 15cc op (trace CH<sub>4</sub>)  
1 m probe went 3/4 m then bent; hard penetration (hit rocks?) in alluvium of valley fill

**E3 381NE** 15cc op (trace CH<sub>4</sub>)  
1 m; east side of main alluvial valley, out of valley fill on hillside on strike with outcrop of mixed shale and sandstone

**D4 593NE** 15cc op  
1 m; probe went in easily on west side of 44 canyon, north of small hill

**D5 447NE** 15cc op (181 ppm CH<sub>4</sub>)  
1 m probe went in 3/4 m and hit rock; on hillside on strike with shale and sandstone at foot of sandstone ridge

**P3 294NE** 15cc op  
1 m; over buried pipeline along fence in E/W roadway on west side of 44 Canyon

**E4 448NE** 15cc op  
1 m; in side-drainage alluvium half way up slope on west side of 44 Canyon (with Brad Boyce and Tom Ann Casey)

**E5 205NE** 15cc op  
1 m; just below ne corner of gas well site (Ladd Petroleum Co. So. Ute 5-7 1020 E 1050N 7/32/11; undrilled) on west side of 44 Canyon on north side of E/W road

**Seep A** two 16oz gas samples in glass bottles; labeled seep A, #1 and #2; one water sample in glass bottle  
in Valencia Canyon at seep at fence line; water sample took 9 sec to fill bottle, estimate caught 60% of flow

**D1 321NE** 15cc op  
1 m; in alluvium on hill slope with mixed in-place sandstone 70 m west of road in Valencia Canyon

- D2 519PE** (3cc) 15cc op  
1 m; middle of east side of Valencia Canyon in alluvial fill
- D3 185NE** 15cc op (12,257 ppm CH<sub>4</sub>)  
0.9 m; 3 m above drainage bottom on east side of side canyon on east side of Valencia Canyon; probably thin-soiled outcrop on opposing (nondip) slope
- Seep B #1; #2 taken under water**  
2 m to south of gas (or water?) well; bubbling spring 3 m from center of road in Valencia Canyon
- C1 453PE** (3cc) 15cc op  
1 m; 30 m north of stream valley axis (6400' el) on north side of Valencia Canyon; on float on nondip slope of fm overlying fm overlying Pictured Cliffs
- C2 188PE** (4cc) 15cc op  
0.9 m, hit rock? 80 m east of ridge (6400' el) on west side of Valencia Canyon
- C3 111PE** (2cc) 15cc op  
1 m; all soft alluvium; different smell to extraction than all others except C5; 30 m south of side stream channel on west side of Valencia Canyon; directly south of C1 in stream valley
- C4 313PE** (5cc) 15cc op  
1 m; directly south of C2; in alluvium 30 m south of stream channel in side stream valley to west of Valencia Canyon
- C5 114PE** (5cc) 15cc op  
1 m; about 13 m to west of road and 7 m to south of side stream channel in valley alluvium on west side of Valencia Canyon; same smell as C3
- C6 178PE** (5cc) 15cc op  
1 m; in valley alluvium west of main stream in Valencia Canyon; about 40 m east of fork of east-flowing and main stream
- B1 285PE** (6cc) 15cc op  
1 m; west of Valencia Canyon; at top of ridge (6510' el) just to west of intersection of N/S and E/W trails; in soil on dip slope of Pictured Cliffs; 50% back pressure
- B2 565PE** (5cc) 15cc op  
1 m; on dip slope (6440' el) in side drainage of major side drainage on west side of Valencia Canyon; 50% back pressure
- B3 449PE** (4cc) 15cc op  
1 m; 17 m to west of road in Valencia Canyon; in side valley alluvium 30 m north of side drainage; 50% back pressure (first try was 17 m west of road; 6 m south of drainage; no flow, 100% back pressure)
- B4 120PE** (5cc) 15cc op  
1 m; in alluvium in small side drainage on east side of Valencia Canyon
- Bkg 142PE** (5cc) 15cc op  
Background air sample taken at B3

**B3N 596PE (4cc) 15cc op**

1 m; about 10 m west of road in Valencia Canyon on small hill of slope outwash above alluvium about 1/2 way between traverses A and B; 30% back pressure

**A1 589PE (4cc) 15cc op**

1 m; on slope outwash about 7 m west of road in Valencia Canyon; 30% back pressure

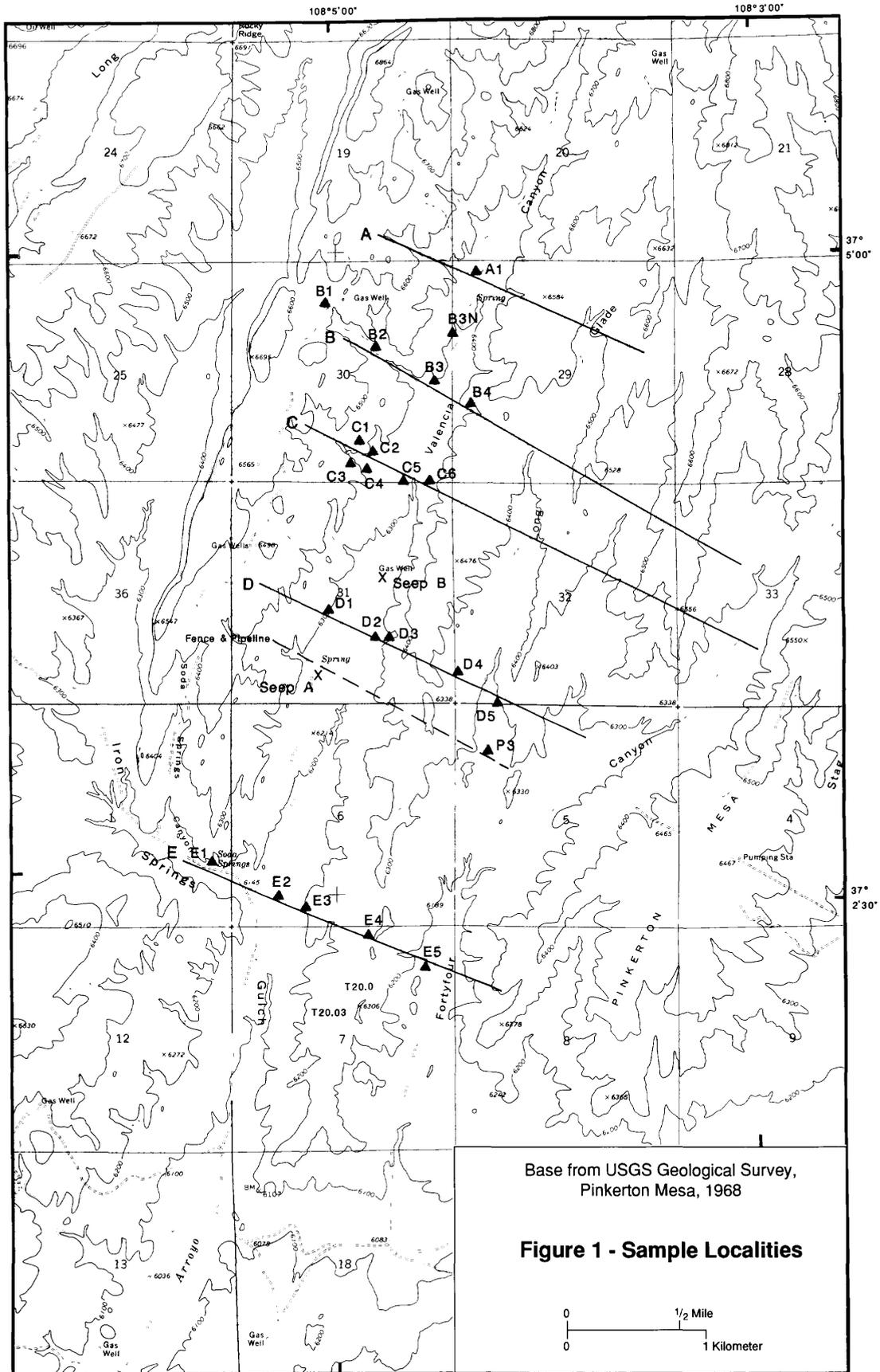
Table 1. San Juan Basin Soil and Seep Gas Samples

Site Location	Sample Order	Analysis Order	Cylinder	CO <sub>2</sub> peak area	CO <sub>2</sub> %	Excess CO <sub>2</sub> %	O <sub>2</sub> peak area	O <sub>2</sub> %	N <sub>2</sub> peak area	N <sub>2</sub> %	CH <sub>4</sub> peak area	CH <sub>4</sub> % (<1 ppm unless specified)	CO <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CH <sub>4</sub> /N <sub>2</sub>
A1	24	2		589	2.94E+04	0.75	0.72	7.04E+05	19.7	2.74E+06	76.1		.0108	0.257	
B1	18	8		285	1.76E+04	0.45	0.41	7.19E+05	20.1	2.75E+06	76.6		.0064	0.261	
B2	19	23		565	2.33E+04	0.59	0.56	7.26E+05	20.3	2.78E+06	77.2		.0084	0.262	
B3	20	21		449	5.11E+04	1.30	1.26	8.33E+05	23.3	3.25E+06	90.3		.0157	0.256	
B3N	23	16		596	2.76E+04	0.70	0.67	7.89E+05	22.1	3.04E+06	84.5		.0091	0.260	
B4	21	17		120	1.21E+04	0.31	0.26	1.03E+06	28.7	3.89E+06	108.1		.0031	0.264	
Bkg. air	22	7		142	3.95E+03	0.10	0.07	7.43E+05	20.8	2.78E+06	77.3		.0014	0.267	
C1	12	18		453	3.95E+04	1.01	0.97	7.00E+05	19.6	2.74E+06	76.3		.0144	0.255	
C2	13	22		188	2.33E+04	0.60	0.56	8.05E+05	22.5	3.09E+06	86.0		.0075	0.260	
C3	14	25		111	4.89E+04	1.25	1.21	8.56E+05	23.9	3.32E+06	92.4		.0147	0.258	
C4	15	5		313	3.79E+04	0.97	0.93	7.17E+05	20.1	2.80E+06	77.9		.0135	0.256	
C5	16	1		114	7.31E+04	1.87	1.83	6.79E+05	19.0	2.85E+06	79.3	tr (~5 ppm)	.0256	0.238	
C6	17	26		178	1.05E+05	2.68	2.64	8.42E+05	23.6	3.51E+06	97.7		.0299	0.240	
D1	9	6		321	2.74E+04	0.70	0.65	1.06E+06	29.7	4.06E+06	112.9		.0067	0.261	
D2	10	24		519	1.89E+04	0.48	0.45	7.71E+05	21.6	2.94E+06	81.7		.0064	0.262	
D3	11	15		185	4.80E+04	1.23	1.19	8.34E+05	23.3	3.10E+06	86.3	1.45	.0155	0.269	0.301318
D4	4	14		593	1.49E+04	0.38	0.34	7.66E+05	21.4	2.94E+06	81.7		.0051	0.261	
D5	5	19		447	2.85E+04	0.73	0.69	7.19E+05	20.1	2.75E+06	76.5	0.02	.0104	0.261	0.005022
E1	1	13		317	2.76E+04	0.70	0.67	7.29E+05	20.4	2.82E+06	78.5		.0098	0.258	
E2	2	9		145	2.40E+04	0.61	0.57	7.86E+05	22.0	3.04E+06	84.4	tr (~2 ppm)	.0079	0.259	
E3	3	12		381	1.92E+04	0.49	0.45	7.46E+05	20.9	2.93E+06	81.5	tr (~2 ppm)	.0066	0.255	
E4	7	20		448	1.97E+04	0.50	0.46	8.48E+05	23.7	3.24E+06	90.0		.0061	0.262	
E5	8	3		205	1.15E+04	0.29	0.26	7.82E+05	21.9	2.96E+06	82.4		.0039	0.264	
P3	6	4		294	2.43E+04	0.62	0.58	7.82E+05	21.9	3.08E+06	85.5		.0079	0.254	
Seep A		10			2.26E+06	57.54	57.53	1.12E+05	3.1	4.09E+05	11.4	47.56	5.5141	0.274	74.88478
Seep B		11			1.95E+06	49.71	49.70	1.17E+05	3.3	4.07E+05	11.3	92.85	4.7815	0.288	146.7411
CALIBRATION SUMMARY:															
				Area/Concn-ppm											
				CO <sub>2</sub> 3.92											
				O <sub>2</sub> 3.58											
				N <sub>2</sub> 3.60											
				CH <sub>4</sub> 64.40											

air = 0.268

Table 2. Isotopic analysis of methane and carbon dioxide from two gas seeps.

	$\delta^{13}\text{C-CH}_4, \text{‰}$	$\delta^{13}\text{C-CO}_2, \text{‰}$	$\text{N}_2, \%$	$\text{CH}_4, \%$	$\text{CO}_2, \%$
Seep A	-46.65	11.39	10.32	45.62	44.06
Seep B	-47.75	10.51	3.59	62.55	33.86



Base from USGS Geological Survey,  
Pinkerton Mesa, 1968

**Figure 1 - Sample Localities**

