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COMPOSITION OF GAS SEEPS IN NORTHWESTERN WYOMING

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ABSTRACT

The natural gases issuing from fumaroles, springs, and seeps in northwestern Wyoming have a wide range of compositions that reflect the varied processes of their genesis. Each source contains hydrocarbons ranging from at least methane up to hexane in a mixture of variable amounts of carbon dioxide, nitrogen, oxygen, argon, and other unmeasured trace gases. In Yellowstone National Park, the Absaroka Range and the Rattlesnake Mountain anticline, all of the samples were taken from fumaroles or hot springs where carbon dioxide is the primary gas ranging in concentration from 65.1 to 96.3%. Total hydrocarbon gases are present in amounts of less than 1%, and the composition ranges from methane to at least the pentanes. Methane is likely derived from organic matter by at least two pathways in these environments; thermal decomposition and microbial activity The hydrocarbons larger than methane are most likely derived from thermal decomposition of sedimentary organic matter, both heated and transported by hydrothermal fluids.

In the Teton-Bridger Wilderness area, carbon dioxide (29.1 to 98.5%, $\delta^{13}C$ from -8.8 to -10.4‰ and nitrogen (0.98 to 58.3%) are co-dominant gases. The variable concentration range of carbon dioxide and nitrogen is believed to result from mixing of CO_2-rich water with waters rich in N_2 recently removed from the atmosphere. Hydrocarbon gases total <0.5% (5000 ppm) and are limited to methane with <1 ppm of ethane and propane. The hydrocarbons appear to be principally the result of microbial activity.

The springs and seeps in Grand Teton National Park are nitrogen dominated (81.0 to 91.2%) with methane concentrations ranging from 0.0023 to 13.5%. Carbon dioxide and oxygen constitute the remainder of the principal gases. At Jackson Lake Hot Springs, methane and ethane were the only hydrocarbons detected. Microbial activity is most likely responsible for the preponderance of these hydrocarbons. The results obtained from samples collected at the same sites in this area in both 1988 and 1989 are highly variable. In 1988 the hydrocarbons ranged from methane to at least the butanes, and methane was present in higher amounts; however, concentrations of carbon dioxide, nitrogen, and oxygen at most sites were similar for both years. Apparently there is a wide range of natural variability with respect to the hydrocarbon gases which in turn is mediated in part by the level and type of microbial activity.

INTRODUCTION

Seepages of natural gas are often observed at the surface of the earth. These seeps provide samples from which subsurface processes of gas generation can be inferred. In northwestern Wyoming, gas seeps are common in and around Yellowstone and Grand Teton National Parks. Yellowstone National Park, in particular, has numerous gas seeps manifest as bubbling hot springs, and a number of previous studies have provided information on gas compositions (Gunter and Musgrave, 1966, 1971; Gunter, 1978; Nehring and Truesdell, 1978; Des Marais et al., 1981; Truesdell and Thompson, 1982). Outside Yellowstone National Park, there apparently has been less interest in gas seep compositions. A preliminary report by Kvenvolden et al. (1989) compares the molecular and isotopic compositions of nine gas seeps sampled in 1988, two in Yellowstone National Park, seven in Grand Teton National Park, and one outside the national park boundaries. That report demonstrated that compositions of seep gases in Yellowstone National Park are dominated by CO_2, whereas in the Grand Teton National Park, CH_4 and N_2 are the principal gases. Concentrations of the low molecular weight hydrocarbon gases in both areas are highly variable.

In order to expand our understanding of the compositions of naturally occurring gas in seeps in northwestern Wyoming, we resampled in 1989 most of the sites visited the previous year (Kvenvolden et al., 1989) and obtained additional samples in the Teton-Bridger Wilderness area and in the area between Yellowstone National Park and the city of Cody, Wyoming (Fig. 1). We sampled seeps in five geographic areas: 1) Yellowstone National Park; 2) Absaroka Range to the east of Yellowstone National Park; 3) Rattlesnake Mountain Anticline on the east flank of the Absaroka Range and west of Cody, Wyoming; 4) Teton-Bridger Wilderness at the northwest end of the Washakie Range along the North Buffalo Fork Thrust Fault, and 5) Grand Teton National Park. Our results are reported relative to these five areas, with comparisons among the areas. Appendix 1 lists simplified lithology, water temperature and pH, and the spring locations by latitude and longitude. Appendix 2 includes topographic maps showing the location of individual seep sites.

The focus of our studies is on the hydrocarbon gases, mainly methane (C_1), and its saturated and unsaturated homologs, ethane (C_2), ethene ($C_{2:1}$), propane (C_3), propene ($C_{3:1}$), and iso-butane (i-C_4) and normal butane ($\underline{n}$-C_4). In addition, we report the concentrations of CO_2, N_2, and Ar. No provisions were taken to correct for the high solubility of CO_2 in water, and thus our results for CO_2, as well as for the other gases, represent the composition of the gas phase in the sample bottle at the time of sampling. We assume that these concentrations approximate the compositions of the natural seep gases.

The results reported here add to a base of recorded analyses, but the interpretations are strictly preliminary because of the small number of analyses. A comparison of the 1988 data of Kvenvolden et al. (1989) with the data of 1989 demonstrates that the gas compositions are highly variable, especially those in Teton National Park. This finding suggests that the gas composition varies with time and may reflect the activity of microorganisms, groundwater levels and flow rates.

METHODS

Field sampling of spring and seep gases involved identifying trains of bubbles rising through water and then trapping the gas in glass containers. Gas samples were collected by water displacement in 350- and 250-ml glass bottles equipped with spring-loaded rubber and ceramic stoppers (Kvenvolden and Pettinga, 1989). Serum vials (100-ml glass bottles) capped with teflon-coated silicone crimp seals were also used. The sample bottles were filled with water from the seep site (natural spring water or river water) and inverted so that the mouth of the bottle was submerged. Gas was directed into the bottles by two different means. At exceptionally slow-bubbling sites (less than about 5 ml/min), a water-filled plastic 40-liter trash bag was anchored over the gas seep and allowed to fill with gas over a period of 1-4 hours. With the bag still under water, a small hole was pierced in the corner allowing the gas to escape into an inverted collecting funnel and finally into the sample bottle. At seeps with sufficient gas flow, an inverted funnel with plastic tubing was submerged in water diverting the bubbles directly into the sample bottle. Wherever the water was too shallow, a water-filled bucket was used as a substitute. After the gas had filled the sample bottle, 1 ml of the bactericide Zephrine Chloride (1:750) was injected into the interior neck of the bottle, then sealed, leaving a small amount of sterilized water in the bottle to enhance the seal against leakage. The samples were stored in an inverted position at room temperature until analyzed.

The samples were analyzed at three different USGS laboratories (Palo Alto, CA, Menlo Park, CA, and Denver, CO) and at Oregon State University's organic geochemistry laboratory. Gas chromatography was utilized to quantitate the gases. The results, reported as volume percent (%) for CH_4, CO_2, N_2, and Ar, and in parts per million (ppm) for hydrocarbon gases other than CH_4, are listed in Table 1, along with the ratios of N_2/O_2, Ar/N_2, $C_1/(C_2 + C_3)$, and $C_2/C_{2:1}$. Carbon isotopic compositions of methane and carbon dioxide were determined by mass spectrometry; results are reported in the δ(‰) notation relative to the Pee Dee Belemnite (PDB) standard:

$$\delta^{13}C(‰) = [R_{sample}/R_{standard} - 1] \times 10^{-3}, \text{ where } R = {}^{13}C/{}^{12}C.$$

SAMPLE SITE DESCRIPTION

Yellowstone National Park

Calcite Springs

The hot springs and seeps of Calcite Springs occur along the Yellowstone River about 1.6 km north of Tower Falls along the east flank of Bumpus Butte (Appendix 2-A). A zone of acid hydrothermal alteration spans both sides of the river for about two km, culminating with the active spring area near the southern end. The host rock at the surface is the hydrothermally altered Eocene Sepulcher Formation, an epiclastic volcanic montage of breccia, conglomerate, sandstone and tuff (Prostka et al., 1975).

The active spring area visited by us spans 0.4 km on the west side of the river, and gas samples were taken at the north and south ends of this active area. Between these two sampling sites is the location of the previous year's sample collection (Kvenvolden et al., 1989). Many black, alkaline springs issue near river level but no higher than about 6 meters above that mark. Numerous gassy springs and acid fumaroles persist from below water level to at least 30 m above river level. The zone of acid hydrothermal alteration extends from river level to about 75 m above the river. The local area is resplendent with deposits of siliceous sinter, sulfur, calcite, barite and fibrous gypsum crystals.

Our gas samples were taken from both ends of the spring area at or near water level. At the north end, a fumarole at water level was sampled. A trickle of acidic spring water (pH 2, 90°C) accompanied the gas discharge. About 0.4 km downstream, one of the southern fumaroles was sampled. Here the discharge of alkali springs is much greater relative to the acidic discharge of the northern location. Bubble trains were spotted below the springs under about 30 cm of water in the Yellowstone River. As gray, clay rich sediment was cleared to minimize bacterial gas contamination, bubbles rising to the surface would burst, each leaving a small hydrocarbon slick on the river.

Some fumaroles, especially those which are elevated highest above the river emit sulfurous gas, and petroleum vapors. The fumaroles are lined with euhedral sulfur crystals coated with a light-brown oil condensate (Clifton et al., 1990). Also unique to these fumaroles are the lithified remains of molten sulfur and petroleum flows which have poured out. Love and Good (1970) counted ten petroliferous flows in varying stages of decomposition, the oldest being gray and white while the youngest look black and fresh. The flows break up rapidly as demonstrated by comparing photographs taken of the area within a 3-year interval. We saw flows made up almost entirely of sulfur and a partially burned sulfur residue which appeared sometime between July 1988 and July 1989; however, we found no lithified petroleum flows.

Jade Hot Springs near Washburn Hot Springs

Approximately 1.2 km southwest of Washburn Hot Springs, just to the northwest of the Eaton Trail, is a group of cool acid springs (Appendix 2-B). The springs emerge along the surficial contact of the Eocene Sulphur Creek Stock, a diorite, and the Sulphur Creek member of the Plateau Rhyolite, a Pleistocene air-fall ash tuff . Less than 0.4 km to the south is the buried scarp of the Yellowstone caldera. The area near the springs is acidic, hydrothermally altered and devoid of flora. The springs form many small pools of tepid water, some with thick, pastel green precipitates of a heavy gelatin-like consistency, and others with sand and gravel floors typical of mountain ponds. The slow flowing spring waters with a temperature of about 30°C contrast with the much warmer fumaroles of Calcite Springs.

We sampled gas from two sites. One sample came from a vent within a pond containing a light dusting of green precipitate, and the other sample came from a vent about 10 m away bubbling through water-saturated hydrothermally-altered debris. Springs in this immediate area were sampled by Kvenvolden et al. (1989) in 1988 and located by the name of Washburn Hot Springs. However, the actual Washburn Hot Springs were never sampled because of the very high temperatures at these springs. In order to be more specific, we use the name Jade Hot Springs to identify this previously unnamed group of springs which are near to the Washburn Hot Springs.

"Jade" refers to the characteristic pastel green-colored precipitate lining many of the spring pools.

Absaroka Range

Sweetwater Mineral Springs

Sweetwater Mineral Springs are located by Sweetwater Creek about 5.5 km north of U.S. Highway 20 and 29 km east of Yellowstone National Park (Appendix 2-C). The area lies at the bottom of a steep-walled canyon, one of many in the Absaroka Range; this canyon is over 700 m deep at the springs. The canyon is cut through thick accumulations of the Eocene Wapiti Formation, a beige colored mafic volcanic conglomerate and agglomerate. Love and Good (1970) estimated the base of the volcanic rocks to be 150 m below the springs, and at greater depth are unknown thicknesses of sedimentary rocks analogous to those in the Big Horn Basin, located 50 km to the east

Historically, oil seeps have occurred here, first described by Hewett (1913) and later by Love and Good (1970). We could not locate any sign of oil in July 1989 nor could Kvenvolden et al. (1989) in 1988. Numerous gas seeps could be seen along the riverbank, and a pervasive petroliferous odor, similar to that of an oil refinery, tainted the air. The springs are cold, yet nearby there are extensive deposits of travertine, siliceous sinter, and sulfur, suggesting previous high temperatures followed by a recent cooling and reduction of water flow. We sampled one gas vent along the bank of the Sweetwater River. Here the gas bubbled up intermittently through river alluvium. Apparently there is a substantial release of gas in the area as evidenced by the pervasive petroleum-like odor in the air.

Sulphur Lake

Sulphur Lake is a shallow pond near a small defunct sulfur mining operation along Sunlight Creek (Appendix 2-D). The area is remote, located about 19.5 km due north of Sweetwater Mineral Springs. Here too the odor of hydrocarbons and sulfur taints the air. An attempt was made to locate a source of the odor along 1.5 km of Gas Creek above Sulfur Camp. No visible gas seeps were located, but a slight petroleum odor was detected. The immediate area shows signs of recent hydrothermal activity; the native volcanic conglomerate is weathered, iron stained, and coated with a white precipitate. Intermittent gas seeps are present in Sulfur Lake, and a sample was collected here. Flow from the seeps was improved by digging into the rubble lining the lake bed.

Rattlesnake Mountain Anticline, Cody Wyoming

De Maris Hot Springs

Originally described as part of "Colter's Hell" in the 1806-1807 travels of John Colter, the springs have since been named De Maris Hot Springs after Bill De Maris, the man who developed the springs for swimming and bathing in the very late nineteenth century (Bartlett, 1926). The springs occur in roughly a 75 m strip adjacent to the north shoreline of the Shoshone River (Appendix 2-E). Seven vents were counted by Breckenridge and Hinckley (1978); in addition, there are evidently more vents under the Shoshone River as evidenced by trains of bubbles from the river bottom. Individual vents flow from less than 4 to over 1900 liters/min (Breckenridge and Hinckley, 1978). Each spring issues directly from fractures in the Permian Phosphoria Formation (Park City Formation), locally an interbedded sequence of hydrothermally fractured massive limestones and shales dipping 16° to the east along the east limb of the Rattlesnake Mountain anticline. The fractures are filled in part with calcite, amethyst, sulfur, and bitumen near the springs. Travertine mounds stipple the immediate area.

Three gas vents were sampled: the largest and easternmost spring surrounded by a defunct bath house, a "middle" spring about 15 m to the west, and the far western spring approximately 45 m beyond the middle spring. The springs increased in temperature from about 28°C to 36°C from east to west corresponding to a decreasing level in the stratigraphic section. A pervasive sulfurous odor permeates the area. Some vents issue from fractures eroded 3 m back into the cliff and contain deadly concentrations of suffocating gases (probably CO_2), at least to the few unlucky birds that flew in but not out.

Teton-Bridger Wilderness Area

Soda Springs

Soda Springs are situated on the upthrown side of the east-west trending Soda Fork fault in the North Buffalo Thrust Fault region (Appendix 2-F). The springs have created two large iron-stained travertine mounds on Archean dark green gneiss and greenstone. The adjacent downthrown side is covered with river alluvium underlain by Paleozoic rocks (see Antweiler et al. 1989 p. 65-66 for a more detailed description of these springs). Soda Springs were the only non-thermal spring waters sampled in this general area. We sampled the easternmost and largest spring. Gas was collected in two 40-liter plastic bags from seeps located 1 m apart in a water depth of about 30 cm. Each seep was excavated by removing some large travertine platters and carbonaceous sand and silt before gas collection. Results are reported for each of the sample collections as samples 1 and 2.

The mound surrounding the pool contains a significant amount of radioactivity as measured by Geiger counter (6,000 cps, maximum). The radionuclide is radium (C. Huh, OSU, personal communication, 1990) from water transported uranium deposited in the iron rich travertine. Radon was not measured.

Junction Springs

Junction Springs, named and sampled here for the first time, are approximately 1 km south of North Buffalo Fork Springs (Appendix 2-F), described by Love in Breckenridge and Hinckley (1978) and Antweiler et al. (1989). The springs rise through alluvial gravel near the junction of two normal faults, named Soda Fork and North Buffalo Fork. Near this area, Love (1956) has mapped Precambrian crystalline rocks which may be in contact with the aquifer. However, the Madison Limestone outcrops on the opposite side of the river just beyond the North Buffalo Fork fault. Old travertine deposits at the North Buffalo Fork Springs and Soda Springs suggest some spring water is in contact with carbonate rock. In 1974, when the springs in this area were surveyed and described by Love (Antweiler et al. 1989, p. 66), gas output and presumably concurrent spring flow appeared to be greater than in 1989, when we visited this area with Love. He could not relocate a previously vigorous spring issuing from the Madison Limestone very near the site of North Buffalo Fork Springs; the old spring is presumed to be dormant or extinct.

Junction Springs emerge in a large meadow. The springs form two interconnected shallow ponds which quietly discharge in the North Buffalo Fork River about 0.2 km to the west. Elk and deer hoof prints cover the floor of the ponds suggesting that the sweet, tepid water is quite an attraction. A thick accumulation of organic debris and silty clays accompanied by a sulfurous odor mantles the floor of the ponds. In some places the accumulation was nearly 0.5 m deep with some peat formation. River alluvium underlies the organic-rich layer. Sporadic gas is released from multiple sites. Vents with the highest outflow in each of two ponds (named East and West) were excavated down to the alluvium to minimize gas input from the organic-rich cover. Plastic bags were anchored over the vents, and gas was collected after sufficient gas accumulation.

Tom Spring

A convoluted fissure in travertine cemented alluvium is the present conduit for Tom Spring which takes its name from Tom Gee, a member of the 1989 sampling party. The spring arises about 0.4 km south of Junction Springs and empties directly into the North Buffalo Fork just a few meters to the west (Appendix 2-F). The north-south trending North Buffalo Fork fault, covered by alluvium, lies nearby and may in part serve as a conduit for this spring as well as for other springs in this valley.

Gas flow from this spring was about 1,200 ml/min, a rate that is fast relative to other springs in the area. Gas vents were numerous and consistent. Taking advantage of the good flow rate, we funneled trains of gas bubbles directly into the sample bottles.

Teton National Park

Teton Valley Ranch Warm Springs

The Teton Valley Ranch Warm Springs emerge in an area of approximately 45 by 365 m along the south terrace of the Gros Ventre River (Appendix 2-G). Deeply fractured Madison Limestone underlies the alluvial deposits from which the many springs and seeps issue. The Paleozoic section dips roughly northward to the east and south of the springs. Immediately to the west, the section terminates on a northwest trending normal fault and to the north under Quaternary glacial deposits .

Gas vents at Teton Valley Ranch Warm Springs appear in many places. We chose three sites, labeled East, Main Pond, and West. Gas was collected in plastic bags in the East and West vents. In the Main Pond, gas was collected from a depth of 1 m by probing the vent area with a shovel, thereby releasing gas trapped in carbonate-rich sediment. The pond floor was extensively colonized with green algae which may contribute gases to the sample. Bubbles could be seen moving upward through these colonies, but it was unclear where they actually originated; however, these areas were avoided to minimize any contribution of gas from the algae.

The west gas seep site was sampled in flowing water from two vents within a meter of one another. To accommodate room for the collection bags, a depression was created by removing some of the overlying alluvial material east of the main pond. Another two close-by vents were sampled in the same manner. The alluvial material here was mostly sand rather than cobbles and gravel.

Kelly Warm Spring

Kelly Warm Spring, two km to the north of Teton Valley Ranch Warm Springs, forms a pool covering approximately 4,000 m^2 (Appendix 2-G). The pool, up to 2 m deep, is fed by many gently bubbling seeps ascending through carbonate-rich grains, possibly of algal origin, underlain by alluvial gravel and Quaternary glacial deposits. The total discharge is estimated to be approximately 19 million liters/day, with a maximum temperature of 30°C (Love and Love, 1987). Kelly Warm Spring and Teton Valley Ranch Warm Springs have nearly identical water chemistries and appearances leading to the speculation of a common aquifer (Breckenridge and Hinckley, 1978). The two springs lie on a Quaternary northwest trending normal fault that roughly terminates at each spring site. At Kelly Warm Spring, the fault splits and a segment extends to the northeast about 3 km.

Gas vents bubbled sporadically in low volumes from numerous vents necessitating agitation of the carbonate-rich sand to enhance bubbling. Samples were collected from many separate vents and mixed together. When one vent bubble train expired, another one was located. The sediment was agitated releasing gas until the bottle was filled. Samples were collected from the east and west sides of the pond.

Jackson Lake Hot Springs

An undetermined number of small springs issue from the Madison limestone along a 900-m section near the shoreline of Jackson Lake (Appendix 2-H). Two northwest-southeast trending faults converge on the Teton fault at the springs (Love and Reed, 1973). Kvenvolden et al. (1989) sampled four gas seeps here, called the Teton Fault seeps, and observed widely variable gas compositions.

The Teton Fault seep sample sites of 1988 were under 6 m of water in 1989. From a boat as an observation point, sporadic gas releases were seen rising through the water. Once identified, a diver with SCUBA descended to the lake bottom and anchored a gas free 40-liter plastic bag over the gas seep. Because the bubbling was slow the sites were marked with a buoy, allowing the diver to return after an hour to retrieve the gas. Two bags breached their anchors and rose to the surface; luckily the openings remained underwater, thereby preserving a valid sample. The bags were sealed, then transferred onboard the boat in a bucket of water to prevent any possible air contamination. Retrieved sediment had a strong hydrogen sulfide odor.

RESULTS AND DISCUSSION

The analyses of the gas seeps are grouped into separate geographic areas. Because the gases are a reflection of source and aquifer chemistry, it is not surprising to find that springs close to one another and sharing the same aquifer have similar gas and water compositions. Although the focus of our analyses is on the hydrocarbon content of spring gases, the presence of other gases and the water chemistries help to explain their origins. Isotopic compositions of carbon in methane and carbon dioxide are most useful in determining gas genesis and are used here along with molecular compositions.

Yellowstone National Park

Yellowstone National Park as well as the Absaroka Range to the east are located in a region of Tertiary volcanic activity. The evolution of the Yellowstone volcanic province is discussed by Smith and Christiansen (1980) and Smith and Braile (1982). Volcanic rocks as old as Early Eocene cover Mesozoic and Paleozoic strata that were folded, uplifted, and eroded during the Cretaceous Laramide Orogeny. Remainders of the pre-Tertiary rocks are inferred by seismic data (Lehman et al., 1986; Smith and Braile, 1982), stratigraphic interpolations (Tonnsen, 1982), and regional mapping (Prostka et al., 1975) to lie under volcanic rocks in the north section of the Park. Buried sedimentary rocks may act as a hydrocarbon source for gases and petroleum found in springs hosted by volcanic rock.

Petroleum seeps have been observed at Calcite Springs, Rainbow Springs, and Tower Bridge (excavated and subsequently buried during road building) inside Yellowstone National Park (Love and Good, 1970). Each seep issues from volcanic rocks and lies within a radius of 10 km of the others. Clifton et al. (1990) critically analyzed the compositions of Calcite and Rainbow Springs oils and concluded that they were derived from thermal alteration by hydrothermal fluids of organic matter in relatively shallow sedimentary rocks. South of the oil-bearing region, Des Marais et al. (1981) conducted carbon isotopic analyses of C_1-C_4 alkanes and concluded that the light hydrocarbon gases originated from the thermal alteration of sedimentary organic matter; this study supported the earlier findings of Gunter and Musgrave (1971), who determined that the isotopic composition of methane and ethane at Washburn Hot Springs was characteristic of conventional natural gas. Our studies concur with these conclusions.

Carbon dioxide is by far the dominant gas in the sampled seeps of Yellowstone National Park. Abundances varied from nearly 97% at Calcite Springs to 80% at Jade Hot Springs. These amounts are typical of hydrothermal areas (White, 1957; Lyons and Hulston, 1984). Hydrocarbon gases at both sites ranged from C_1 to C_{6+}. Benzene or hexane may be present, but this identification has not been unequivocally ascertained. A most unusual lack of C_2 and i-C_4 and just traces of n-C_4 (0.15 ppm) contrasts with the relatively high abundance of C_1, C_3, $C_{3:1}$, and C_5, showing a remarkable odd to even carbon number preference in the gas at Calcite Springs. It should be noted that an unusual chromatographic interference occurred in the Calcite Springs samples. Normally, good separation is achieved between $C_{2:1}$ and C_2 with elution of $C_{2:1}$ about 0.3 minutes before C_2; however, Calcite Springs gas consistently produced a single peak exactly in between the expected elution times of $C_{2:1}$ and C_2. Additionally, a thermal conductivity detector recorded an unknown gas, perhaps causing the coelution of $C_{2:1}$ and C_2. Consequently, the presence of $C_{2:1}$ or C_2 here is inconclusive, but it is assumed that one or both compounds are present at a total amount of about 2 ppm. A C_{6+} component (a back flush peak) was a major constituent in the gas from the south site. Sediment extracted from this site revealed a variety of polycyclic aromatic hydrocarbons.

Hydrocarbon gas distributions at Calcite Springs are perplexing. The north and south sample sites collectively emit C_1 through C_{6+}, except i-C_4; however, the seep at Calcite Springs south contained C_2 and n-C_4, but Calcite Springs north did not. The close proximity of sample sites, and the similarity of seep characteristics imply that the most volatile and therefore most mobile chemical components in these seeps should match, but this result shows that is not the case. It appears that this system is not completely homogeneous and may be accessing different sources of hydrocarbons. Analyses of the 1988 site very near Calcite Springs south show even larger discrepancies supporting this conclusion. For example, C_1 concentrations at the 1988 site were 5800 ppm as compared to 89.7 ppm at Calcite Springs south and 39.0 ppm at Calcite Springs north. C_2 concentrations were similarly depleted in 1989. In 1988, i-C_4 was present, but not in 1989. $C_{3:1}$ was not found in 1988, but was present at both sites in 1989. A comparison of the non-hydrocarbon gases between sites and years revealed compositional consistency implying that the parent hydrothermal flow system is constant on a time scale of years.

Clifton et al. (1990) studied the organic geochemistry of oil seeps at Calcite Springs and determined that the oil was derived from three discrete sources, each with a characteristic fingerprint: 1) the major component is a complex mixture of aromatic and polar compounds with a minor amount of saturated hydrocarbons derived from thermally immature, shallow sedimentary rocks heated by hydrothermal waters; 2) a high temperature component of residual polycyclic aromatic hydrocarbons and thio-polyaromatic hydrocarbons which may be derived from previously leached sedimentary rock in contact with deeper, hotter circulating fluids, perhaps at temperatures greater than 270°C (Fournier, 1989); and 3) contemporaneous input from plant waxes, bacteria, and algae heated by hydrothermal fluids. The preponderance of gas at Calcite Springs is most likely formed by process (1) with minor inputs of metagenic gas from process (2) and microbial respiration and decomposition gas products from process (3). The presence of higher molecular weight hydrocarbon gases, visible oil nearby, and $C_1/(C_2+C_3)$ ratios of 25 (south seep) and 55 (north seep) indicate the gases are thermogenetically derived and are consistent with process (1). The presence of $C_{2:1}$ and $C_{3:1}$ highlight the probability of microbial activity (Davis and Squires, 1954; Oremland, 1981), although a thermal origin of these hydrocarbons cannot be discounted. Catagenetic temperatures associated with process (2) would primarily produce C_1, and this source of gas could not be distinguished from other sources with our present body of data. On a speculative note, a temporary shut-off of deep, hot hydrothermal circulation carrying C_1 could explain the lack of C_1 in 1989 relative to 1988.

Extensive sulfur flows are present at Calcite Springs. Sulfur flows are not common, but have previously been reported to occur in active volcanic areas: for example, Siretoko-Iôsan, Japan; Sierra Negra and Azufre Volcanoes, Galapagos Islands; Mauna Loa, Hawaii; Lastarria Volcano, Northern Chile; and Volcan Poás, Costa Rica (Naranjo, 1985; Oppenheimer and Stevenson, 1989). At Lastarria and Volcan Poás, a rapid temperature increase caused by magmatic intrusion or draining of a fumarole capping lake, respectively, cause the melting of fumarolic sulfur.

To explain the sulfur flows at Calcite Springs, we initially thought that hot gases could melt the sulfur forming an ever increasing subterranean reservoir of molten sulfur. At some point the mass of sulfur would restrict the escape of gas causing the gas to push the sulfur out as if to clear the throat of the vent.

During the summer of 1988, extensive fires swept through Yellowstone National Park generating clouds of red-hot embers. Some embers settled on sulfur deposits and ignited them. The deposits subsequently became molten sulfur flows. Firefighters witnessed one such flow and were threatened by the toxic SO_2 gases emitted by the combustion of sulfur (Rick Hutchinson, Yellowstone National Park Geologist, personal communication, 1990). In addition, the sulfur flows at Calcite Springs were absent in July 1988, before the fires started, and first noted in July 1989, after the fires. At present it appears that ignition is the most likely mode of formation for the sulfur flows at Calcite Springs, although volcanic-like hydrothermal sulfur flows cannot be ruled out.

Both gas samples taken at Jade Hot Springs had identical compositions. The hydrocarbons were dominated by C_1 (approximately 3,200 ppm) followed by much lower amounts of C_2, C_3, i-C_4, n-C_4, and $C_{3:1}$, given in order of their respective concentrations; the pattern is characteristic of natural gas. It is interesting to note that the hydrocarbon gas distribution of Jade Hot Springs is distinctly more similar to the 1988 Calcite Springs gas composition than to the distributions observed at Calcite Springs in 1989. Based on the work done at Calcite Springs and the presence of C_2 through C_5 hydrocarbon gases, it is reasonable to suggest that subsurface hydrothermal alteration and transportation of organic matter is occurring here, or gases are being transported by hydrothermal waters from a nearby source. High C_1 concentrations (13.2 and 16.25%) were also found previously at Washburn Hot Springs (Allen and Day, 1935; Gunter and Musgrave, 1971). These concentrations are an order of magnitude higher than those found at Jade Hot Springs just 1.5 km south. According to the areal distributions of hydrocarbons, a source of gas may be located near Washburn Hot Springs or perhaps northeast towards Calcite Springs.

It is also important to note that the oils associated with Calcite Springs contain highly toxic, naturally-generated organic compounds such as benz(a)-pyrene and nitrogen containing heterocyclic polar compounds known to be health hazards. Therefore these substances must be handled with appropriate caution (Clifton et al. 1990 p.19).

Absaroka Range

The Sulphur Lake seep gases and those of Sweetwater Mineral Springs appear to have little in common. Sulphur Lake gas is mainly nitrogen (83.7%) and the low amount of methane (1,100 ppm) is likely from microbial sources, probably generated by bacteria utilizing fermentation to digest organic matter which sinks to the lake bed. In contrast, the gases present at Sweetwater Mineral Springs are CO_2-rich (94.2%) and contain significant hydrocarbon gases . C_1 to at least C_6 gases are present in concentrations of 5,400 ppm C_1 to 41 ppm n-C_4. The observed values are similar to those reported by Kvenvolden et al. (1989) suggesting that a stable source is responsible for these gases. The $\delta^{13}C$ values of -1.5 and -2.1‰ indicate that the CO_2 is most likely derived from the dissolution of carbonate rock.

The sustained presence of higher molecular weight gases, coupled with CO_2 derived from carbonate dissolution, strongly suggests that there is a nearby sedimentary source rock underlying the volcanic cover. Hydrothermal waters, though absent at the surface now, but present in the past, have leached an organic-rich horizon and passed through a carbonaceous rock. It cannot be determined with the present data if the source rock is oil-bearing or if the hydrothermal waters were hot enough to generate oil and gas from organic-rich sediments analogous to those reported in Yellowstone National Park by Clifton et al. (1990).

The Rattlesnake Mountain Anticline, Cody, Wyoming

Gas seeps at De Maris Hot Springs demonstrate a good example of systematic changes in hydrocarbon gas concentrations as well as other gases. From east to west, corresponding to an increase in depth within the Phosphoria Formation, the following increases in concentrations were noted: CO_2 from 65.2 to 80.0%, $\delta^{13}C$ of CO_2 from -9.22‰ to -5.68‰, and temperature from 27° to 36°C; the following decreases were observed: N_2+Ar+O_2 from 28.7 to 9%, C_1 from 2,690 to 1,357 ppm, C_2 from 100.8 to 58.5 ppm, C_3 from 0.81 to 0.64 ppm, $C_{3:1}$ from a trace to not detected, and i-C_4 from 0.87 to 0.51 ppm. Water analysis from other workers [Wyoming State Lab No. 7-1571 and 1572 (1976), reported in Breckenridge and Hinckley (1978)] also showed increases in common cations and anions from east to west. The sharp increase in water temperature from 27° to 36°C over about 20 m of stratigraphic section is difficult to explain. However, the temperature increase with a concomitant increase in solubility of ionic species accounts for most of the previously noted changes in chemistry.

The highest concentrations of hydrocarbon gases are found at the most eastern spring which has the lowest temperature and CO_2 concentrations. The ratios of $C_1/(C_2+C_3)$ are nearly equal at each seep (ranging from 23 to 27), supporting the notion of a common, finite hydrocarbon gas source; different sources would likely produce distinct $C_1/(C_2+C_3)$ ratios. The western spring contains CO_2 at the highest concentrations and hydrocarbons at the lowest concentrations. This observation suggests that the hydrocarbon gas fractions are increasingly diluted by CO_2 released from the parent hydrothermal water. The $\delta^{13}C$ values of CO_2 of -9.2 (west spring) and -5.7‰ (middle spring) can be explained as mixing of limestone derived CO_2 ($\delta^{13}C$ ~ 0‰) and CO_2 from the oxidation of oil ($\delta^{13}C$ ~ -28‰) (Faure, 1977).

Heasler (1982) modeled the Cody Hydrothermal System and determined that the groundwater flow was from west to east, and fluids in the Phosphoria Formation reached a maximum temperature of 46°C at a depth of 1.7 km. The maximum occurs in a synform southwest of the Rattlesnake Mountain Anticline with an associated northeast groundwater flow towards the springs. This model supports the possibility that the warm waters leach the oil-rich Phosphoria Formation thereby carrying previously generated thermogenic hydrocarbons regionally from west to east, occasionally surfacing at springs.

On the western side of the anticline, more hydrocarbon-rich springs exist. John Colter's "boiling tar spring," described in Love and Good (1970), is now submerged under Buffalo Bill reservoir. When the water levels are low in winter, an ice-free region remains above the springs (approximately 20 m below the water surface) with gas bubbles smelling of hydrogen sulfide and sometimes leaving an oil slick where they burst (Doug Lumis, Bureau of Reclamation, personal communication, 1990). The springs appear to emerge from the Phosporia Formation as do De Maris Springs and presumably represent a more petroleum-rich source.

Teton-Bridger Wilderness

The gas compositions are quite diverse in springs of the Teton-Bridger Wilderness (Soda Springs, Junction Springs and Tom Spring). Tom Spring is characterized by a very high concentration of CO_2 (98.5%) and only 20 ppm methane. The balance gases are N_2, O_2, and Ar. The N_2/Ar ratio of 33 and the N_2/O_2 ratio of 2 suggest that the dissolved air gases have been stripped by CO_2 (Bill Evans, personal communication, 1990). The $\delta^{13}C$ value of CO_2 of -9.36‰ implies a mixed source of CO_2 from limestone and oxidized organic matter. The two sample sites at Junction Springs, east and west, had surprisingly different amounts of N_2 and CO_2. The western seep contained 50.2% N_2 and 47.5% CO_2, whereas the eastern seep contained 19.8% N_2 and 78.4% CO_2. This difference is striking, considering that the seeps are within 50 m of one another. Both seep gases contained C_1, C_2, and $C_{2:1}$ in similar amounts. The major compositional differences may be caused by mixing of gases from different local sources. The isotopic values of CO_2, and the N_2/Ar and N_2/O_2 ratios support the idea of multiple sources. From west to east $\delta^{13}C$ of CO_2 decreases from -9.0 to -8.8‰, whereas the value at Tom Spring is -9.4‰. Other values decrease from west to east, such as N_2/Ar ratios (46 to 33) and N_2/O_2 ratios (55 to 30).

The observed N_2 and CO_2 values could also be attributed to differences in gas solubilities. The gases we sampled represent degassing spring waters that are supersaturated with CO_2 and N_2 at surface pressure. At 20°C, CO_2 is about 50 times more soluble than N_2, therefore N_2 will be released first from solution. Thus, water that is just starting to degas will generate a gas composition enriched N_2. As the solution continues to degas, CO_2 will become the predominate gas. In this context the bubbles of the seep gases could represent an earlier stage in the degassing process. N_2/Ar and N_2/O_2 ratios also support this supposition in that Ar and O_2 are about 2 times more soluble than N_2 at 20°C.

Basalt cobbles in intimate contact with both the spring discharge and the organic-rich sediments become finely plated with an undetermined form of iron sulfide, creating the appearance of a gilded basalt nugget. For unknown reasons, cobbles of other compositions were not plated. Perhaps the basalt acts as a nucleus for the precipitation of iron sulfide. As spring water is injected into the overlying sediment, water-borne ferrous (Fe^{+2}) ions may combine with sulfur derived from the hydrogen sulfide-rich sediment. The high iron and magnesium content of basalt relative to the other sedimentary and metamorphic cobbles may be an important factor in nucleation.

Conversely, the basalt may provide the source of iron in the proposed reaction. Iron sulfide plating was not observed away from the spring discharge. When spring discharges move, apparently plated cobbles slowly oxidize, leaving no hint of their previous contact with spring water. Within 3 months of exposure to the atmosphere, plating on the cobbles became oxidized. The cobble plating process does not appear to be unique to Junction Springs. Less spectacular, poorly plated basalt cobbles were also excavated at Calcite Springs.

Soda Springs, with large travertine mounds, are distinct from the previous swamp-like seeps. The presence of travertine mounds here is peculiar because the spring water is only 9°C; perhaps they represent former thermal features. The inorganic gas composition here is most similar to Junction Springs west with a tenfold decrease in C_1. This composition also reflects groundwater mixing. The $\delta^{13}C$ value of CO_2 of -10.4‰ suggests a more ^{13}C-depleted source here than at Junction Springs.

Grand Teton National Park

The seeps in and near the Grand Teton National Park (Jackson Lake Hot Springs, Kelly Warm Spring, and Teton Valley Ranch Warm Springs) were nearly all dominated by N_2 gas (81.0, 91.2, and 87.5%, respectively). O_2, CO_2, N_2, and Ar were present in amounts characteristic of groundwater in recent contact with the atmosphere. Jackson Lake Hot Springs gas contained a notable amount of CO_2 (3.28%). These waters are the warmest of the three sites (37°C measured at a nearby underwater vent with no apparent gas). Previously temperatures of 72° have been reported in this area by Love (Breckenridge and Hinckley, 1978), and the seeps emerge from the Madison Limestone, a possible source for CO_2. C_1 and C_2 were the only hydrocarbon gases detected. The concentrations of these hydrocarbons were significant only at Jackson Lake Hot Springs (C_1, 13.5% and C_2, 45 ppm). Kelly Warm Spring and Teton Valley Ranch Warm Springs contained only C_1 (1,172 and 65 ppm, respectively). Three seeps were analyzed at Teton Valley Ranch Warm Springs, and C_1 increased from 23 ppm at the western seep, to 40 ppm in the main pond, to 65 ppm at the eastern seep. The increase in C_1 corresponds to the flow direction of the spring's surface runoff, perhaps reflecting an input of more microbially generated C_1 as the distance from the spring sources increases.

In 1988, four seeps were analyzed by Kvenvolden et al. (1989) at Jackson Lake Hot Spring, included in Table 1 for reference. These seeps are labeled "Teton Fault numbers 1 through 4". In addition, Kelly Warm Spring and Halfmoon Lake Spring (Appendix 2-I) were sampled. The samples from the Teton Fault all contained measurable C_1 through C_4 hydrocarbons in contrast to the 1989 samples which contained only C_1 and C_2. As a check, the old samples were rerun and the presence of $C_{2:1}$, C_3, $C_{3:1}$, i-C_4, and n-C_4 were confirmed at levels comparable to those originally reported. The compositional difference between the 1988 and 1989 samples appears to be real and perhaps best explained by natural variability or by variations in sampling methods. For example, a bactericide was not used in the 1988 samples. Growing bacterial colonies could give rise to hydrocarbon gases; however, the production of 3 and 4-carbon chain hydrocarbon gases by microorganisms is not well established.

An experiment was preformed with the plastic bag collection technique in order to evaluate the possibility of gas adsorption into the plastic. A saturated hydrocarbon gas mixture of C_1 to C_4 in nitrogen was released underwater and collected in a plastic bag. Samples were removed from the headspace and analyzed every hour for seven hours, about twice as long as any field sample remained in a bag. The results showed a decrease in each hydrocarbon gas over time; furthermore, the longer the carbon chain the less gas was recovered. By the end of the experiment C_1 had decreased 20%, C_2 by 39%, C_3 by 40%, and n-C_4 by 65%. The solubility of these compounds in water varies with $C_1 < C_2 < nC_4 < C_3$, with C_2, C_3, and n-C_4 having nearly equal solubilities. C_1 through C_3 gas concentrations are consistent with removal from the gas phase into solution; however, the behavior of n-C_4 is not. The accelerated removal of n-C_4 is not due to its solubility alone; perhaps adsorption accounts for the extra loss, but this observation was not confirmed.

The Jackson Lake Hot Springs (Teton Fault seeps) contained higher molecular weight hydrocarbons in 1988. Because of the deeper water present 1989, the Jackson Lake Hot Springs were resampled in 1989 by the bag method; the later analyses lacked hydrocarbons greater than C_2. In addition, samples collected by direct water displacement at other sites also lacked higher molecular weight hydrocarbon gases. There is no positive correlation between the bag sampling method with possible gas adsorption and the direct sampling method; both techniques were used at sites lacking higher molecular weight hydrocarbon gases. Based on these results and the seemingly infinite variability of processes within the crust, the lack of these gases is best explained by natural variation in gas genesis and destruction.

The 1988 carbon isotope data set from this area offers some potential insight into the generation processes of the hydrocarbon gases (Table 1). As discussed previously, multiple sources of C_1 need to be considered. Isotopic composition is one of the best means available to ascertain sources. The carbon isotopic composition of C_1 ranges from -49.7‰ at Halfmoon Lake to -61.9‰ at Teton Fault seep #2, and the carbon isotopic composition of CO_2 ranges from -20.4‰ at Halfmoon Lake to -6.6‰ at Teton Fault seep #4. The C_1 isotopic values lie in a region of source ambiguity according to the criteria established by previous work (Claypool and Kaplan, 1974; Stahl, 1974; Fuex, 1977; Rice and Claypool, 1981; Schoell, 1983). Traditionally values of -60‰ and less are considered good evidence of microbially generated C_1, whereas those values heavier than -50‰ indicate a thermogenic source (Schoell, 1983). Values in between are commonly interpreted as mixtures from different sources. Recently several workers have focused on environments where $\delta^{13}C$ values of C_1 are in this zone of ambiguity (Jenden and Kaplan, 1986; Whiticar et al., 1986; Woltemate et al., 1984). These studies have demonstrated the existence of microbially generated C_1 within this range of values . The differences in isotopic composition are attributed to differing contributions from the methanogenic pathways of CO_2 reduction and acetate fermentation (Whiticar et al., 1986).

Jenden and Kaplan (1986) compared two marine environments: 1) Scripps Submarine Canyon, California, a shallow submarine canyon head filled with sand and decaying kelp, and 2) cored sediments of the Middle America Trench. They found a distinct isotopic difference which they attributed to fermentation as the primary C_1 source at Scripps Canyon and to CO_2 reduction at the Middle America Trench. They noted that the C_1 fermentation pathway produced $\delta^{13}C$ values for C_1 of -44 to -65‰ with a fractionation factor of approximately 50‰ between C_1 and CO_2, whereas CO_2 reduction produced values of -39 to -84‰ and a fractionation factor of about 70‰. CO_2 isotopic fractionation was also evident, and values range from -3 to -16‰ at Scripps Canyon and from -2 to +15‰ at the Middle America Trench. Results similar to those observed at Scripps Canyon were obtained by Whiticar et al. (1986) and Woltemate et al. (1984), who examined shallow sediments in freshwater lakes and attributed the C_1 to acetate fermentation. These workers point out that important factors for fermentation are very young sediments (detritus) and a herbaceous, woody substrate. CO_2 reduction occurs only after the entire series of metabolic oxidants are depleted (NO_3^-, MnO_2, Fe_2O_3, and SO_4^{-2}) and is usually common in older marine sediments.

Several lines of evidence, taken together, point to microbial acetate fermentation as a major contributor of hydrocarbons in the gases of the Grand Teton National Park. Figure 2 shows the carbon isotopic compositions of the gases at Yellowstone National Park (Gunter and Musgrave, 1966) and Grand Teton National Park (Kvenvolden et al., 1989). Values from Scripps Canyon (Jenden and Kaplan, 1986) are added for comparison. Each of the values for the Jackson Lake samples falls near the 50‰ line, whereas the value for the Halfmoon Lake gas seep falls near the 30‰ line, a characteristic of Yellowstone National Park geothermal samples. The Halfmoon Lake spring area is underlain by subbituminous coal beds in the Bacon Ridge Sandstone [for detailed stratigraphy see Love et al. (1951) and for a description of the seep, see Love and Love (1983) and Antweiler et al. (1989)]. Blackstone (1989) has suggested that coal in the Bacon Ridge Sandstone may produce methane. Thus the methane (94.5%) in the Halfmoon Lake gas seep may be derived in part from coal. In the Halfmoon Lake seep gas, the carbon isotopic composition of CO_2 of -20‰ is light, much lighter than any other sample. This composition can be explained by the aerobic decomposition of organic matter such as algae and terrestrial plants by microbes, and the degassing of coal. The carbon of these substances falls within the range of -12 to -34 ‰; coal averages about -25‰ (Faure, 1977).

The carbon isotopic composition of CO_2 in the Jackson Lake seeps is quite consistent ranging from -6.6 to -10.8‰ and, taken alone, offers little insight into source; however, there is a correlation between concentrations of C_1 and CO_2, and of $\delta^{13}C$ of CO_2. As C_1 concentrations increase CO_2 concentrations decrease, and the isotopic compositions become lighter. The same pattern was observed in Scripps Canyon. Figure 3 shows the relationship between the carbon isotopic composition of CO_2 and the amount of CO_2 gas present. Again, values for gases from Scripps Canyon are included along with the values for our gas samples. The respective data overlap, supporting the idea that fermentation is occurring. The samples with the isotopically light CO_2 (Halfmoon Lake, Kelly Warm Spring, and Sulphur Lake) represent environments where microbial respiration or coal degassing (Halfmoon Lake) can account for the isotopic compositions of CO_2, and fermentation can explain the carbon isotopic values of C_1. O_2 is most depleted in these samples, an indication that it is being utilized. Each process is a continuum, and several processes are occurring concurrently. The proportion of one process over another determines the geochemical signature.

Dilution of near-suface groundwater by geothermal fluids possesing distinct carbon isotopic signatures is important when interpreting the $\delta^{13}CO_2$ values. Geothermal waters in the Yellowstone region carry a characteristic carbon isotopic signature for CO_2 of roughly -2 to +2‰, derived principally from the dissolution of limestone in the area (dissolved atmospheric CO_2 with a $\delta^{13}C$ of -7‰ is also a consideration, but this source is effectively diluted by much greater amounts of geothermal CO_2 in most cases). Dilution of sampled gases by geothermally derived CO_2 is observed in the Jackson Lake Hot Springs gases where the $\delta^{13}C$ values of the CO_2 are intermediate between those in Yellowstone Park and those from Halfmoon Lake. This conclusion is supported by the fact that the Jackson Lake Hot Springs are the warmest of the seeps in the Teton National Park and Teton-Bridger Wilderness areas, and the overall CO_2 volumes are the highest, suggesting an important geothermal source. By addition of CO_2 from fermentation and respiration (?) to CO_2 from geothermal sources, the resulting $\delta^{13}C$ values should be intermediate between two end members as are the isotopic values obtained at Jackson Lake Hot Springs . Determination of $^{14}CO_2$ would be a test for this system because geothermal CO_2 would be "dead" (carbon derived from the dissolution of limestone in this area should not contain measureable amounts of ^{14}C) and the resulting CO_2 should be low in^{14}C. Another approach to evaluating the possible role of microorganisms in gas generation would be the determination of the isotopic composition of hydrogen in C_1. Numerous studies, including those of Jenden and Kaplan (1986), Whiticar et al. (1986), and Woltemate et al. (1984), have noted that the characteristic $\delta D(CH_4)$ of < -250 ‰ as a signature for C_1 derived from fermentation. Finally, the molecular compositions of the hydrocarbon gases indicate microbial activity. $C_{2:1}$ and $C_{3:1}$ are known to be produced by microbes (Davis and Squires 1956, Vogel et. al. 1982) and the $C_1/(C_2+C_3)$ ratios (3,400 to 41,000) are well above 1000, the guideline commonly used in denoting microbially generated C_1.

CONCLUSIONS

The cross section of natural gases sampled in northwestern Wyoming fall into four categories based on the results of this study:

1. CO_2 dominated, where the source of CO_2 is likely the dissolution of limestone by ascending hydrothermal fluids associated with hydrocarbon gases principally derived from the thermal decomposition of sedimentary organic matter.

2. N_2 dominated, where atmospherically derived N_2 has apparently been introduced into the groundwater during the recharging process. The remainder of the gas is made of variable amounts of C_1, CO_2, or O_2. Microbial processes are likely responsible for producing the majority of C_1.

3. CO_2 and N_2 co-dominant warm springs, where discrete groundwaters apparently mix or locally come into contact with a CO_2 source such as limestone bedrock. The principal hydrocarbon gas is C_1 and is probably produced primarily by microbial action, with, at times the possibility of a dilute influx of thermogenetically derived hydrocarbons from unknown sources.

4. C_1 dominated, where C_1 is probably generated by microbial processes or by the degassing of coal.

A comparison of samples taken in Grand Teton National Park in two different years demonstrated a high degree of variability in the composition of hydrocarbon gases . We evaluated sampling techniques and analytical compatibilities between years, and found some minor discrepancies; however, natural variability in the system mediated by microbial processes or changes in the spring plumbing system are the most likely causes of the observed variabilities.

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Table 1

	C_1	C_2	$C_{2:1}$	C_3	$C_{3:1}$	i-C_4	n-C_4	CO_2	N_2	O_2	Ar	N_2	O_2	Ar	$\frac{N_2}{O_2}$	$\frac{N_2}{Ar}$	$\frac{C_1}{C_2+C_3}$	$\frac{C_2}{C_{2:1}}$	$\delta^{13}C_{CH4}$	$\delta^{13}C_{CO2}$
	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(%)	(%)	(%)								(‰)	(‰)
YELLOWSTONE NATIONAL PARK																				
Calcite Springs S.	0.0090	nd	2.1	1.3	2.1	nd	0.2	96.3	na	na	na	na	na	na	na	na	69	na	na	na
Calcite Springs N.	0.0039	nd	0.01	0.76	2.0	nd	nd	92.4	na	na	na	na	na	na	na	na	55	na	na	na
Calcite Springs '88	0.58	36	1.0	11	nr	1.7	2.8	94.7	4.3	0.3	0.10	4.3	0.3	0.10	14.3	43	120	36	na	-1.6
Jade Hot Springs (vent)	0.32	59	nd	15	0.14	1.2	2.3	82.7	na	na	na	na	na	na	na	na	44	na	na	na
Jade Hot Springs (pool)	0.30	53	nd	13	trace	1.1	2.1	na	na	na	na	na	na	na	na	na	45	na	na	na
Jade Hot Springs '88	0.36	62	0.2	16	nr	1.9	3.2	91.0	7.1	1.3	0.16	7.1	1.3	0.16	5.5	44	46	310	na	+0.5
(Washburn Hot Springs area)																				
ABSAROKA MOUNTAINS																				
Sweetwater Mineral Springs	0.54	12.2	nd	67	nd	16	41	93.8	4.4	1.2	0.10	4.4	1.2	0.10	37	43	28	na	na	-1.5
Sweetwater Mineral Springs '88	0.67	126	0.9	63	nr	17	32	95.4	2.8	1.1	0.07	2.8	1.1	0.07	2.6	40	35	140	na	-2.1
Sulphur Lake	0.11	nd	nd	0.02	nd	nd	nd	2.2	84.3	12.4	0.95	83.7	12.3	0.95	6.8	88	na	na	na	-12.0
RATTLESNAKE MOUNTAIN																				
De Maris Springs E.	0.27	101	nd	0.81	trace	0.87	nd	65.1	na	na	na	na	na	na	na	na	27	na	na	na
De Maris Springs middle spring	0.24	91	nd	0.71	nd	0.68	nd	70.9	28.1	0.20	0.59	27.9	0.20	0.59	140	47	26	na	na	-9.2
De Maris Springs W.	0.14	59	nd	0.64	nd	0.51	nd	80.0	na	na	na	na	na	na	na	na	23	na	na	-5.7
TETON-BRIDGER WILDERNESS																				
Soda Springs 1	0.024	0.16	nd	nd	nd	nd	nd	29.1	na	na	na	na	na	na	na	na	810	na	na	-10.4
Soda Springs 2	0.024	nd	0.24	nd	nd	nd	nd	39.7	58.3	1.15	0.89	57.4	1.13	0.88	51	65	na	na	na	nd
Tom's Spring	0.0021	nd	nd	nd	nd	nd	nd	98.5	0.98	0.49	0.03	0.98	0.49	0.03	2	33	na	na	na	-9.4
Junction Springs W.	0.30	0.54	0.12	nd	nd	nd	nd	47.5	50.2	0.91	1.09	49.1	0.89	1.07	55	46	5,400	4.5	na	-9.0
Junction Springs E.	0.46	0.46	trace	0.13	nd	nd	nd	78.4	19.8	0.67	0.60	19.5	0.66	0.59	30	33	8,400	na	na	-8.8
GRAND TETON NATIONAL PARK																				
Kelly Warm Spring	0.12	nd	nd	nd	nd	nd	nd	0.66	91.2	6.86	1.12	89.5	6.73	1.10	13	81	na	na	na	na
Kelly Warm Spring '88	0.060	4	0.4	2.7	nr	0.6	0.9	0.7	89.1	9.0	1.2	89.1	9.0	1.2	9.9	74	90	10	na	-18.6
Teton Valley Ranch E.	0.0065	nd	nd	nd	nd	nd	nd	na	na	na	na	na	na	na	na	na	na	na	na	na
Teton Valley Ranch W.	0.0023	nd	nd	nd	nd	nd	nd	0.67	87.5	10.7	1.10	86.3	10.6	1.08	8.1	80	na	na	na	na
Teton Valley Ranch N.	0.0040	nd	nd	nd	nd	nd	nd	na	na	na	na	na	na	na	na	na	na	na	na	na
Jackson Lake Hot Springs	13.5	45	nd	nd	nd	nd	nd	3.28	81.0	1.17	1.05	82.8	1.2	1.07	69	77	3,400	na	na	na
(located closest to Seep 2)																				
Jackson Lake H.S. Seep 1 '88	20.5	37	3.5	1.2	nr	0.4	0.4	7.8	69.4	1.1	1.2	69.4	1.1	1.2	63	58	5,400	11	-59.8	-9.4
Jackson Lake H.S. Seep 2 '88	83.7	16	13	4.5	nr	1.8	0.9	5.1	10.4	0.6	0.22	10.4	0.6	0.22	17	47	41,000	1.2	-61.9	-10.8
Jackson Lake H.S. Seep 3 '88	18.6	34	3.2	1.1	nr	0.4	0.3	9.7	na	na	na	na	na	na	na	na	5,300	11	-59.8	-8.1
Jackson Lake H.S. Seep 4 '88	7.6	12	3.4	0.7	nr	0.2	0.2	7.9	81.8	1.4	1.3	81.8	1.4	1.3	58	63	6,000	3.5	-59.2	-6.6
Halfmoon Lake Seep '88	94.5	185	3.1	1.7	nr	0.4	0.6	1.3	3.6	0.5	0.08	3.6	0.5	0.08	7.2	45	5,100	60	-49.7	-20.4

Abbreviations used:
nd = not detected
na = not ascertained
nr = not reported

Table 1. Composition of gases from natural gas seeps in Northwertern Wyoming.

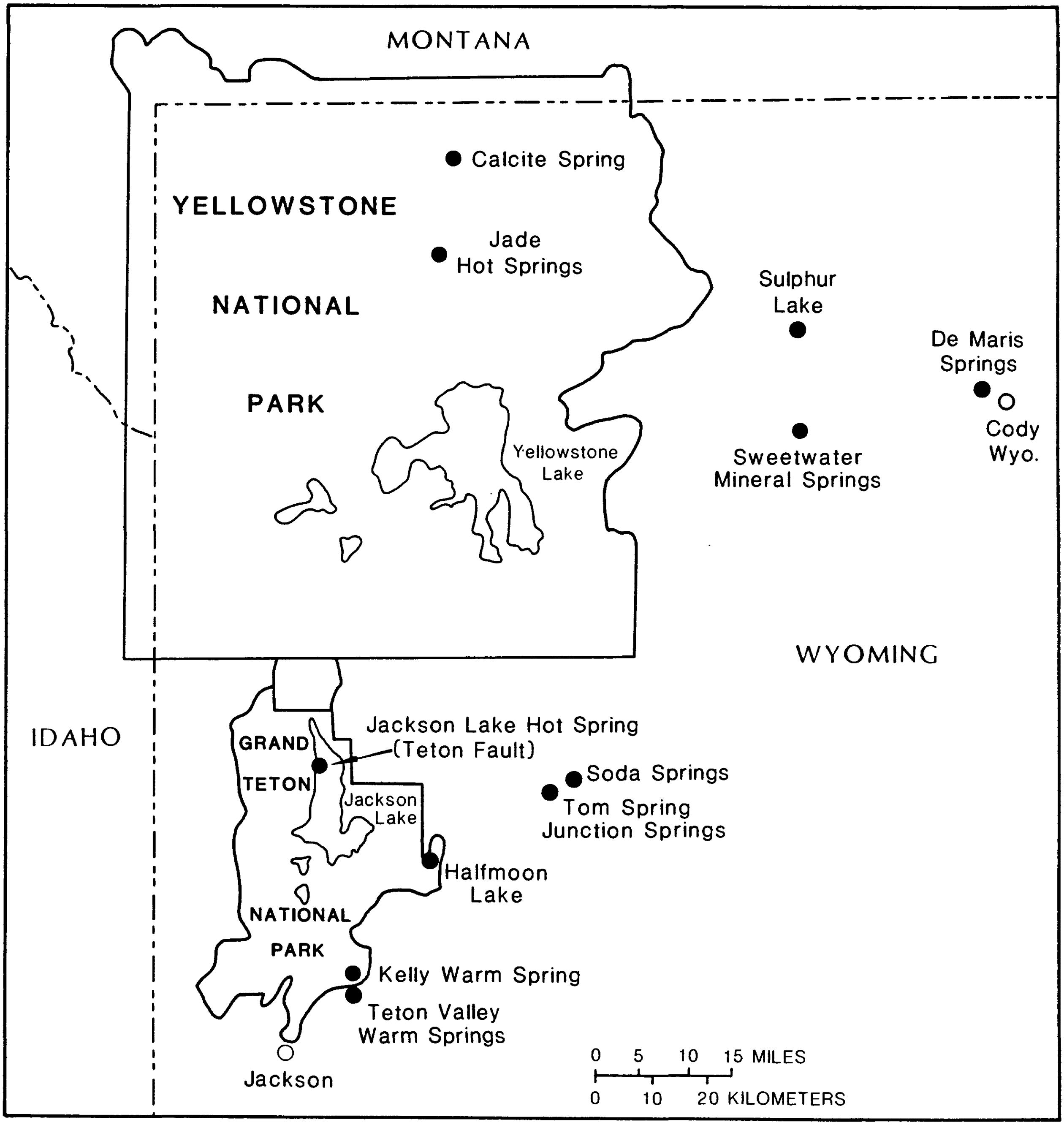


Figure 1. Locations of natural gas seeps sampled for this study and by Kvenvolden et al. (1989) in northwestern Wyoming.

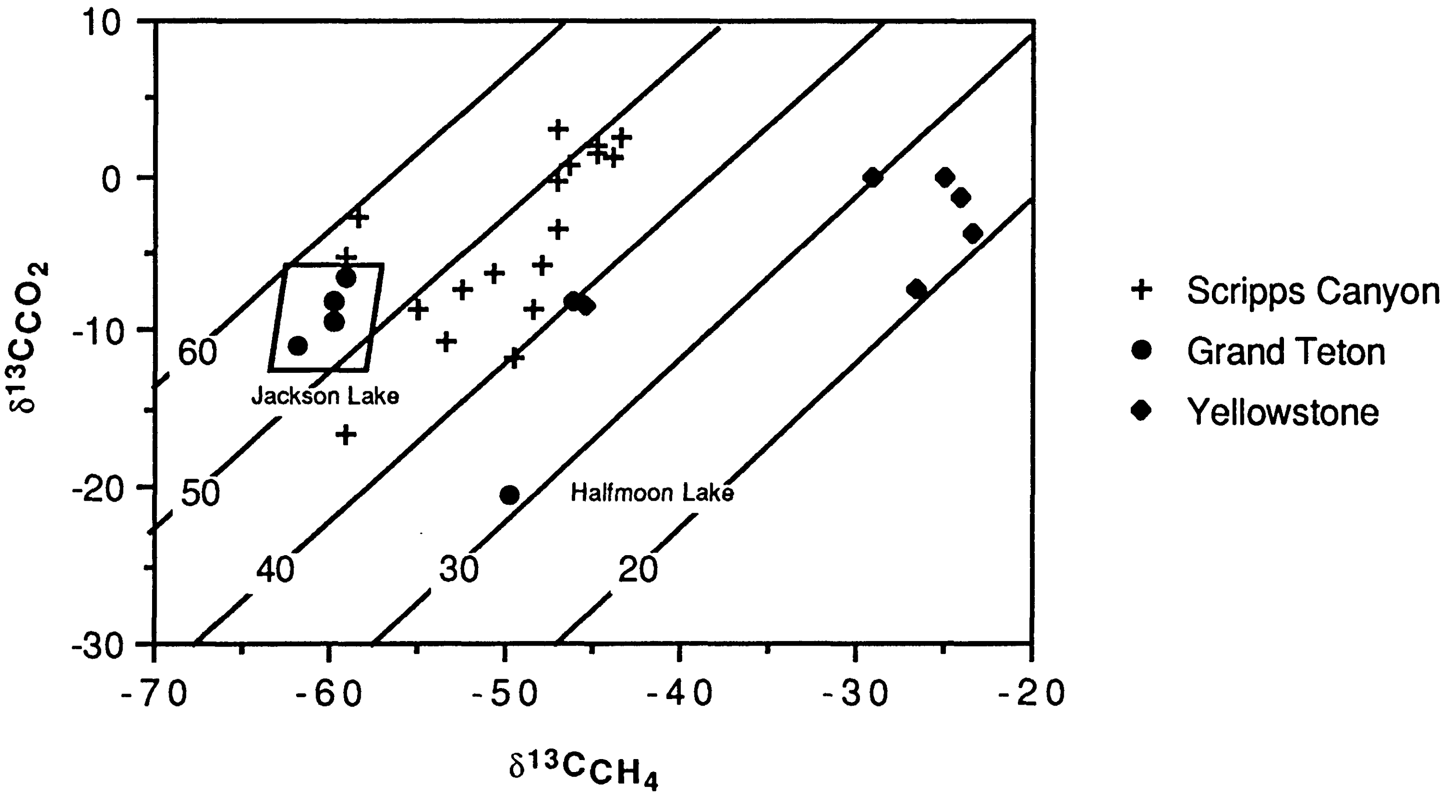


Figure 2. Plot of carbon dioxide $\delta^{13}C$ vs. methane $\delta^{13}C$ for three sets of gases: Grand Teton National Park data (Kvenvolden et al., 1989), Yellowstone National Park data (Gunter and Musgrave, 1971), and the Scripps Submarine Canyon data (Jenden and Kaplan, 1986). The lines represent carbon isotope fractionations of 1.020 through 1.060 between carbon dioxide and methane.

The fractionation factor α is defined by the equation: $\alpha = \frac{(1000+\delta^{13}C_{CO_2})}{(1000+\delta^{13}{}_{CH_4})}$

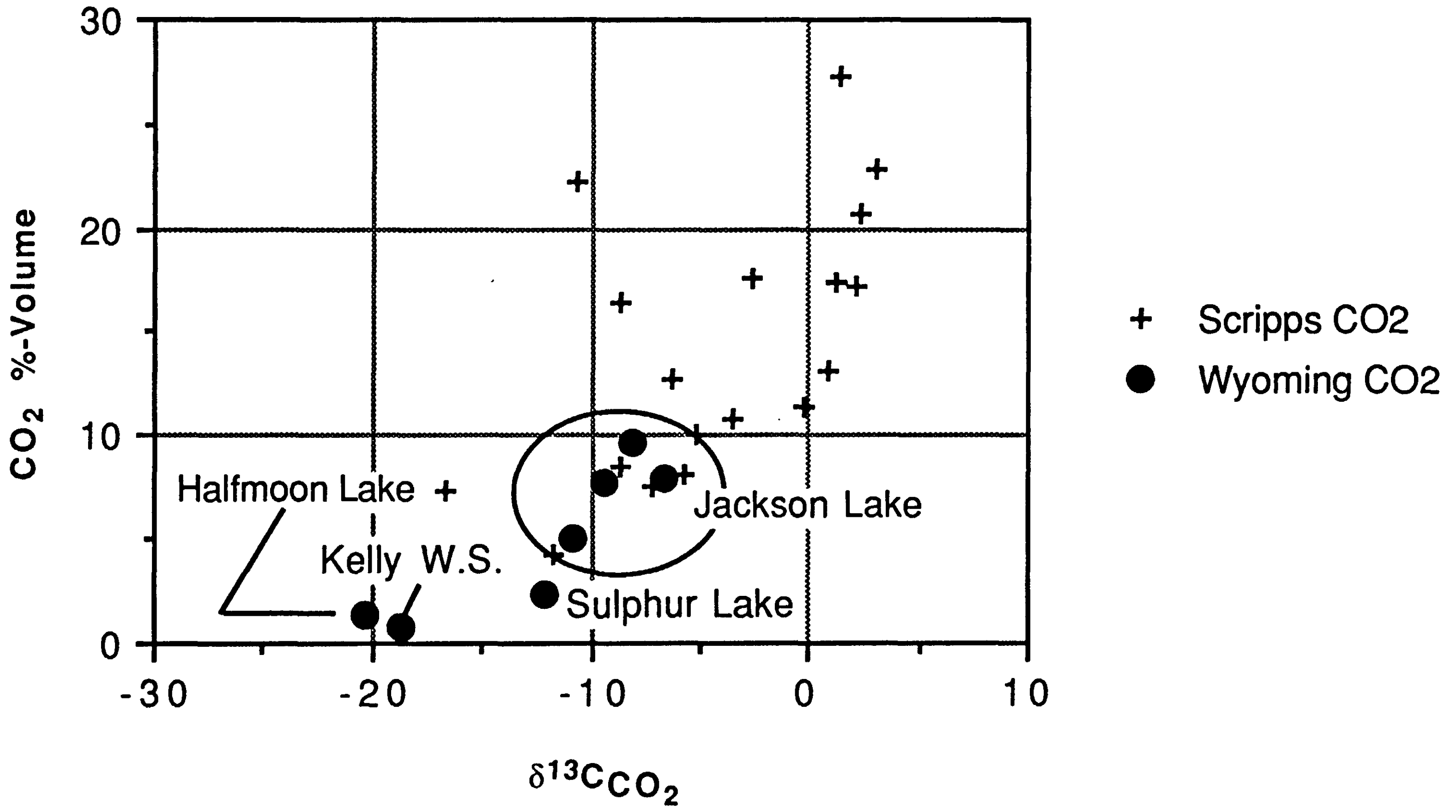


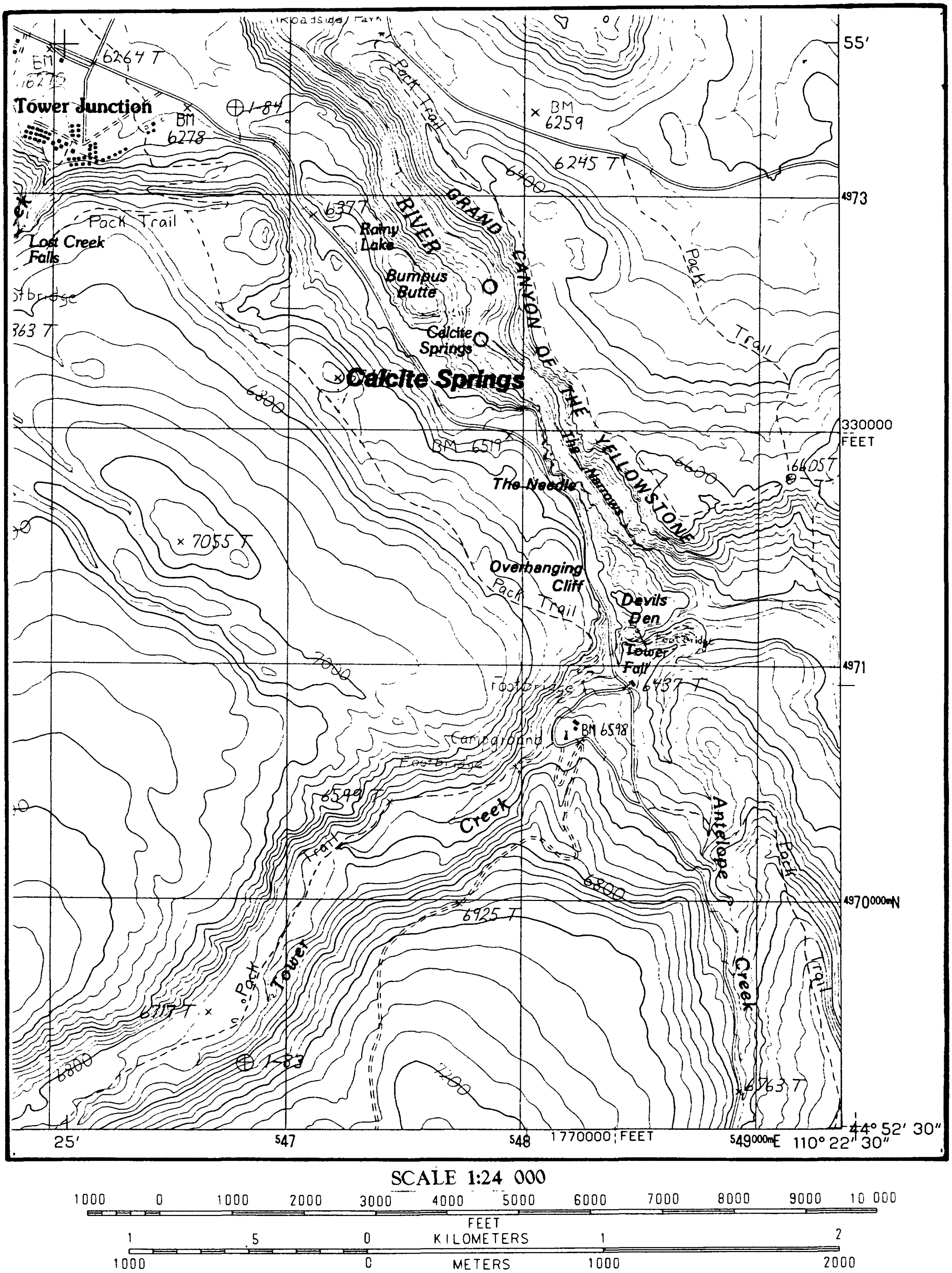
Figure 3. Plot of carbon dioxide δ13C vs. carbon dioxide concentration for the Yellowstone-Grand Teton seeps (Kvenvolden et al., 1989), Sulphur Lake, and the Scripps Submarine Canyon gases (Jenden and Kaplan, 1986).

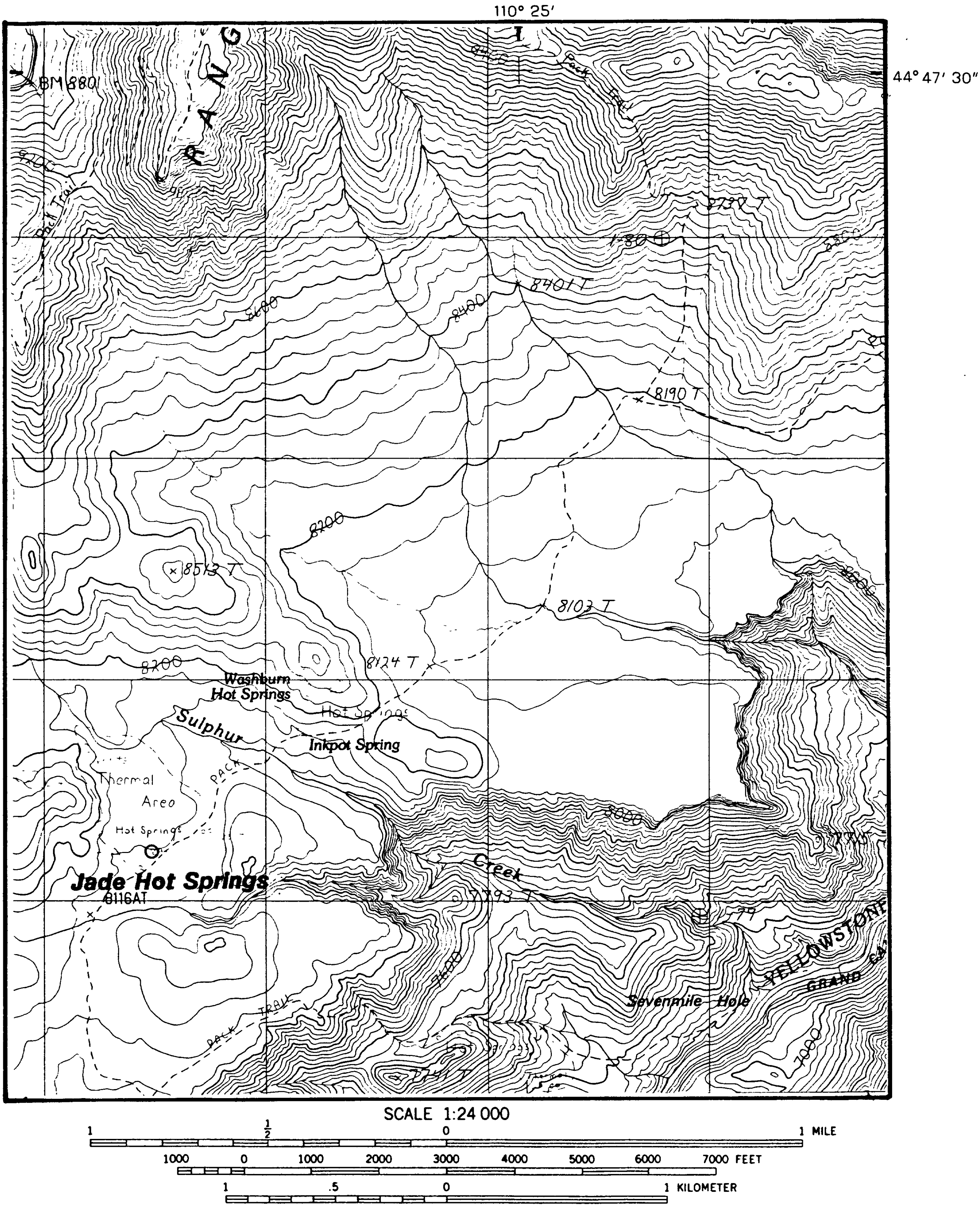
Appendix 1

Yellowstone-Teton Spring Gas Sites, 1989

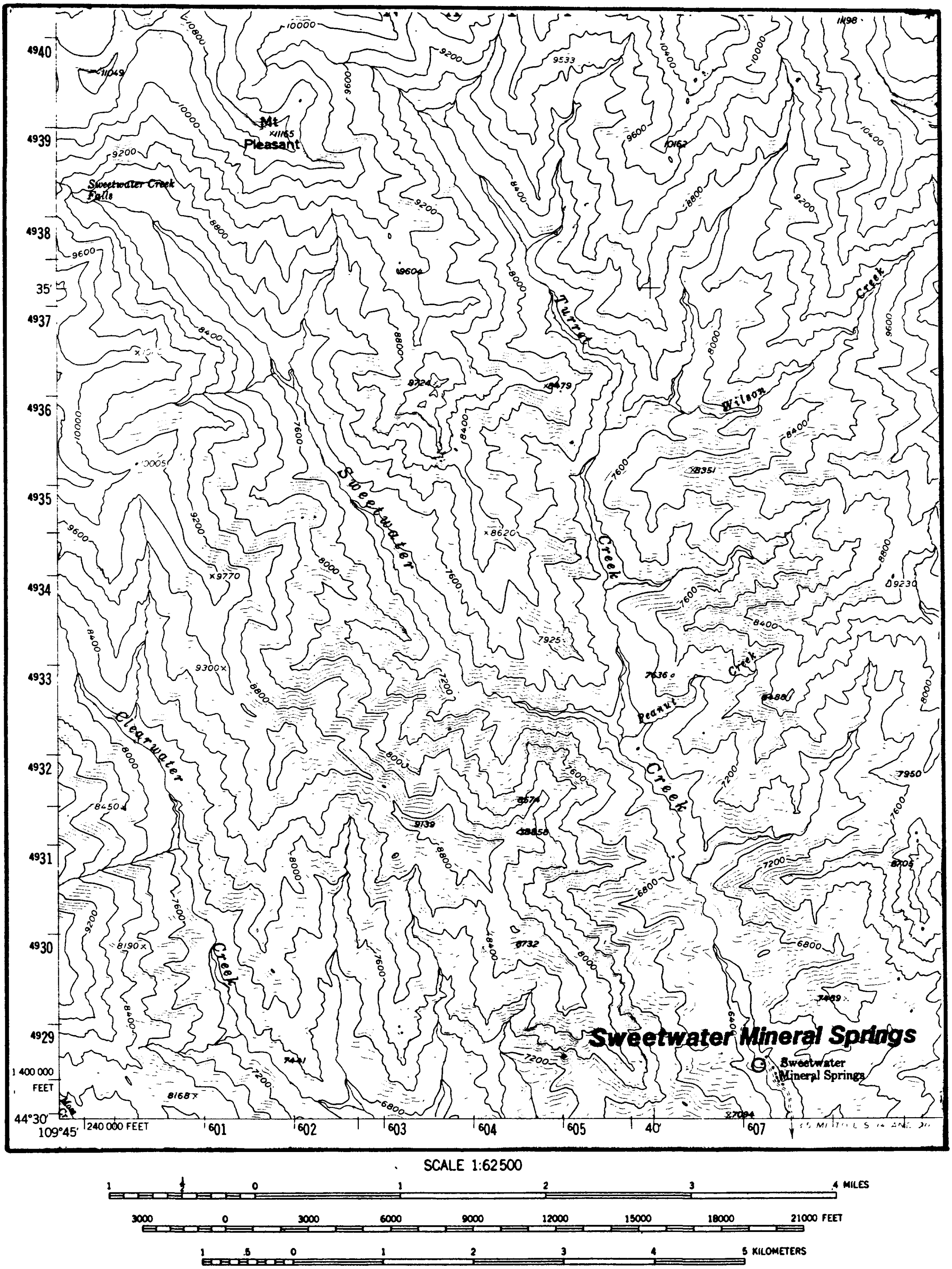
Sample Site	Latitude,Longitude	Lithology ,Water pH,Temp.
Yellowstone Nat. Park		
Jade Hot Springs	44°45'54"N,110°25'45"W	Altered rhyolite, pH=2,30°C
Calcite Springs	44°54'24"N,110°23'41"W	Altered rhyolite, pH=2,94°C
Absaroka Mountains		
Sweetwater Min. Springs	44°30'15"N,109°34'01"W	Alluvium overlying andesitic volcaniclastics
Sulphur Lake	44°40'19"N,109°37'08"W	Alluvium overlying andesitic volcaniclastics
Rattlesnake Mountain		
De Maris Springs	43°30'49"N,109°06'50"W	Phosphoria Fm., (leached dolomite here), pH=8,28-36°C
Teton Nat. Park		
Jackson Lake Hot Springs	43°57'45"N,110°41'42"W	H_2S rich sediment overlying Madison Ls.
Kelly Warm Spring	43°38'21"N,110°36'54"W	carbonate rich sediment overlying glacial deposits pH=6.9,27°C
Teton Valley Ranch	43°37'27"N,110°36'18"W	Alluvium overlying Madison Ls., pH=6.6,7-19°C
Teton-Bridger Wilderness		
Tom Spring	43°53'54"N,110°12'19"W	Travertine cemented alluvium overlying Madison Ls., pH=6.6,28.7°C
Junction Springs	43°54'04"N,110°12'17"W	Organic rich clay and peat overlying alluvium, 25°C
Soda Springs	43°54'34"N,110°10'41"W	Travertine overlying Precambrian metasediments pH=7.0,12.1°C

Appendix 2

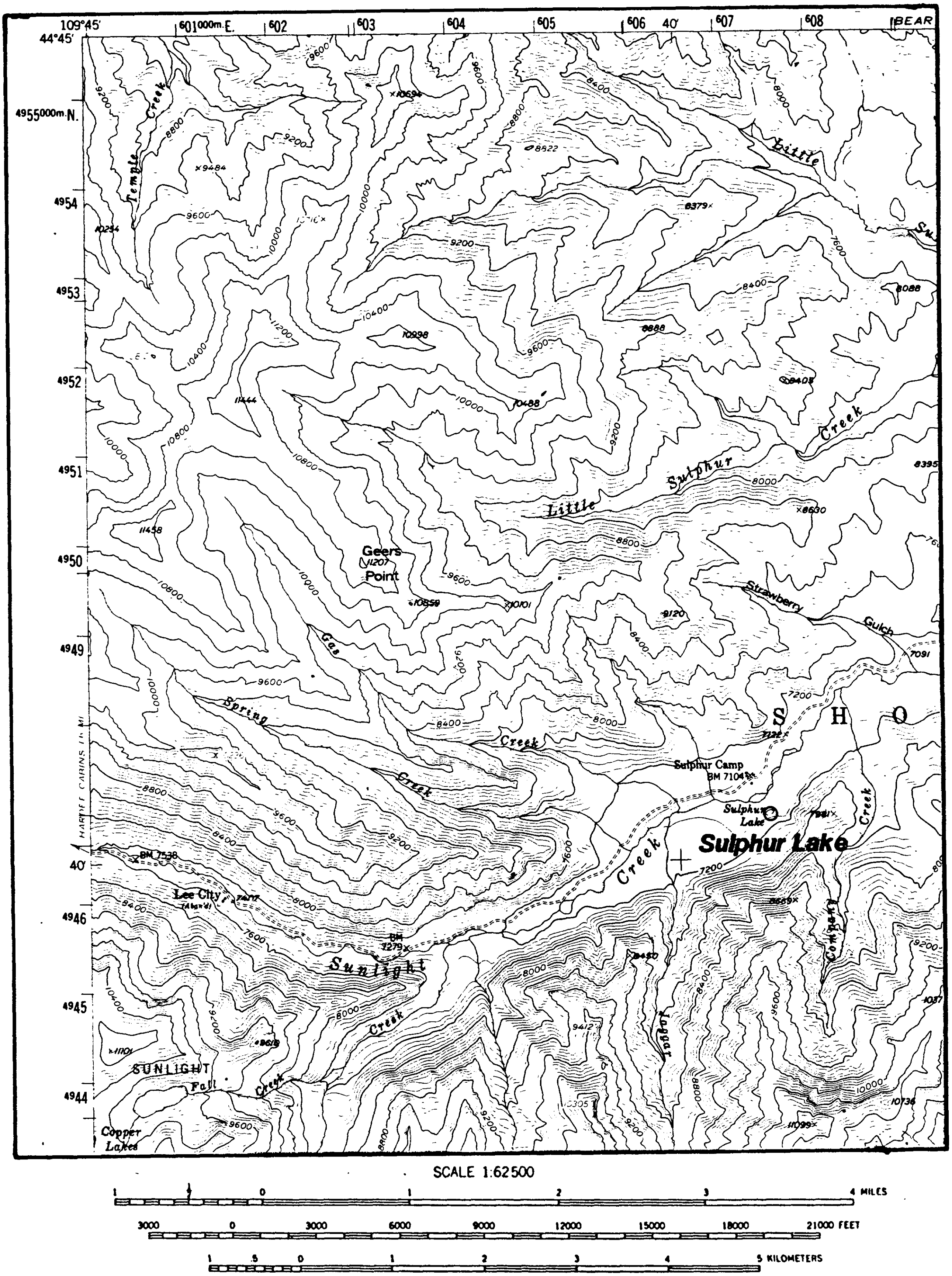

Roadside Park
Tower Junction
BM 6275
6264 T
BM 6278
1-84
Pack Trail
BM 6259
6245 T
Lost Creek Falls
6377
Rainy Lake
RIVER
GRAND CANYON OF THE YELLOWSTONE
Bumpus Butte
Calcite Springs
Calcite Springs
6400
Pack Trail
Footbridge
363 T
6800
BM 6519
The Narrows
The Needle
6600
6605 T
7055 T
Overhanging Cliff
Pack Trail
Devils Den
Footbridge
Tower Fall
6437 T
7000
Footbridge
BM 6598
Campground
Footbridge
6599 T
Creek
Trail
Antelope
Pack
6800
6925 T
Tower
Pack
6717 T
1-83
6800
7100
Creek
Trail
6763 T
55′
4973
330000 FEET
4971
4970000mN
44° 52′ 30″
25′
547
548
1770000 FEET
549000mE
110° 22′ 30″
SCALE 1:24 000
1000
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10 000
FEET
1
.5
0
KILOMETERS
1
2
1000
0
METERS
1000
2000


110° 25′
44° 47′ 30″
BM 8801
RANG
Pack Trail
8732 T
8401 T
8400
8190 T
8513 T
8200
8103 T
8124 T
Washburn Hot Springs
Hot Springs
Sulphur
Inkpot Spring
Thermal Area
PACK
Hot Springs
Jade Hot Springs
8116AT
Creek
8000
7793 T
7600
PACK TRAIL
7741 T
Sevenmile Hole
YELLOWSTONE
GRAND CA
7000
SCALE 1:24 000
1
½
0
1 MILE
1000
0
1000
2000
3000
4000
5000
6000
7000 FEET
1
.5
0
1 KILOMETER

2-B


Mt Pleasant
11165
Sweetwater Creek Falls
Turret Creek
Wilson Creek
Sweetwater Creek
Peanut Creek
Clearwater Creek
Sweetwater Mineral Springs
Sweetwater Mineral Springs
11049
10162
9604
8724
8479
8351
10005
8620
9770
9230
7925
9300
7636
8488
7950
8574
9139
8858
8705
8190
8732
7489
8450
7441
8168
7094
11198
9533
10000
10400
10800
9600
9200
8800
8400
8000
7600
7200
6800
6400
4940
4939
4938
35'
4937
4936
4935
4934
4933
4932
4931
4930
4929
1 400 000 FEET
44°30'
109°45'
240 000 FEET
601
602
603
604
605
40'
607
SCALE 1:62500
1
½
0
1
2
3
4 MILES
3000
0
3000
6000
9000
12000
15000
18000
21000 FEET
1
.5
0
1
2
3
4
5 KILOMETERS

2-C


109°45′
44°45′
601000m.E.
602
603
604
605
606
40′
607
608
BEAR
4955000m.N.
4954
4953
4952
4951
4950
4949
40′
4946
4945
4944
Temple Creek
Little Su
Little Sulphur Creek
Geers Point
11207
Strawberry Gulch
Gas Spring Creek
Spring Creek
S H O
Sulphur Camp
BM 7104
Sulphur Lake
Sulphur Lake
Creek
Lee City
BM 7538
BM 7279
Sunlight Creek
Company Creek
Jaggar
SUNLIGHT
Fall Creek
Copper Lakes
HARVEY CABINS
SCALE 1:62500
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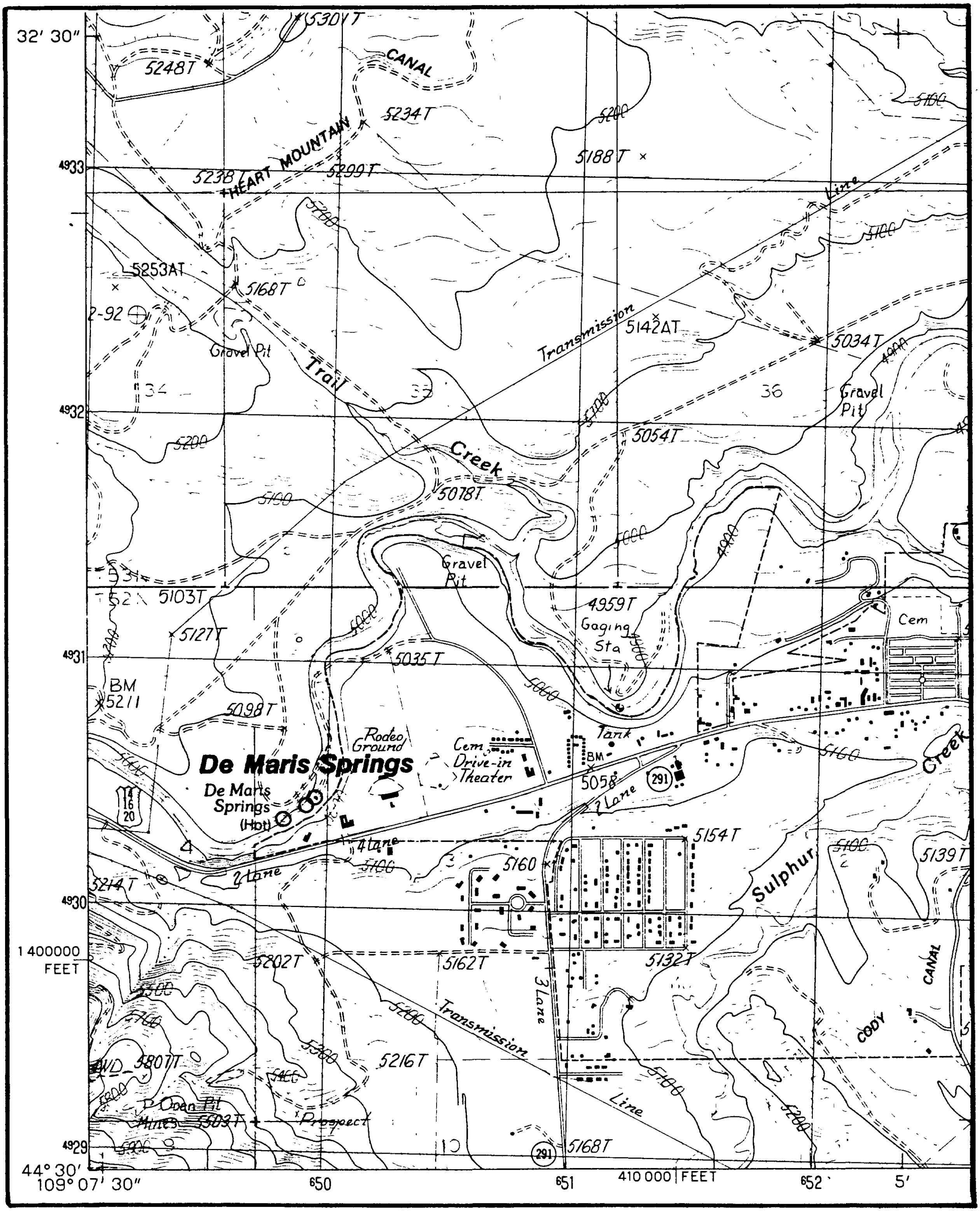
3000 0 3000 6000 9000 12000 15000 18000 21000 FEET
1 .5 0 1 2 3 4 5 KILOMETERS

2-D



32′ 30″
5301T
5248T
CANAL
5234T
HEART MOUNTAIN
5238T
5299T
5188T
5200
5100
Line
Transmission
5253AT
5168T
2-92
Gravel Pit
Trail
5142AT
5034T
34
35
36
Gravel Pit
Creek
5054T
5018T
5100
Gravel Pit
5103T
5127T
4959T
Gaging Sta
5035T
BM 5211
5098T
Cem
Rodeo Ground
Cem Drive-in Theater
Tank
BM 5058
De Maris Springs
De Maris Springs (Hot)
14 16 20
4 lane
2 Lane
291
5154T
5160
Sulphur
Creek
5139T
5214T
5202T
5162T
3 Lane
5132T
CANAL
CODY
Transmission
Line
5216T
5807T
Open Pit Mines
5503T
Prospect
5168T
291
4933
4932
4931
4930
4929
1 400000 FEET
44° 30′
109° 07′ 30″
650
651
410 000 FEET
652
5′
SCALE 1:24 000
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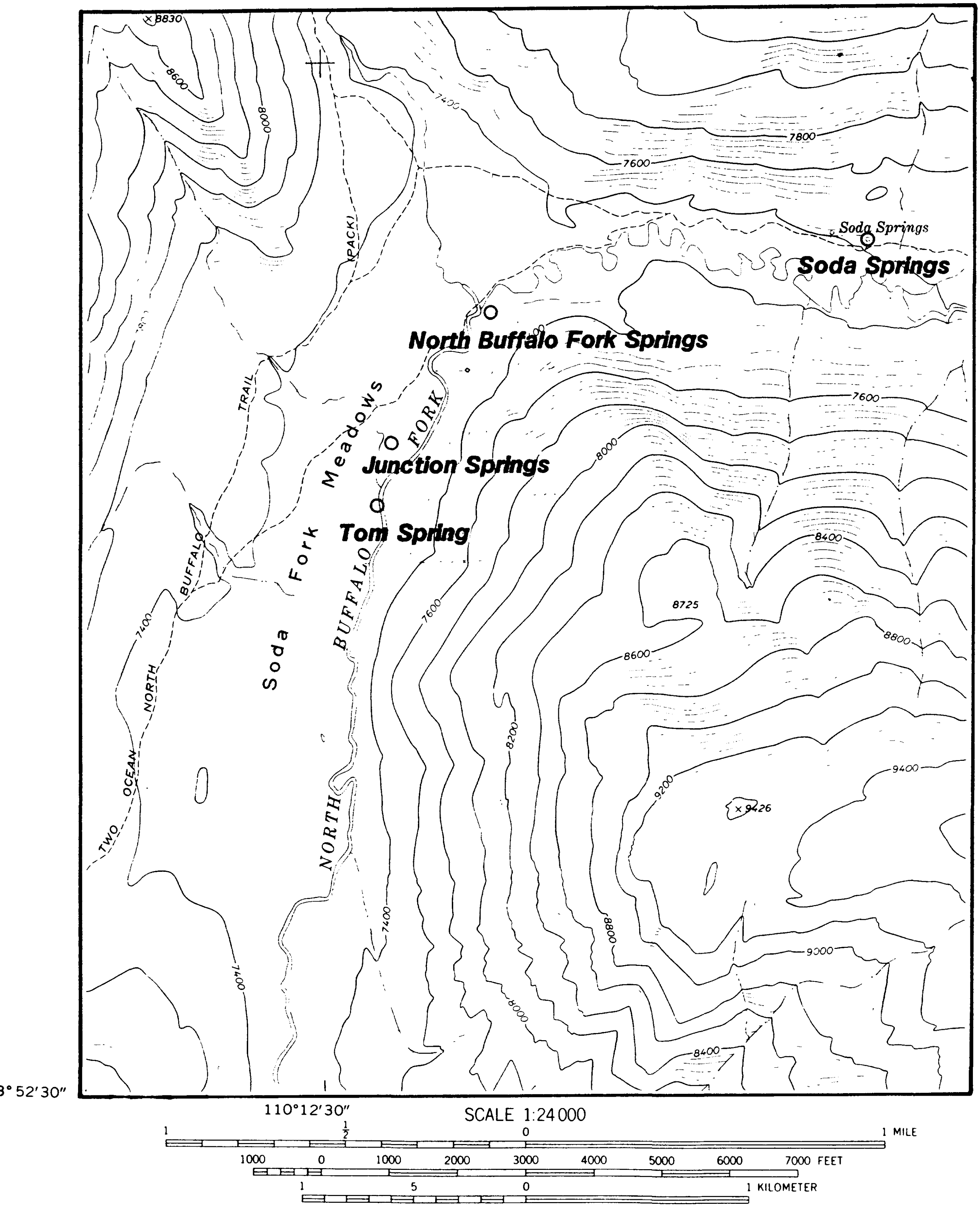
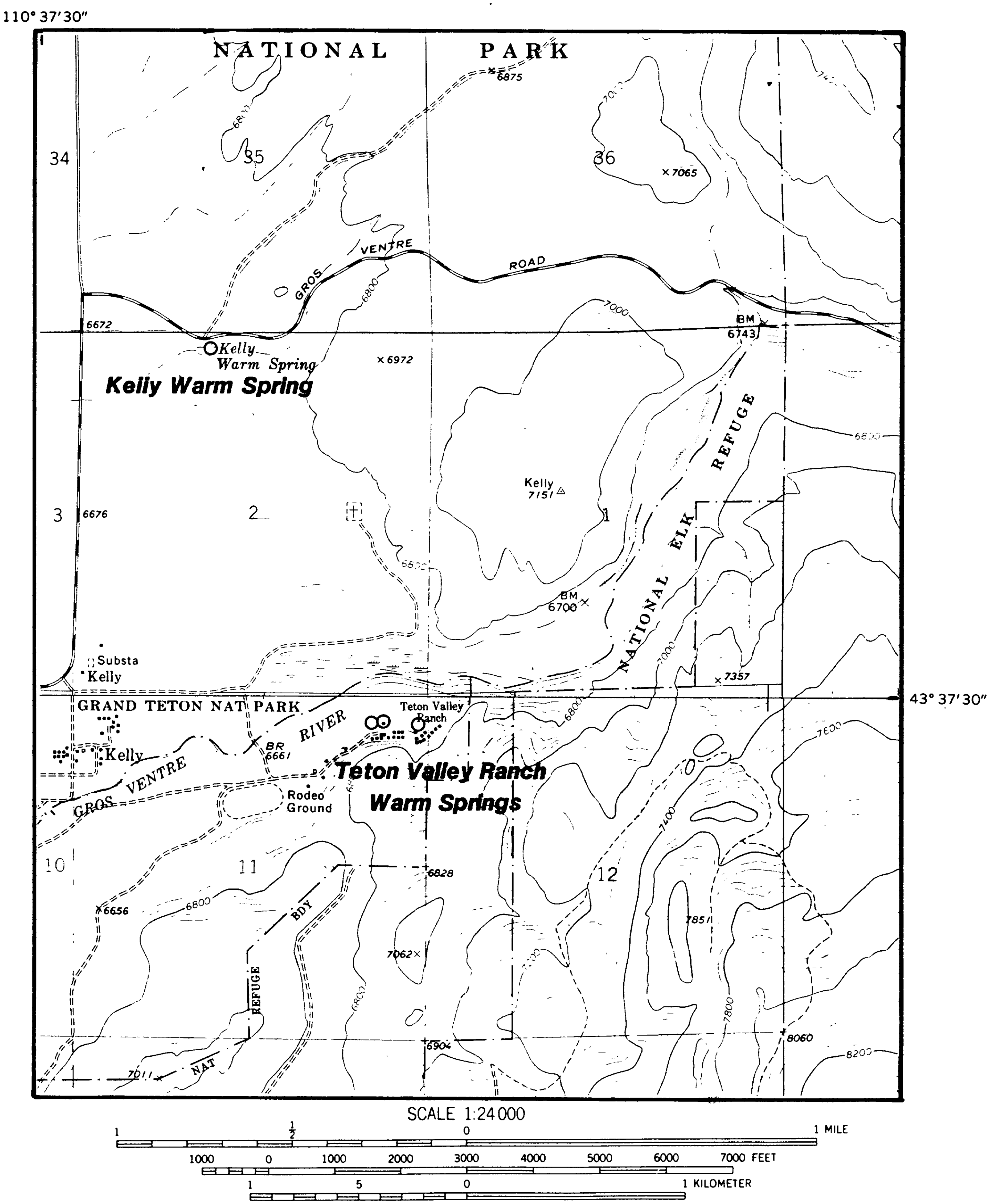
1000 0 1000 2000 3000 4000 5000 6000 7000 FEET
1 .5 0 1 KILOMETER

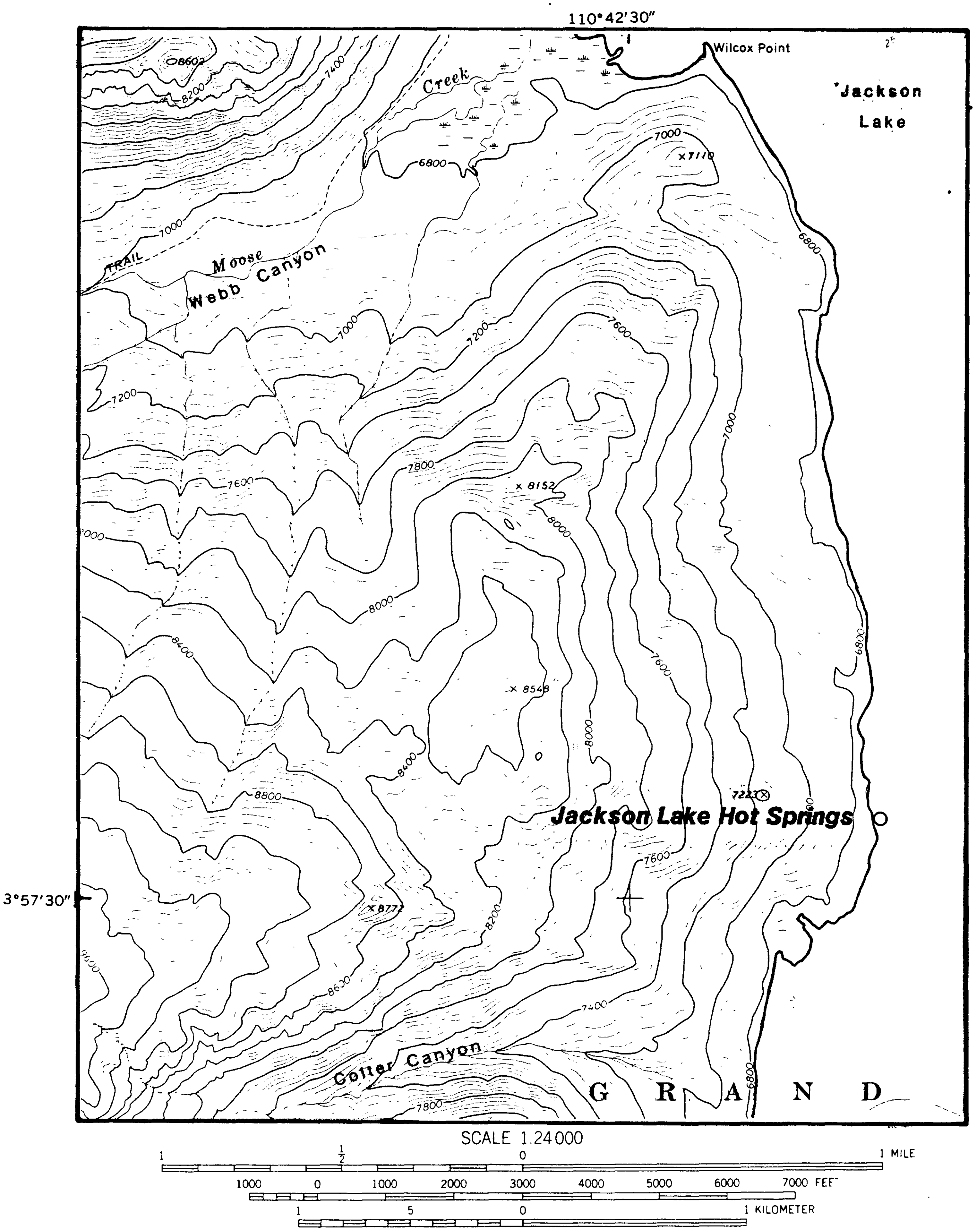
2-E


8830
8600
8000
7400
7800
7600
(PACK)
Soda Springs
Soda Springs
North Buffalo Fork Springs
7600
TRAIL
Soda Fork Meadows
NORTH BUFFALO FORK
Junction Springs
8000
Tom Spring
8400
BUFFALO
8725
7600
8800
7400
8600
NORTH
Soda
8200
OCEAN
9400
9200
9426
TWO
7400
8800
9000
7400
8000
8400
3°52'30"
110°12'30"
SCALE 1:24 000
1 ½ 0 1 MILE
1000 0 1000 2000 3000 4000 5000 6000 7000 FEET
1 .5 0 1 KILOMETER

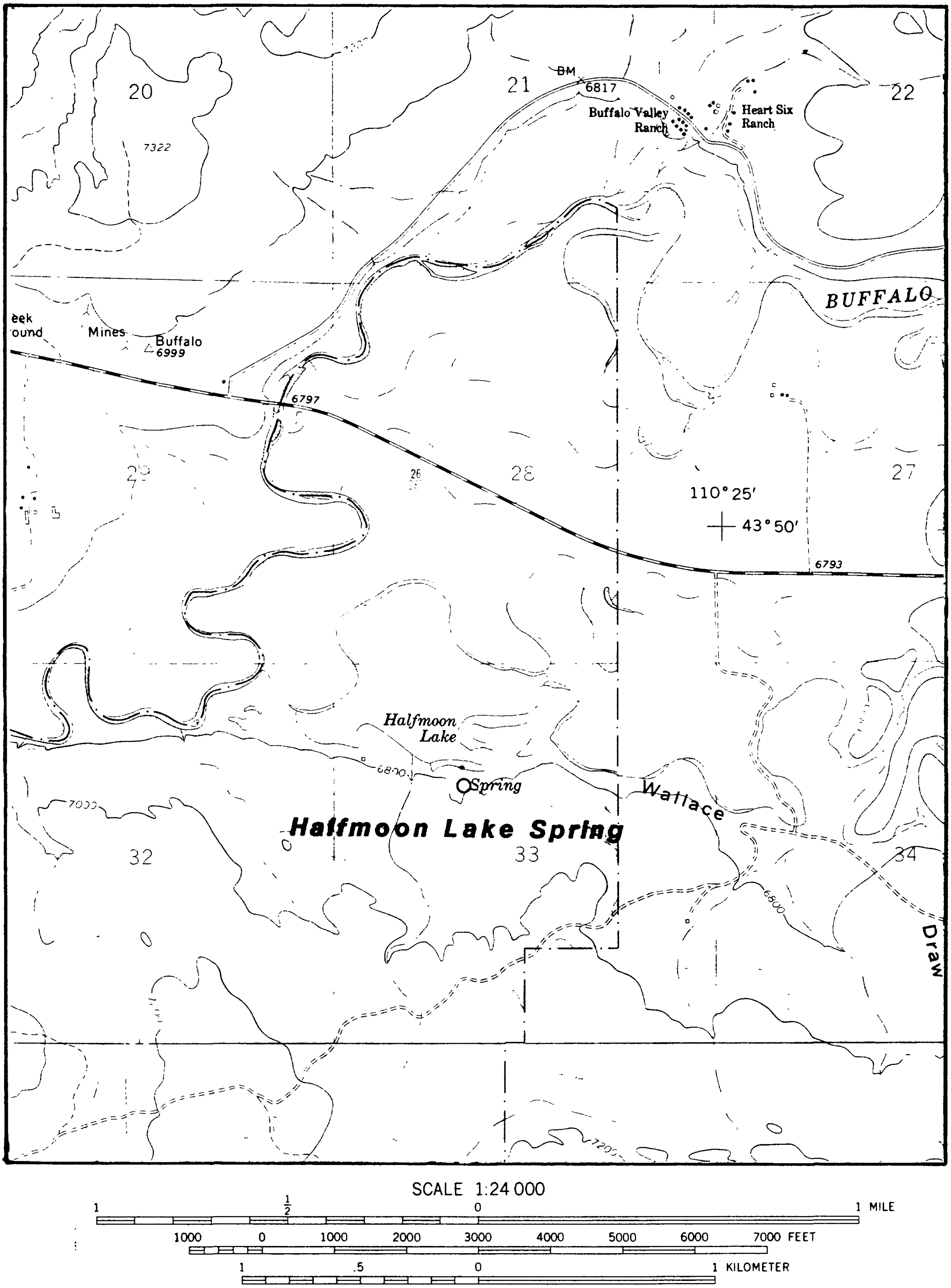
2-F


110° 37'30"
NATIONAL PARK
6875
34
35
36
7065
GROS VENTRE ROAD
6800
7000
6672
BM 6743
Kelly Warm Spring
6972
Kelly Warm Spring
REFUGE
6800
Kelly 7151
3
6676
2
1
NATIONAL ELK
6800
BM 6700
7000
Substa
Kelly
7357
43° 37'30"
GRAND TETON NAT PARK
RIVER
Teton Valley Ranch
7600
Kelly
BR 6661
GROS VENTRE
Teton Valley Ranch Warm Springs
Rodeo Ground
7400
10
11
12
6828
6656
6800
BDY
7851
7062
REFUGE
6800
7800
8060
8200
6904
7011
NAT
SCALE 1:24 000
1
½
0
1 MILE
1000
0
1000
2000
3000
4000
5000
6000
7000 FEET
1
5
0
1 KILOMETER

2-G


110°42'30"
Wilcox Point
Jackson
Lake
Creek
Moose
Webb Canyon
TRAIL
Jackson Lake Hot Springs
Colter Canyon
G R A N D
3°57'30"
8602
8200
7400
7000
6800
7110
7200
7600
7800
8152
8000
8400
8548
8800
8772
8600
8200
7223
9000
SCALE 1:24000
1
½
0
1 MILE
1000
0
1000
2000
3000
4000
5000
6000
7000 FEET
1
5
0
1 KILOMETER

2-H


20
21
22
BM
6817
Buffalo Valley Ranch
Heart Six Ranch
7322
BUFFALO
eek
ound
Mines
Buffalo
6999
6797
29
26
28
27
110° 25′
43° 50′
6793
Halfmoon Lake
6800
Spring
Wallace
Halfmoon Lake Spring
7000
32
33
34
6800
Draw
7200
SCALE 1:24 000
1
½
0
1 MILE
1000
0
1000
2000
3000
4000
5000
6000
7000 FEET
1
.5
0
1 KILOMETER