

Upper Cretaceous Microbial Petroleum Systems in North-Central Montana¹

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ABSTRACT

Cenomanian to Campanian rocks of north-central Montana contain shallow economic accumulations of dry natural gas derived from microbial methanogenesis. The methanogens utilized carbon dioxide derived from organic matter in the marginal marine sediments and hydrogen from *in situ* pore water to generate methane. The most recent USGS assessment of the shallow gas resources of eastern Montana used a petroleum systems approach, identifying the critical components of a petroleum system (source rock, reservoir rock, seal rock, and trap) and their temporal relationships. As a part of this effort, geochemical data from natural gas wells and associated formation waters were used to identify two microbial gas systems and the timing of methanogenesis.

Two microbial gas families are identified in north-central Montana based on stable carbon isotope and gas composition. The Montana Group gas family has heavier $\delta^{13}\text{C}$ methane values, slightly lighter δD methane values, and a lower carbon dioxide and nitrogen content than the Colorado Group gas family. The two gas families may reflect, in part, the source rock depositional environments, with the Colorado Group rocks representing a more offshore marine depositional environment and the Montana Group rocks representing proximal marine, deltaic and nonmarine depositional environments. Assuming the gas families reflect only source rock characteristics, two microbial petroleum systems can be defined. The first petroleum system, called the Colorado Group microbial gas system, consists of Colorado Group rocks with the shales in the Belle Fourche Formation, Greenhorn Formation, and the Carlile Shale as the presumed source rocks and the interbedded Phillips and Bowdoin sandstones and the Greenhorn Formation limestones as reservoirs. The second petroleum system, called the Montana Group microbial gas system, consists of the Montana Group rocks that include the Gammon Shale and possibly the Claggett Shale as source rocks and the Eagle Sandstone and the Judith River Formation as reservoirs. The Niobrara Formation is tentatively placed in the former system. The geographic extent of the two microbial systems is much larger than the study area and includes an area at least from the Alberta basin to the northwest to the Powder River basin to the southeast. Upper Cretaceous microbial gas accumulations have been recognized along these basin margins at burial depths less than 3000 ft, but have not been recognized within the deeper parts of the basins because subsequent charge of thermogenic oil and gas masks the preexisting microbial gas accumulations.

Methanogenesis began soon after the deposition (early-stage methanogenesis) of the Cenomanian to Campanian source sediments, and was either sustained or rejuvenated by episodic meteoric water influx until sometime in the Paleogene. Methanogenesis probably continued until CO_2 and hydrogen were depleted or the pore size was compacted to below tolerance levels of the methanogens. The composition of the Montana and Colorado Group gases and coproduced formation water precludes a scenario of late-

stage methanogenesis like the Antrim gas system in the Michigan basin. Some portion of the methane charge was originally dissolved in the pore waters, and subsequent reduction in hydrostatic pressure caused the methane to exsolve and migrate into local stratigraphic and structural traps. The critical moment of the microbial gas systems is this timing of exsolution rather than the time of generation (methanogenesis). Other studies suggest that the reduction in hydrostatic pressure may have been caused by multiple geologic events including the lowering of sea level in the Late Cretaceous, and subsequent uplift and erosion events, the youngest of which began about 5 Ma.

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INTRODUCTION

Microbial gas is generated in anaerobic, sulfate-free sediments at low temperatures (usually less than 75°C) by a community of microbes that include fermentative bacteria, acetogenic bacteria and a group of Archaea called methanogens (see Winfrey, 1984, for detailed discussion). The term “microbial gas” is used here rather than “biogenic gas” to avoid a conflict in terminology (Jenden and Kaplan, 1986). Methanogens can produce methane by either carbon dioxide reduction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) or acetate fermentation ($\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$) with the former pathway being far more common in marine settings and the latter more common in fresh water settings (Whiticar et al., 1986). Although microbial methane is ubiquitous in marine and fresh water sediments, economically recoverable accumulations of microbial gas are less common than thermogenic gas accumulations and require a combination of favorable geological and biological conditions (Rice and Claypool, 1981). These conditions developed in Upper Cretaceous marginal marine sediments throughout eastern Montana, southeastern Alberta and southwestern Saskatchewan (Fig. 1) to produce several shallow microbial gas fields (Rice, 1975b; Rice and Claypool, 1981; Rice, 1993a). The largest field, Medicine Hat, has merged with adjacent gas fields in southeastern Alberta and southwestern Saskatchewan with continued development and is collectively called Southeast Alberta gas field (Fig. 1). The reservoir and presumed source of methane is the Cenomanian to Campanian marginal marine sequence

that was deposited along the western margin of the Cretaceous seaway. The stratigraphic section from oldest to youngest includes the Belle Fourche Formation, Greenhorn Formation, Carlile Shale and Niobrara Formation of the Colorado Group, and the Gammon Shale, Eagle Sandstone, Claggett Shale and Judith River Formation of the Montana Group (Fig. 2). The depositional environment of the Colorado Group is mostly offshore marine, whereas the Montana Group is proximal marine, deltaic and nonmarine (Rice and Shurr, 1980). The reader is referred to Shurr and Ridgley (2002) for a more detailed discussion of the stratigraphic section.

The U.S. Geological Survey (USGS) has previously assessed the Northern Great Plains area for shallow microbial gas resources (Rice and Shurr, 1980; Rice and Spencer, 1996). The most recent assessment (Fig. 1) of the shallow gas resources of eastern Montana (Ridgley et al., 1999a, 1999b; Ridgley et al., 2001) used a petroleum systems approach (Magoon, 1988) and a continuous gas accumulation assessment methodology modified from Schmoker (1999). The critical components of a petroleum system — source rock, reservoir rock, seal rock, and trap — must exist prior to petroleum generation and migration from the source rock. A modified petroleum systems approach is necessary when applied to microbial gas systems. Most importantly, the timing of microbial gas generation is not controlled by the burial history and thermal cracking kinetics of kerogen but by the timing of the development of optimal living conditions (temperature, nutrient and pore-water chemistry requirements) of methanogens. Early-stage

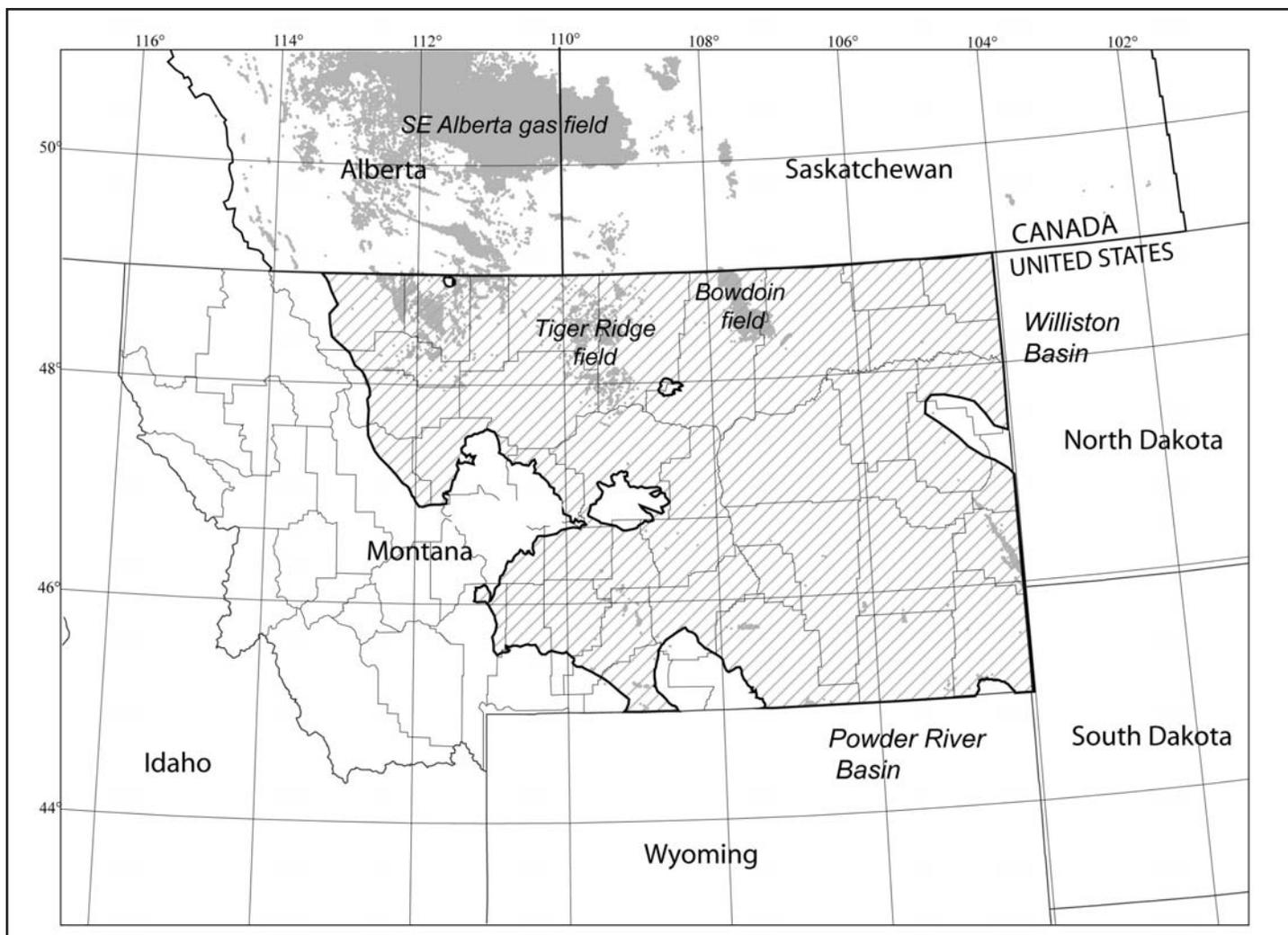


Figure 1. Map of the northern Great Plains of eastern Montana, southeast Alberta and southwest Saskatchewan showing gas wells and the USGS 2000 assessment area of the shallow gas resources of eastern Montana (hachured area, Ridgley et al., 2001). The Southeast Alberta gas field includes Medicine Hat, Alderson, Suffield, Hatton and Big Stick fields.

methanogenesis (also called primary) begins soon after deposition of sediments (Claypool and Kaplan, 1974; Rice and Claypool, 1981), and late-stage methanogenesis (also called secondary) occurs later in geologic time in sedimentary rocks inoculated with methanogens and nutrients by meteoric groundwater (Rice, 1993a, 1993b; Scott et al., 1994; Martini et al., 1996; Shurr and Ridgley, 2002). According to Rice (1993a) most microbial gas accumulations are the product of early-stage methanogenesis, but late-stage methanogenesis is well documented in coals of the northern San Juan basin (Scott et al., 1994) and in organic-rich marine source rocks of northern Michigan basin (Martini et al., 1996).

Significant isotope fractionation of carbon ($\delta^{13}\text{C}$) and hydrogen (δD) occurs during the process of methanogenesis

and the degree of fractionation is controlled, in part, by the methanogenic pathway (Whiticar et al., 1986). For example, the $\delta^{13}\text{C}$ value of microbial methane is 40 to 80 per mil lower than the dissolved inorganic carbon in the associated pore water. Therefore, important genetic information can be obtained not only from the $\delta^{13}\text{C}$ and δD values of the gas but also the $\delta^{13}\text{C}$ of the dissolved inorganic carbon and δD of the associated pore water. In this report, geochemical data from produced natural gas and associated formation water are used to identify two microbial gas systems in the north-central Montana area (Fig. 3). Included in the discussion of the petroleum systems are the approximate boundaries, the timing of generation, trapping mechanism and critical moment. Preliminary results of this study have been previously presented (Condon et al., 2000;

System	Series	Stage		Alberta	Saskatchewan	Montana	
Cretaceous	Upper	Campanian	MONTANA GROUP	Belly River Formation	Belly River Formation	Judith River Formation	
				Pakowki and Lea Park Formations	Pakowki and Lea Park Formations	Claggett Shale	
				Milk River Formation	Milk River Formation	Eagle Sandstone and Gammon Shale ☼	
		Santonian	COLORADO GROUP	Niobrara Formation	Niobrara Formation	Martin sandy zone ☼	
				Medicine Hat Formation	Medicine Hat Formation	Niobrara Formation	
		Coniacian					
		Turonian		Cardium Sandstone	Carlile Shale	Carlile Shale	Bowdoin sandstone ☼
							Carlile Shale
		Cenomanian		Second White Specks Formation	Second White Specks Formation	Second White Specks Formation	Greenhorn Formation ☼
				Phillips sandstone*	Phillips sandstone* ☼	Phillips sandstone	Mosby Sandstone
				Belle Fourche Formation	Belle Fourche Formation	Belle Fourche Shale	

Figure 2. The Cretaceous stratigraphic section of northern Great Plains of eastern Montana, southeast Alberta and southwest Saskatchewan (modified from Shurr and Ridgley, 2002). ☼ denotes gas sample. *In Canada, the Phillips sandstone in the upper Belle Fourche Formation is referred to as Second White Specks Sandstone by industry (Bloch et al., 1993).

Fishman et al., 2001; Ridgley et al., 2001, Rowan et al., 2001, Ridgley et al., 2002; Fishman et al., 2002; Lillis et al., 2002; Shurr and Ridgley, 2002).

METHODS

Gas and water samples (where possible) were collected from 31 gas wells in north-central Montana and southern Saskatchewan, predominantly in the areas of Bowdoin and Tiger Ridge fields (Fig. 3, Table 1). Samples were taken from wells with a single producing horizon, where possible, and include samples from Phillips sandstone, Bowdoin sandstone, Martin sandy zone of the Niobrara Formation, and the Eagle Sandstone (Fig. 2). Gas samples were collected by displacing sterile water in inverted citrate bottles. Gas composition was determined using a Wasson-Hewlett Packard gas chromatograph (GC), and stable carbon isotopes ($\delta^{13}C$) were determined using an Optima continuous flow isotope ratio mass spectrometer. The Wasson GC technique introduced a small quantity of air into the analysis yielding an anomalously high argon plus oxygen (coeluting GC peak) and nitrogen content. Because oxygen and argon concentrations are generally very low in natural gas (see Appendix I for gas analyses from north-

central Montana by the U.S. Bureau of Mines), the nitrogen content of the gas data was corrected assuming oxygen plus argon equals zero and nitrogen content is reduced using the ratio $(O_2+Ar)/N_2=0.2802$ (Mason and Moore, 1982, p.211). Deuterium values (δD) of gas and water, stable oxygen isotopes ($\delta^{18}O$) of water and other stable carbon isotope data were determined on selected samples by Isotech Laboratories, Champaign, Illinois and by Mountain Mass Spectrometry, Evergreen, Colorado. Stable carbon isotope data are reported in per mil relative to the PDB standard, and oxygen and deuterium isotope data are reported in per mil relative to the standard mean ocean water (SMOW). Gas wetness is reported as $\% C_{2+} = [(\sum C_2 \text{ to } C_7) / (\sum C_1 \text{ to } C_7)] \times 100$ and as the ratio $C_1 / (C_2 + C_3)$.

RESULTS

Gas Chemistry

All of the gas samples are composed of predominantly methane with minor amounts of nitrogen and trace amounts of carbon dioxide and other gases (Table 2). Methane $\delta^{13}C$ values range from -71.0 to -64.6 per mil and the C_{2+} component of hydrocarbon gases is very low (wetness ranges

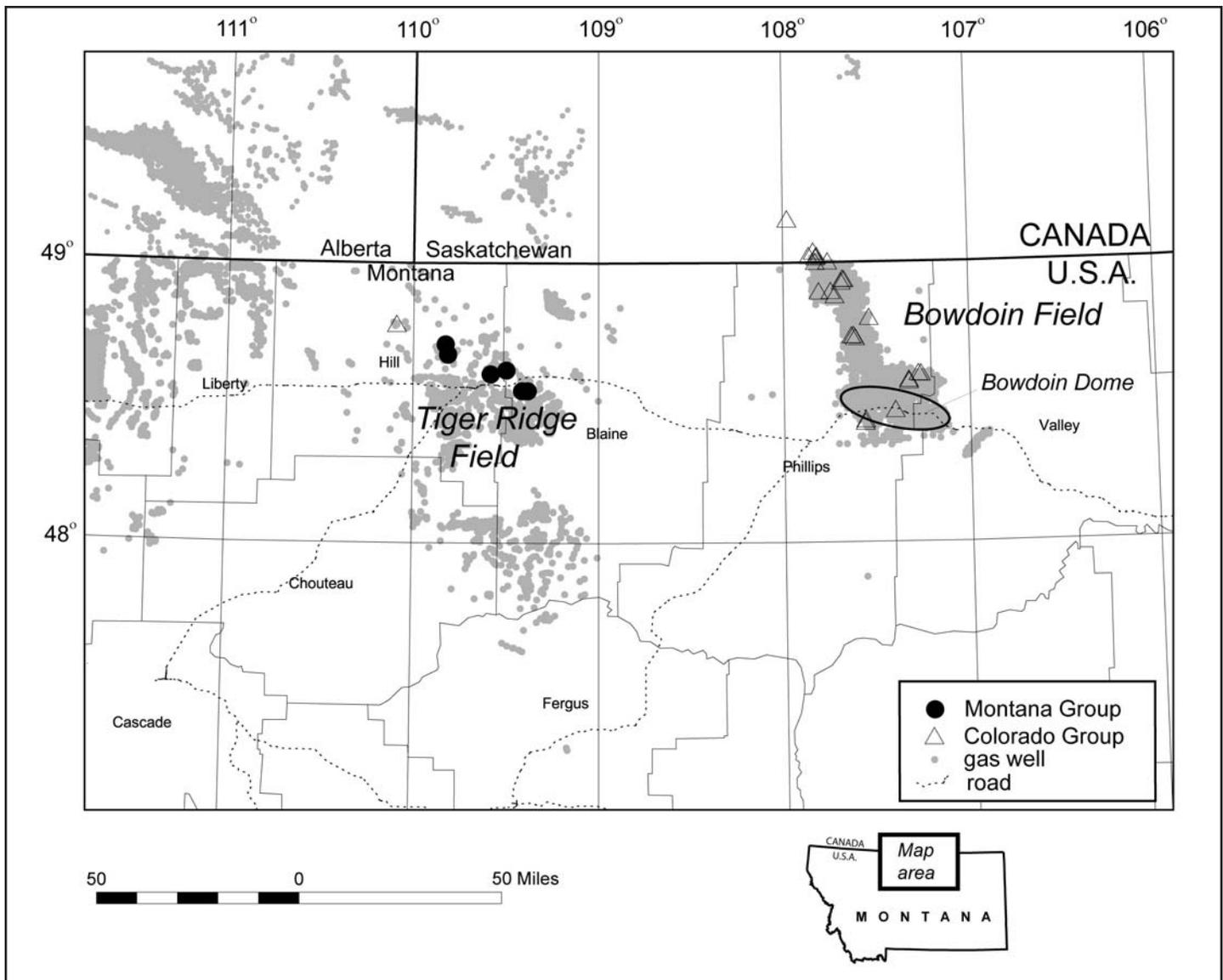


Figure 3. Map of the study area showing locations of gas and water samples collected from gas wells in north-central Montana and south-eastern Saskatchewan, predominantly in the areas of Bowdoin Dome and Tiger Ridge Field.

from 0.12 to 0.58 % C₂₊) which is consistent with a microbial origin (Nakai, 1960; Rice, 1975b; Fuex, 1977). As shown on the Bernard diagram in Figure 4, the gases plot within the microbial field but near the mixed field. These results are similar to previous studies in the same area of Montana (Rice, 1975a, 1975b, 1980) and in Southeast Alberta gas field (Fuex, 1977; Rice and Claypool, 1981).

Selected gas samples were analyzed for $\delta^{13}\text{C}$ ethane and δD methane values (Table 2). Ethane $\delta^{13}\text{C}$ values are isotopically very light (-61 to -52 per mil) which is consistent with a microbial origin (Oremland et al., 1988; Claypool, 1999; Taylor et al., 2000). Methane δD values range from -251 to -224 per mil (Fig. 5) indicating that the methanogenic

pathway is carbon dioxide reduction (Whiticar et al., 1986; Whiticar, 1994). Rice (1993a) reports $\delta^{13}\text{C}$ and δD methane data for unspecified gas fields in Montana and South Dakota; his δD values (-245 to -234 per mil) are from Bowdoin field (Threlkeld, 2004) and are within the range of this study.

The gases in the study area show compositional distinctions with respect to producing formation in that the Montana Group (Eagle Sandstone) gases generally have heavier $\delta^{13}\text{C}$ methane values by 2 to 5 per mil (Fig. 6), slightly lighter δD methane values (Fig. 5), and have a lower carbon dioxide and nitrogen content (Fig. 7) than gases from the Colorado Group. Within the Colorado Group, gases

Table 1.
Sample information, north-central Montana and southern Saskatchewan.

Sample No.	Field	Area	Well Name	Location	Producing Zone	Depth (ft)	Comments
001	Ashfield	B	Ashfield 2112-3	C NE NE 21-31N-32E	upper Phillips sandstone	1045-1141	---
002	Ashfield	B	Federal 2112-2	NW SE SE 21-31N-32E	lower Phillips sandstone	1042-1116	---
003	Bowdoin	B	Federal 0213-1	NW SE SW 2-31N-33E	Bowdoin sandstone	861-757	1
004	Whitewater, East	B	Federal 3134-1	NW SE NW 31-33N-34E	upper and lower Phillips sandstone	1164-1194	2
005	Whitewater, East	B	Orval S. Hillman 3134-3	SW NE SW 31-33N-34E	upper and lower Phillips sandstone	1129-1218	2
006	Bowdoin	B	Federal 0241-4	SW NE NE 2-34N-31E	upper Phillips sandstone	1172-1152	2
007	Bowdoin	B	Federal 0241-1	NW SE NW 2-34N-31E	lower Phillips sandstone	1162-1222	---
008	Bowdoin	B	Federal 0141-2	SE NW SW 1-34N-31E	upper and lower Phillips sandstone	1120-1158	3
009	Bowdoin	B	Federal 1861-1	NW SE NW 18-36N-31E	Bowdoin sandstone	1307-1404	---
010	Bowdoin	B	Federal 1260-1	NW SE NW 12-36N-30E	Bowdoin sandstone	1335-1446	---
011	Bowdoin	B	Federal 0960-1	NW SE NW 9-36N-30E	Bowdoin sandstone	1254-1299	---
012	Loring, East	B	Federal 2971-2	SE NW NE 29-37N-31E	Phillips + Greenhorn + Bowdoin	1556-1761	---
013	Loring, East	B	Federal 2971-4-11	NW NW 29-37N-31E	Martin sandy zone	1179-1308	---
014	Loring, East	B	Federal 3071-4-44	SE SE 30-37N-31E	Phillips + Bowdoin sandstones	1545-1881	---
015	Loring, East	B	Loring 0952-3	NE SW SE 9-35N-32E	Phillips + Greenhorn	1766-1822	---
016	Swanson Creek	B	Federal 2-21	SE NW SE 21-33N-34E	Phillips sandstone	1164-1177	---
017	Swanson Creek	B	State 1-22	NW SE SW 22-33N-34E	Phillips sandstone	1049-1060	4
018	Monchy	B	Altana Monchy 4-4-1-14	4-4-1-14 W3	upper Belle Fourche (Phillips)*	1900-1978	5,6
019	Monchy	B	ARL Monchy 4-1-1-14	4-1-1-14 W3	Greenhorn + upper Belle Fourche (Phillips)*	1850-1929	5
020	Orkeny	B	Altana Orkeny 11-29-2-15	11-29-2-15 W3	upper Phillips sandstone	2152-2172	5,7
021	Monchy	B	Altana Monchy 10-17-1-14	10-17-1-14 W3	upper Belle Fourche (Phillips)*	1909-2001	5,8
022	Monchy	B	ARL Monchy 10-7-1-14	10-7-1-14 W3	Greenhorn + upper Belle Fourche (Phillips)*	1785-1893	5,8
023	Monchy	B	ARL Monchy 10-9-1-14	10-9-1-14 W3	Greenhorn + upper Belle Fourche (Phillips)*	1654-1798	5
024	Monchy	B	Altana Monchy 6-9-1-14	6-9-1-14 W3	upper Belle Fourche (Phillips)*	1863-1952	5,9
025	Spring Coulee	TR	Larson 19-4	SE NW NW 19-35N-13E	Phillips sandstone	2160-2178	---
026	Browns Coulee, East	TR	State Velk 18-34-15	18-34N-15E	Eagle Sandstone	1316-1321	---
027	Browns Coulee	TR	Long 30-34-15	S2 SE 30-34N-15E	Eagle Sandstone	1038-1165	---
028	Red Rock	TR	State 24-33-16B	NE SW 24-33N-16E	Eagle Sandstone	706-764	---
029	Red Rock	TR	Baltruoch 15-33-17	NW SW 15-33N-17E	Eagle Sandstone	1082-1084	---
030	Havre	TR	Sheppard 8-32-18B	NW SE SE 8-32N-18E	Eagle Sandstone	1195-1198	---
031	Three Mile	TR	Sullwold 10-32-18-B	NE SW SW 10-32N-18E	Eagle Sandstone	1060-1080	---

Area abbreviations: B, Bowdoin field area, TR, Tiger Ridge field area. *In Canada, the Phillips sandstone in the upper Belle Fourche Formation is referred to as Second White Specks Sandstone by industry (Bloch and others, 1993; Shurr and Ridgley, 2002). Comments: 1, close to Dome Unit; 2, no water production; 3, very dirty water; 4, Greenhorn reported producer; 5, shut-in well; 6, sampled after 2 min flow; 7, gas flow died; 8, hydrocarbon smelli; 9, milky water sample.

Table 2. Natural gas composition and stable carbon isotope data from gas production, north-central Montana and southern Saskatchewan.

Sample No.	Gas Type	$\delta^{13}C_{C_1}$	δD_{C_1}	$\delta^{13}C_{C_2}$	N_2^*	O_2+Ar	CO_2	H_2	C_1	C_2	C_3	$n-C_4$	$i-C_4$	C_{2+} %	C_1/C_2+C_3	N_2/N_2+CH_4 %
001	C	-70.38	-239.2	-56.22	5.83	0.34	0.14	nd	92.06	0.22	0.03	0.004	0.006	0.28	368	6.0%
002	C	-70.35	---	---	6.31	0.35	0.10	nd	91.59	0.20	0.02	tr	0.005	0.25	416	6.4%
003	C	-70.64	---	---	4.98	0.29	0.12	nd	93.25	0.16	nd	tr	0.001	0.17	583	5.1%
004	C	-70.33	---	---	5.74	0.36	0.11	nd	92.11	0.21	0.02	0.001	0.005	0.26	400	5.9%
005	C	-69.96	---	---	5.79	0.26	0.13	nd	92.46	0.23	0.02	0.001	0.006	0.28	370	5.9%
006	C	-67.96	---	---	4.85	0.29	0.09	nd	93.22	0.30	0.03	0.003	0.005	0.36	282	4.9%
007	C	-69.22	---	---	5.50	0.40	0.08	nd	92.07	0.30	0.03	0.003	0.006	0.37	279	5.6%
008	C	-68.72	---	---	4.60	0.21	0.09	nd	93.84	0.30	0.03	0.002	0.006	0.36	284	4.7%
009	C	-69.18	-224.5	-60.57	4.92	0.34	0.07	nd	92.93	0.32	0.03	0.003	0.004	0.38	266	5.0%
010	C	-69.34	---	---	4.85	0.30	0.07	nd	93.17	0.32	0.03	tr	0.004	0.38	266	4.9%
011	C	-68.92	---	---	5.58	0.30	0.06	nd	92.47	0.30	0.03	tr	0.004	0.36	280	5.7%
012	C	-68.75	-232.2	-60.74	5.21	0.27	0.04	nd	92.99	0.31	0.03	0.001	0.004	0.37	274	5.3%
013	C	-70.76	-237.9	-61.15	6.99	0.42	0.06	nd	90.59	0.26	nd	0.004	tr	0.29	348	7.2%
014	C	-69.06	---	---	5.31	0.31	0.03	nd	92.71	0.32	0.03	0.002	0.004	0.38	265	5.4%
015	C	-69.28	---	---	6.65	0.31	0.09	nd	91.32	0.30	0.03	0.003	0.007	0.37	277	6.8%
016	C	-70.76	-240.5	---	6.73	0.26	0.03	0.04	91.71	0.11	nd	nd	0.002	0.12	834	6.8%
017	C	-70.50	---	---	7.48	0.36	0.05	nd	90.54	0.11	nd	tr	0.002	0.12	823	7.6%
018	C	-70.06	-232.4	-60.01	5.91	0.38	nd	nd	91.83	0.30	0.03	0.003	0.005	0.37	278	6.1%
019	C	-70.16	---	---	5.82	0.36	nd	nd	92.00	0.31	0.03	0.001	0.006	0.38	271	5.9%
020	C	-70.07	---	---	19.04	0.41	4.67	nd	74.00	0.20	0.04	0.003	0.008	0.34	308	20.5%
021	C	-70.82	---	---	9.23	0.82	0.05	0.69	85.58	0.25	0.03	0.002	0.007	0.34	306	9.7%
022	C	-70.96	---	---	5.99	0.36	0.14	nd	91.73	0.27	0.03	0.001	0.006	0.33	306	6.1%
023	C	-70.75	---	---	6.42	0.47	0.11	0.18	90.43	0.34	0.07	0.047	0.027	0.58	221	6.6%
024	C	-70.45	---	---	6.13	0.38	0.56	0.14	90.94	0.27	0.03	0.005	0.007	0.34	303	6.3%
025	C	-67.81	-250.3	-55.72	4.52	0.47	0.04	nd	92.77	0.27	0.04	0.005	0.006	0.34	299	4.6%
026	M	-67.83	-239.1	-59.31	3.00	0.42	nd	nd	94.57	0.27	0.03	0.003	0.005	0.32	315	3.1%
027	M	-66.35	---	---	2.71	0.47	nd	nd	94.60	0.33	0.03	0.003	0.005	0.39	263	2.8%
028	M	-66.85	---	---	2.44	0.41	0.02	nd	95.25	0.22	nd	tr	0.004	0.23	433	2.5%
029	M	-68.42	-251.4	-58.42	2.85	0.39	nd	nd	94.96	0.22	nd	nd	nd	0.23	432	2.9%
030	M	-64.83	---	---	2.80	0.33	0.03	nd	95.17	0.29	nd	tr	0.005	0.31	328	2.9%
031	M	-64.56	-241.9	-52.52	2.78	0.37	0.02	nd	94.99	0.31	0.02	tr	0.006	0.35	288	2.8%

Gas Type; C, Colorado; M, Montana. $\delta^{13}C$ in per mil (± 0.2) relative to PDB standard, δD in per mil (± 1.0) relative to SMOW standard. Gas composition in mole %. N_2^* , corrected nitrogen content = $[N_2\text{-measured} - ((O_2+Ar)\text{measured}/0.2802)]$ (see Methods). O_2+Ar , mostly oxygen, argon values less than 0.01 based on Bureau of Mines data. C_{2+} % (wetness) = $[(\sum C_2 \text{ to } C_7)/(\sum C_1 \text{ to } C_7)] \times 100$. ---, not measured. nd, not detected. tr, trace quantity (less than 0.001 mole percent). sample 020, $\delta^{13}C_{CO_2} = -67.38$. sample 021, $CO = 0.22$ mole%. sample 023, $C_2\text{ene}=0.02$, $C_3\text{ene}=0.008$, $C_4\text{ene}=0.0096$, $iC_4\text{ene}=0.0091$, $iC_5=0.0005$ mole%. No C_{5+} gases detected except sample 023. Helium less than 0.1 mole% based on Bureau of Mines data. No H_2 , S detected.

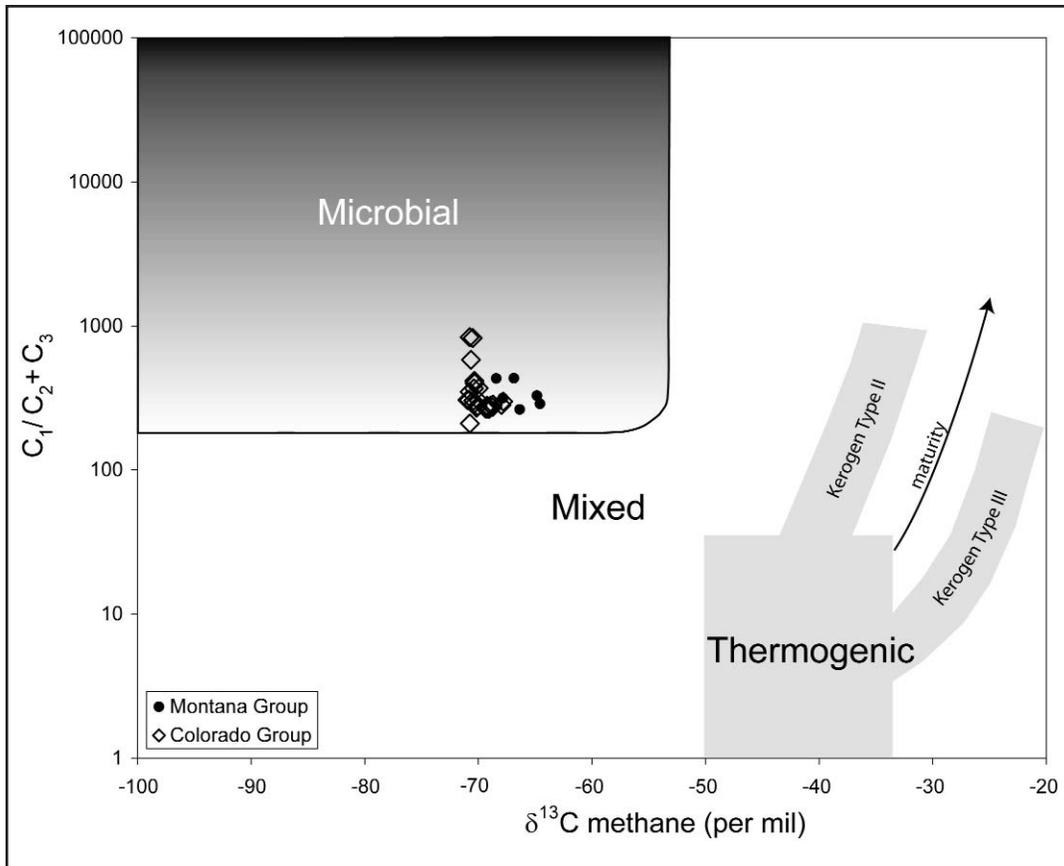


Figure 4. Bernard plot of $\delta^{13}\text{C}$ methane versus gas wetness expressed as C_1/C_2+C_3 to identify the origin of natural gas (modified from Bernard, 1977; Whiticar, 1994).

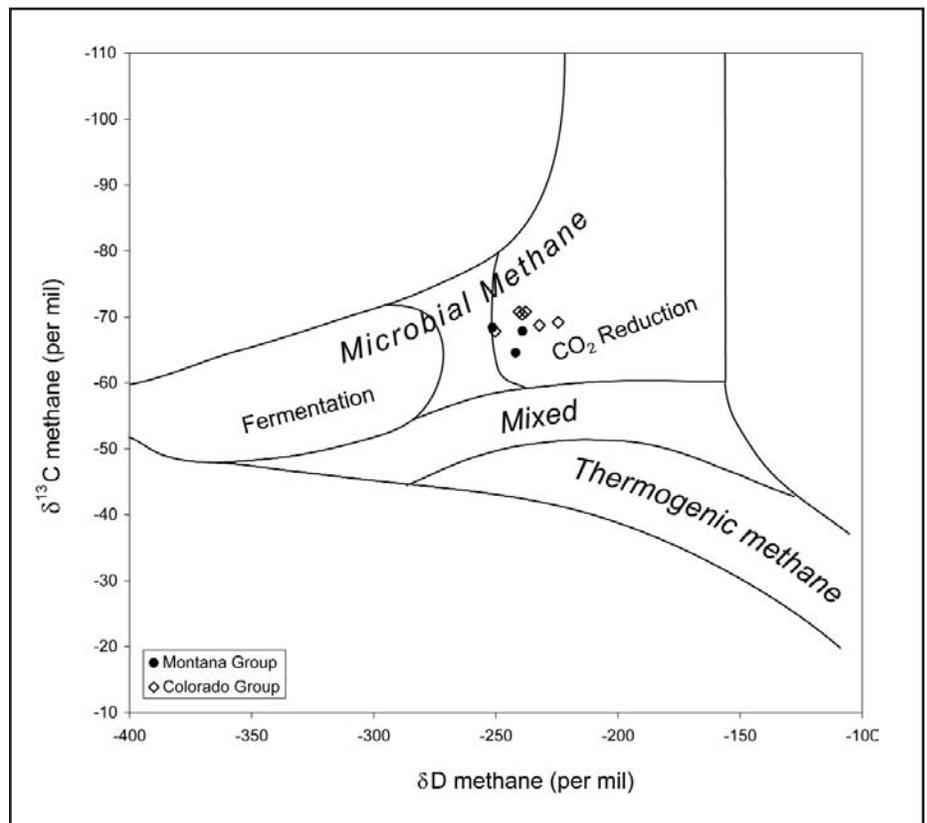


Figure 5. Natural gas genetic classification diagram using of δD methane versus $\delta^{13}\text{C}$ methane (Whiticar et al., 1986).

from the different reservoirs are similar in composition except that the Bowdoin sandstone gas generally has lower nitrogen content (Fig. 7) and heavier $\delta^{13}\text{C}$ methane values (Fig. 6) than Phillips sandstone gas. A plot of gas wetness or % C_{2+} vs. $\delta^{13}\text{C}$ methane (Fig. 6) shows four groupings of data based on geographic area: Bowdoin Dome, northwest Bowdoin field, and Monchy field in Saskatchewan, and the Tiger Ridge area. Notably, gases from Bowdoin Dome are the driest and have lighter $\delta^{13}\text{C}$ methane values.

Four of the seven gas samples from the Canadian wells (samples 020, 021, 023, and 024; Table 2) show some distinctive chemical characteristics which may be related to the fact that the wells were all recently drilled and shut-in (at the time of collection in 1999), and the gas flow of one well (020) died during sample collection. Three samples (021, 023, and 024) contain small amounts of hydrogen

and two (020 and 024) have anomalously high carbon dioxide concentrations. Sample 020 has the highest nitrogen and carbon dioxide content with an extremely depleted $\delta^{13}\text{C}$ CO_2 value of -67 per mil. The latter anomalous sample could be explained by the presence of air in the well bore and the generation of light carbon dioxide by microbial oxidation of methane.

Water Chemistry

Selected coproduced waters were analyzed for $\delta^{13}\text{C}$ dissolved inorganic carbon (also called total dissolved carbon dioxide), δD water and $\delta^{18}\text{O}$ water values (Table 3). Dissolved inorganic carbon (DIC) exists in natural water mostly in the form of bicarbonate (HCO_3^-) but also may include dissolved carbon dioxide ($\text{CO}_2(\text{aq})$), carbonic acid

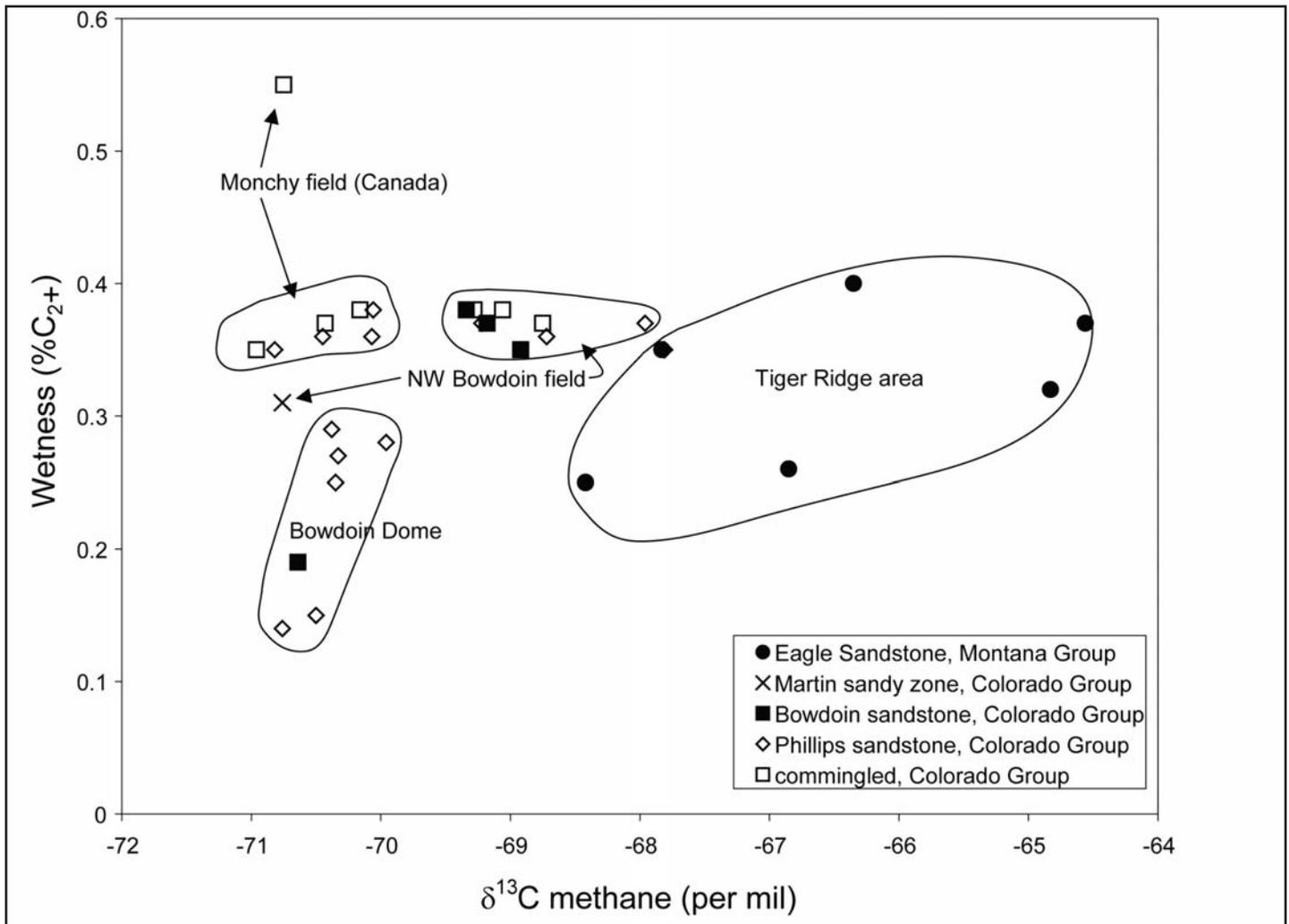


Figure 6. Plot of $\delta^{13}\text{C}$ methane versus gas wetness or % C_{2+} ($[(\Sigma\text{C}_2 \text{ to } \text{C}_7)/(\Sigma\text{C}_1 \text{ to } \text{C}_7)] \times 100$) showing relationships of geochemical data to producing formation and geographic area. Commingled gases are from more than one horizon within the Colorado Group.

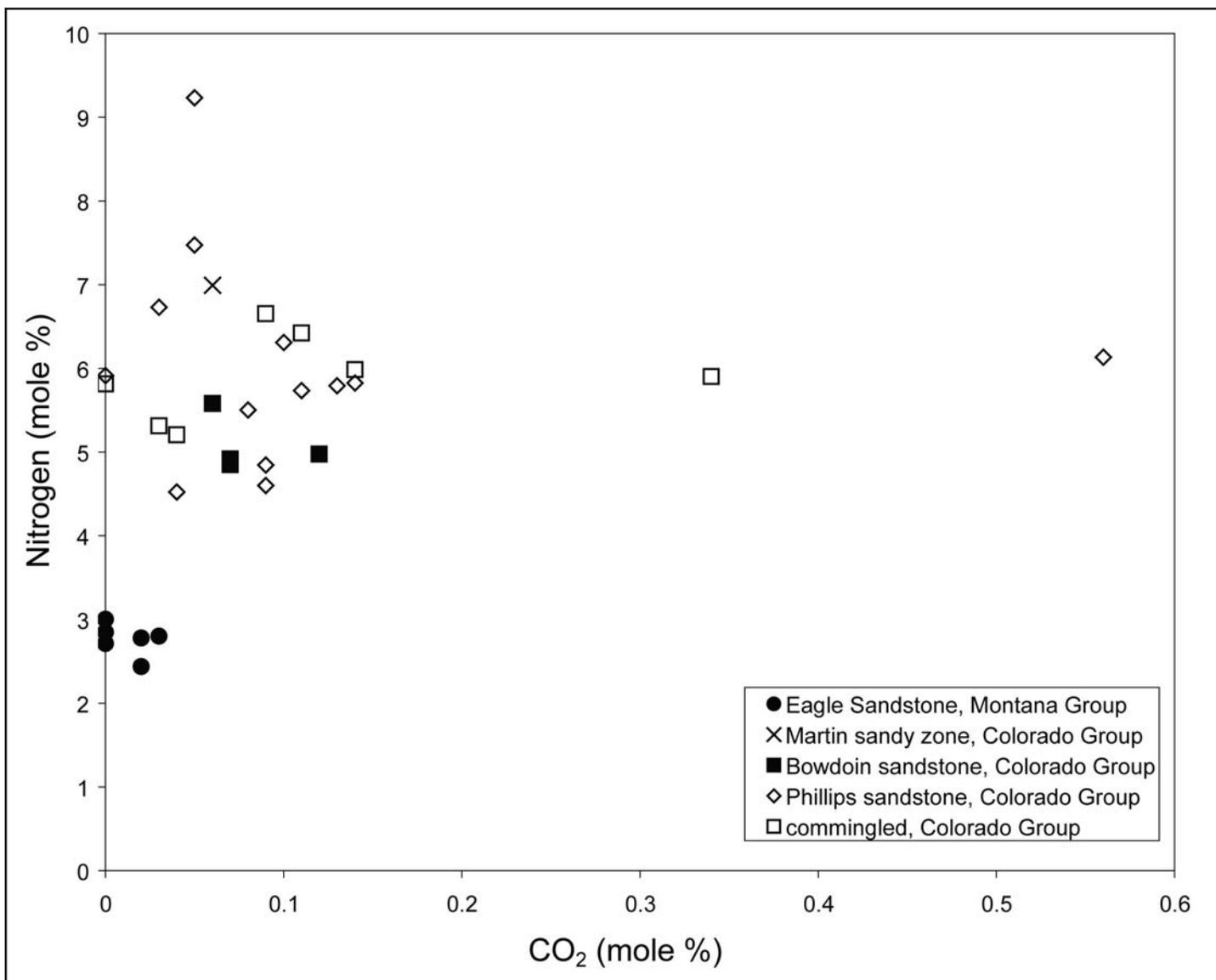


Figure 7. Plot of carbon dioxide versus nitrogen content showing composition differences between Montana Group gas and Colorado Group gas. Commingled gases are from more than one horizon within the Colorado Group. Nitrogen content has been corrected for minor air contamination (see Methods). Outlier sample 020 is not plotted.

(H₂CO₃), and carbonate ion (CO₃²⁻) depending on the pH. The δ¹³C DIC values reported here are the sums of all dissolved forms measured on carbon dioxide gas exsolved from the water by acidification. The δ¹³C DIC values in the water range from -9.96 to +1.14 per mil with one outlier at -45.9 per mil. The δ¹³C methane and δ¹³C DIC values are plotted on a diagram by Whiticar (1994) that differentiates carbon dioxide reduction and methyl fermentation pathways of methanogenesis based on the degree of isotopic fractionation (Fig. 8). The isotopic fractionation factor (α) is the ratio of the precursor to the product (for example, δ¹³C CO₂ +1000)/(δ¹³C methane +1000). Excluding the

outlier, the data in this study fall in the region greater than α=1.055, which is consistent with methanogenesis by carbon dioxide reduction.

Produced water δD values range from -92.1 to -74.1 per mil with one heavy outlier data point at -59.2 per mil (Table 3). A plot of δD water versus δD methane (Fig. 9) shows that most of the data fall near the linear relationship where δD methane is depleted by about 160 per mil relative to the coproduced water (δD methane = δD water - 160 per mil). This relationship has been observed in microbial gas systems worldwide and has been interpreted to be caused by hydrogen isotope fractionation during methano-

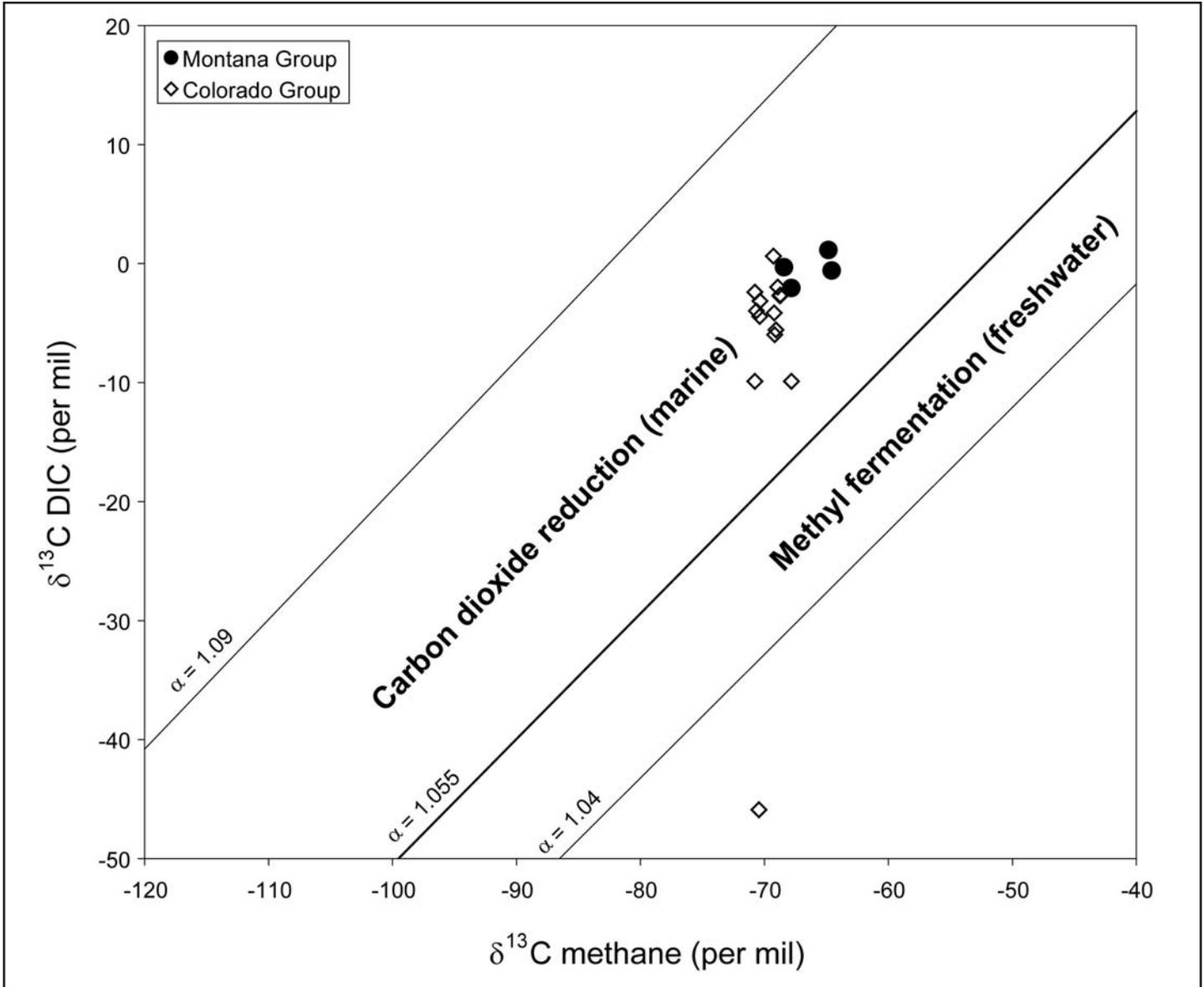


Figure 8. Plot of $\delta^{13}\text{C}$ methane versus $\delta^{13}\text{C}$ carbon dioxide calculated from the $\delta^{13}\text{C}$ dissolved inorganic carbon in the coproduced water. Lines of equal fractionation are shown for $\alpha = 1.04, 1.055$ and 1.09 (Whiticar, 1994). $\alpha = (\delta^{13}\text{C CO}_2 + 1000)/(\delta^{13}\text{C methane} + 1000)$.

genesis by carbon dioxide reduction (Schoell, 1980). However, Waldron et al. (1999) suggest that this relationship more accurately represents the isotope fractionation from methanogenesis in marine environments. In any case, the relationship shows that the hydrogen in the methane was derived from the associated pore water. In contrast, the lack of a relationship between the methane and water data in the Milk River aquifer (Eagle Sandstone equivalent in southern Alberta) northwest of the study area (Fig. 9) indicates that the microbial methane is not derived from the water currently in the aquifer (Andrews et al., 1991).

Stable hydrogen and oxygen isotope ratios of modern meteoric water in the study area (Fig. 10) were obtained from the interpolation of contours on regional $\delta^{18}\text{O}$ and δD maps of river water constructed by Kendall and Coplan (2001). The degree of uncertainty of this interpolation (± 0.5 and ± 5 per mil for $\delta^{18}\text{O}$ and δD , respectively) is based on the contour interval of the maps. The $\delta^{18}\text{O}$ and δD coproduced water values in the current study plot off the global meteoric water line (Craig, 1961) and are isotopically much heavier than modern meteoric water in northern Montana, as well as Holocene (0 to 10 ka) and

Table 3.

Stable carbon, hydrogen and oxygen isotope data from produced water, north-central Montana and southern Saskatchewan.

Sample No.	Original analyses			Repeat analyses			¹²⁹ I Age H ₂ O
	δ D H ₂ O	δ ¹⁸ O H ₂ O	δ ¹³ C DIC*	δ D H ₂ O	δ ¹⁸ O H ₂ O	δ ¹³ C DIC*	
001	-84.87	-10.03	-4.45	-83.71	-10.09	-4.51	35.6 ± 2.1 Ma
002	-83.48	-9.98	-3.15	-83.66	-9.93	-3.21	---
003	-91.00	-10.14	-3.97	---	---	---	---
007	-84.60	-9.17	-4.15	---	---	---	---
008	-86.70	-9.00	-2.63	---	---	---	---
009	-82.10	-9.43	-5.97	---	---	---	---
011	-87.10	-9.26	-1.97	---	---	---	---
012	-92.10	-10.40	-2.71	---	---	---	---
013	-74.05	-9.28	-9.89	-74.84	-9.30	-9.96	---
014	-84.80	-9.07	-5.56	---	---	---	---
015	-88.00	-9.55	0.62	---	---	---	---
016	-85.70	-9.32	-2.39	---	---	---	---
024	-77.87	-8.87	-45.89	-78.55	-8.86	-45.93	51.0 ± 3.1 Ma
025	-82.90	-8.54	-9.90	-82.98	-8.60	-9.91	53.6 ± 3.3 Ma
026	-92.10	-9.25	-2.06	---	---	---	---
029	-82.89	-9.46	-0.31	-84.00	-9.48	-0.42	65.6 ± 3.5 Ma
030	-59.20	-6.33	1.14	---	---	---	---
031	-80.90	-9.26	-0.58	---	---	---	---

δ D and δ¹⁸O in per mil relative to SMOW standard. δ¹³C in per mil relative to PDB standard.
 *DIC, dissolved inorganic carbon. ¹²⁹I data from Ridgley et al. (2002), Shurr and Ridgley (2002).
 --, not measured.

Pleistocene (50 to 600 ka) recharge water in the Milk River aquifer in southeastern Alberta (Drimmie et al., 1991). The coproduced waters from this study have similar δ¹⁸O and δD values as Bow Island Formation (lower Colorado Group) coproduced water in southeastern Alberta (Schwartz et al., 1981) and slightly older Lower Cretaceous (Colorado Group and Mannville Group) formation water in central Alberta (Connolly et al., 1990).

Four water samples were analyzed for ¹²⁹I/I ratios to determine the age of the water, and show uncorrected ages from 35.6 ± 2.1 Ma to 53.6 ± 3.3 Ma for the Colorado Group and 65.6 ± 3.5 Ma for the Montana Group (Table 3) (Ridgley et al., 2002; Shurr and Ridgley, 2002).

DISCUSSION

Gas Origin

The results of this study support previous studies that the shallow Upper Cretaceous gas accumulations in north-central Montana are microbial in origin. For example, the

isotopically light methane δ¹³C values and high C₁/C₂+C₃ values (low wetness) are well within the microbial methane region on the Bernard plot (Fig. 4). Methanogens utilize *in situ* pore water to generate methane and fractionate carbon and hydrogen stable isotopes in a systematic way (for example, the δ¹³C value of microbial methane is about 65 per mil lower than the dissolved inorganic carbon in the associated pore water). The coupled δ¹³C and δD values of the methane and coproduced water in this study (Figs. 8-9) show systematic isotopic fractionations consistent with a microbial origin by the carbon dioxide reduction pathway (Schoell, 1980; Whiticar, 1994). Because the methane and water appear to be cogenetic, the gas and water are either locally derived, or both migrated together to the producing reservoir. However, the low nitrogen/methane ratio of the gas (N₂/N₂+CH₄ generally less than 10%, table 2) suggests minimal migration distance of methane in solution; Clayton (1992) observed that migrated microbial gas accumulations have high nitrogen/methane ratios (generally greater than 10%) because nitrogen is less soluble in water than methane. Therefore,

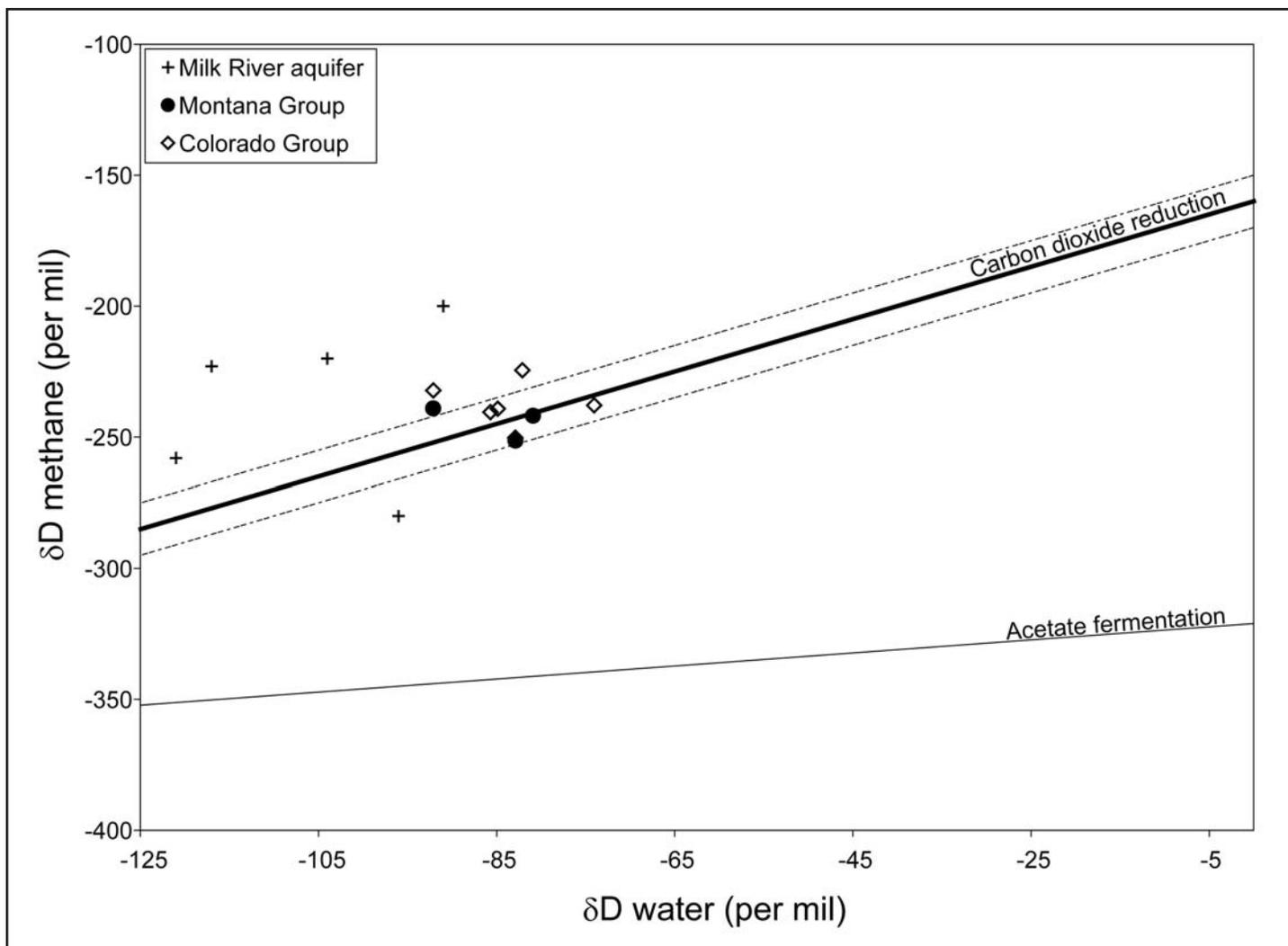


Figure 9. Plot of produced water and methane δD values showing that most of the Montana and Colorado Group data fall near the carbon dioxide reduction line: δD methane = δD water - 160 per mil (Nakai et al., 1974; Schoell, 1980). Dashed lines are ± 10 per mil. Acetate fermentation line is δD methane = $0.25 \times \delta D$ water - 321 per mil (Schoell, 1980).

the data in this study are consistent with the proposal by Rice (1980) and Rice and Claypool (1981) that the gases in the reservoirs are locally derived from adjacent mudstones.

Ethane $\delta^{13}C$ values in this dataset are among the lightest values ever reported from commercial gas production (-61 to -52 per mil) and are consistent with a microbial origin (Oremland et al., 1988; Claypool, 1999; Hinrichs et al., 2006). Thermogenic ethane $\delta^{13}C$ values from gas wells are usually heavier than -45 per mil; all but 13 of the ethane $\delta^{13}C$ values in two large data sets of commercial gas production (803 gases, Jenden et al., 1993; 638 gases, Threlkeld, 2004) fall between -45 and -20 per mil. Claypool (1999) proposes that isotopically light ($\delta^{13}C$ values lighter than -50 per mil) microbial ethane may be formed from the reduction of two-carbon carboxylic acids (acetic,

oxalic) in a process analogous to microbial methanogenesis. In a study of the Judith River and Milk River aquifers and commercial gas in southern Alberta, Taylor et al. (2000) suggest a microbial origin for ethane with $\delta^{13}C$ values lighter than -45 per mil. However, microbial ethanogenesis remains controversial. Ethane with $\delta^{13}C$ values less than -45 per mil also have been attributed to diagenetic or low-temperature thermogenic processes (Schoell, 1983; Jenden and Kaplan, 1989; Coleman, 1999; Rowe and Muehlenbachs, 1999; Coleman, 2001). In this study, a microbial origin for the ethane is proposed considering that the ethane $\delta^{13}C$ values are significantly lighter than the normal range of thermogenic ethane from commercial gas wells and are similar to other examples of microbial ethane in the literature. The origin of the trace amounts of

propane detected in this study is unknown ($\delta^{13}\text{C}$ values could not be measured), but a microbial origin cannot be excluded (Hinrichs et al., 2006).

Gas Families

The gas data presented here (Figs. 4-7) indicate two microbial gas families—Montana Group gas produced from the Eagle Sandstone, and Colorado Group gas produced from several stratigraphic units (Fig. 2). The Montana Group gas family has heavier $\delta^{13}\text{C}$ methane values by up to 5 per mil (Fig. 6), slightly lighter δD methane values (Fig. 5), and has a lower carbon dioxide and nitrogen content (Fig. 7) than the Colorado Group gas family. The two gas families can be explained by differences in source rock depositional environments; the Colorado Group source rocks are mostly offshore marine and more likely contain a higher proportion of marine algae, whereas the Montana Group source rocks are proximal marine, deltaic and non-marine, and likely have a higher proportion of terrestrial organic matter. The heavier $\delta^{13}\text{C}$ methane values of the Montana Group gas family may reflect greater amounts of terrestrial organic matter (Dean et al., 1986) or oxidized organic matter (Pratt et al., 1986) in the source rock. The lighter δD methane values of the Montana Group gas (Fig. 5) may reflect a slightly more fresh water depositional environment (Whiticar et al., 1986). However, other factors may control microbial gas chemistry including the relative contributions of carbon dioxide from decarboxylation and fermentation, and the carbon dioxide production rate relative to the rate of methanogenesis (Rice and Claypool, 1981). Another explanation for the heavier $\delta^{13}\text{C}$ methane values of the Montana Group gas family could be that the gas contains a contribution of thermogenic gas from the much deeper oil accumulations in Middle Jurassic reservoirs (about 2,500 ft deeper). However, a thermogenic mixing scenario would require higher wetness and heavier δD methane values than those observed in the Montana Group gas.

Rock-Eval pyrolysis data reported by Shurr and Ridgley (2002) support the difference in depositional environment between the Colorado Group and Montana Group source rocks, with the former rocks having total organic carbon (TOC) values up to four percent and hydrogen index (HI) values up to 420 mg hydrocarbon/g organic carbon, and the latter rocks having TOC values less than 1.2 percent and HI values less than 30 mg hydrocarbon/g organic carbon. Offshore marine rocks (Colorado Group) typically have higher TOC values because of higher organic productivity, lower proportion of clastic sediment, and better organic matter preservation due to lower oxygen content in the depositional environment (Demaison and Moore, 1980). Similarly, offshore marine rocks typically have

higher HI values because of better organic matter preservation and because the hydrogen/carbon values of marine algae are higher than land plants (Tissot et al. 1974; Espitalie et al., 1977).

Gas Correlation

Results of this study were compared with published gas data from the surrounding areas, including southeastern Alberta, eastern Montana, and northwestern South Dakota, to determine if the Montana or Colorado gas families may be genetically related to other microbial gas accumulations. The $\delta^{13}\text{C}$ methane values of the Montana Group gas family (-68.4 to -64.6 per mil) are similar to the gases from the Eagle equivalent (Milk River) and Niobrara equivalent (Medicine Hat) pools of the Southeast Alberta gas field ($\delta^{13}\text{C}$ methane values from -68.3 to -66 per mil) based on data by Fuex (1977) and Rice and Claypool (1981). However, Krouse (1983) reports significantly lighter $\delta^{13}\text{C}$ methane values (-75 to -66 per mil) from the same reservoirs (Milk River and Medicine Hat pools). The $\delta^{13}\text{C}$ methane values of the Colorado Group gas family (-71 to -68 per mil) are isotopically lighter than gases from equivalent age reservoirs (Second White Specks) in the Southeast Alberta gas field ($\delta^{13}\text{C}$ methane values generally between -68 and -65 per mil) (Rice and Claypool, 1981; Krouse, 1983). The heavier isotopic values in Alberta are possibly due to mixing of thermogenic or diagenetic methane (Fuex, 1977; Rice and Claypool, 1981; James, 1983).

The $\delta^{13}\text{C}$ methane values of the Montana Group gas family are similar to most of the gases reported by Rice and Claypool (1981) in equivalent age reservoirs from eastern Montana (Black Coulee, Guinn, Liscom Creek, and Tiger Ridge fields; their table 3). However, the gases they report from fields in easternmost Montana (Cedar Creek) and northwestern South Dakota (West Short Pine Hills fields) have lighter $\delta^{13}\text{C}$ methane values (-69.7 to -70.0 per mil). These lighter values may be derived from more distal marine sediments of the Montana Group, based on the facies maps of Cretaceous rocks of the northern Great Plains (Rice and Shurr, 1980).

Identification of Petroleum Systems

Given that the gas families are locally derived from adjacent mudstones and reflect only source rock characteristics, two microbial petroleum systems can be defined (Lillis et al., 2002). The first petroleum system, called the Colorado Group microbial gas system, consists of Colorado Group rocks with the shales in the Belle Fourche Formation, Greenhorn Formation, and the Carlile Shale as the

presumed source rocks and the interbedded Phillips and Bowdoin sandstones and the Greenhorn Formation limestones as reservoirs (Fig. 2). The second petroleum system, called the Montana Group microbial gas system, consists of the Montana Group rocks that include the Gammon Shale and possibly the Claggett Shale as source rocks and the Eagle Sandstone and the Judith River Formation as reservoirs. Based on a single gas sample (sample 013 from the Martin sandy zone), the Niobrara Formation is tentatively placed in the Colorado Group gas system (Figs. 6-7). However, the gas from the Niobrara equivalent (Medicine Hat) reservoir in the Southeast Alberta gas field is similar to the Montana Group gas in this study, suggesting that in southeast Alberta the Niobrara has a more proximal marine depositional environment with higher proportion of terrestrial organic matter than in the Bowdoin field area of Montana. The low HI values (89 to 152 mg hydrocarbons/g organic carbon) reported by Shurr and Ridgley (2002) for the Niobrara/Medicine Hat are consistent with the unit containing predominantly terrestrial organic matter. Consequently, the Niobrara Formation in southeast Alberta is assigned to the Montana Group gas system, whereas in north-central Montana the unit is tentatively assigned to the Colorado Group gas system.

The geographic extent of a petroleum system is defined by a line that circumscribes the pod of active source rock and the locations of all shows, seeps and accumulations of petroleum that originated from that pod (Magoon and Dow, 1994). For thermogenic petroleum systems, mapping the pod of active source rock involves using burial history and thermal maturity data to determine where and when the source rock was actively generating petroleum. However, mapping the geographic extent of a microbial gas system is more problematic because the pod of active source rock is constrained by the optimal conditions of methanogenesis such as temperature, food supply, and porosity (Rice and Claypool, 1981; Rice, 1993a), which are reflected, only in part, in the rock record (porosity, depositional environment, sedimentation rate, thermal history, organic carbon content). For late-stage methanogenesis, the burial history (or more correctly the uplift history) of the source rock could be used to constrain the areal extent of the pod of active source rock because uplifted portions of the source rock attain optimal temperature and nutrient conditions for methanogenesis. For early-stage methanogenesis, the entire geographic extent of the source rock is optimal for microbial methane generation soon after deposition, and thus the pod of active source rock is equal to its entire geographic extent. Because the Colorado and Montana microbial gas systems are considered early-stage (timing of methanogenesis discussed later), their geographic extent includes the entire area of source rock between the Alberta basin to the northwest, the Williston basin to the east, and the Powder River basin to the south

(Rice and Shurr, 1980; Rice et al., 1990). Upper Cretaceous microbial gas accumulations have been recognized throughout this area at burial depths less than 3000 ft, many of which correlate with the gases in this study. However, Upper Cretaceous microbial gas accumulations have not been recognized within the deeper parts of the surrounding basins because methanogenesis ends with increasing burial (methanogens generally cannot survive in fully compacted shale below about 6600 ft of burial, or in temperatures greater than about 100°C) (Rice, 1993a), and the subsequent charge of thermogenic oil and gas masks the preexisting microbial gas accumulations.

Timing of Gas Generation

It is critical to know the timing of gas generation as it relates to the timing of migration and trap formation. As stated previously, the timing of methanogenesis falls into two end members: early stage and late stage. Early-stage methanogenesis begins soon after sedimentation and may continue at an appreciable rate for tens of millions of years as long as optimal living conditions and nutrient supply exist (Claypool and Kaplan, 1974). Late-stage methanogenesis occurs millions of years after source rock lithification and requires inoculation of fresh methanogens and nutrients by way of meteoric groundwater flow into permeable rocks (Rice, 1993a). The best example of late-stage methanogenesis is the Upper Devonian Antrim Shale microbial gas system of the Michigan basin that has developed since the Pleistocene (Martini et al., 1996). In southeastern Alberta, uplift and unroofing of the Cretaceous strata since the Pliocene has provided meteoric recharge to the Milk River Formation (Eagle/Gammon equivalent) allowing for some late-stage methanogenesis (Andrews et al., 1991; Drimmie et al., 1991). However, data presented here indicate that the Upper Cretaceous microbial gases of north-central Montana (Bowdoin and Tiger Ridge areas) are not the result of late-stage methanogenesis.

As stated previously, the methane and coproduced formation water from the Montana and Colorado Group microbial gas systems appear to be cogenetic based on the observed relationships between δD methane and δD water (Fig. 9), and between $\delta^{13}C$ methane and $\delta^{13}C$ dissolved inorganic carbon in the water (Fig. 8). Thus, the age of the coproduced formation water constrains the timing of methanogenesis. The coproduced water is not modern meteoric water based on $\delta^{18}O$ and δD values. The values plot away from the global meteoric water line (GMWL), and are isotopically much heavier than modern meteoric water in northern Montana and Holocene recharge water in the Milk River aquifer in southern Alberta (Fig. 10). However, the coproduced formation water has a similar $\delta^{18}O$ and δD composition as formation water from the

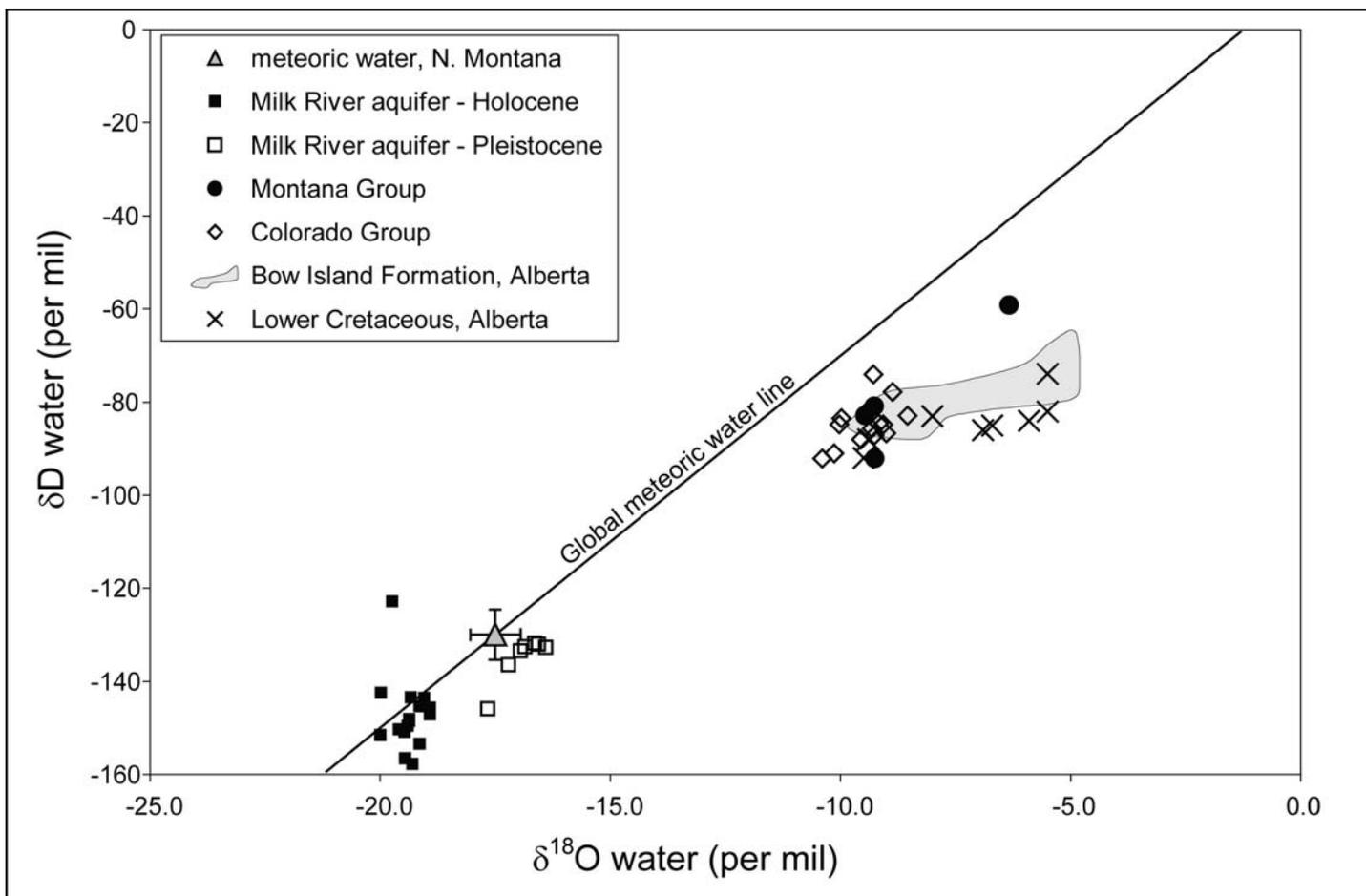


Figure 10. Plot of $\delta^{18}\text{O}$ water versus δD water showing that the coproduced formation water values in this study (Montana and Colorado Group) fall off the global meteoric water line (Craig, 1961) and are isotopically much heavier than modern meteoric water in northern Montana (Kendall and Coplan, 2001), and Holocene (0 to 10 ka) and Pleistocene (50 to 600 ka) groundwater in the Milk River (Eagle Sandstone equivalent) aquifer in southeastern Alberta, Canada (Drimmie et al., 1991). Error bars show the degree of uncertainty of the modern meteoric water value in northern Montana (± 0.5 and ± 5 per mil for $\delta^{18}\text{O}$ and δD , respectively). The waters in this study are similar in composition to Bow Island Formation (lower Colorado Group) coproduced water in southeastern Alberta (Schwartz et al., 1981) and slightly older Lower Cretaceous (Colorado Group and Mannville Group) formation water in central Alberta (Connolly et al., 1990).

Lower Cretaceous Bow Island Formation in southeastern Alberta, which is believed to be a mixture of ancient meteoric water and connate water (Schwartz et al., 1981), and as Lower Cretaceous formation water from central Alberta, which is believed to be a mixture of Neogene meteoric water and connate brines (Connolly et al., 1990). These data suggest that the coproduced water in this study is a mixture of paleometeoric water and connate water. Several mixing events may have occurred including meteoric flushing as a result of regression near the end of the Campanian, regional fluid recharge from Late Cretaceous to Eocene orogenic events (Laramide) west of the study area, or recharge associated with local uplift since the late Miocene (Toth and Corbet, 1986). The ages of four water samples in

this study based on $^{129}\text{I}/\text{I}$ ratios (35.6, 51.0, 53.6 and 65.6 Ma) and the $\delta^{18}\text{O}$ and δD water data are consistent with Cretaceous to Paleogene mixing or migration events. Shurr and Ridgley (2002) propose that the older ages (65.6 and 53.6 Ma) reflect fluid migration related to Laramide orogeny events in the thrust belt west of the study area.

The gas and water data in this study provide further evidence against late-stage methanogenesis. For example, documented cases of late-stage microbial gas contain higher concentrations of carbon dioxide, and heavier $\delta^{13}\text{C}$ values of methane, carbon dioxide and coproduced dissolved inorganic carbon (DIC) than samples in this study (Table 4). The reasons for these observations are unclear. The high carbon dioxide content observed in cases of late-

Table 4.

Comparison of late-stage microbial gas systems with gases from north-central Montana and southern Saskatchewan.

Petroleum system	CO ₂ mol %	$\delta^{13}\text{C}_{\text{methane}}$ per mil	$\delta^{13}\text{C}_{\text{DIC}}$ per mil	References
Late stage				
Antrim Shale, Michigan	8.0 (avg)	-47 to -56	+19 to +31	1*
Fruitland Coal, Colorado	6.5 (avg)	-46.6 to -49.7	+16 to +26	2*, 3
Fort Union Coal, Wyoming	1.4 to 3.2	-56.6 to -53.8	+10 to +20	4, 5
This study				
Upper Cretaceous, Montana	0.2 (avg)	-65 to -71	-10 to +1	

$\delta^{13}\text{C}$ in per mil relative to PDB standard. DIC, dissolved inorganic carbon. * possible mixed thermogenic gas noted in reference. Reference: 1, Martini et al. (1998); 2, Scott et al. (1994); 3, P.G. Lillis, unpublished data; 4, Rice (1993b); 5, C.A. Rice, pers. comm. (2004).

stage methanogenesis suggests that carbon dioxide is being generated at a faster rate than methane generation. Heavier $\delta^{13}\text{C}$ methane and cogenetic $\delta^{13}\text{C}$ DIC values may reflect the isotopic composition of the reactive carbon in the source rock that was altered by microbial or chemical processes prior to late-stage methanogenesis. In contrast, the low carbon dioxide content of samples from this study may reflect complete consumption by methanogens in the geologic past, and the methane and DIC isotopic composition probably reflect a lighter $\delta^{13}\text{C}$ value carbon dioxide from the source sediments by processes of sulfate reduction, fermentation and low-temperature nonbiologic decarboxylation (Rice and Claypool, 1981).

Other evidence for early methane generation in the Upper Cretaceous marine sediments is the timing and isotopic composition of authigenic carbonate cementation in the Gammon Shale east of the study area (Gautier, 1981; Gautier and Claypool, 1984). In addition, Fishman et al. (2001) used authigenic carbonate, fluid inclusion, and burial history data to suggest that methane generation in the Milk River Formation in the Southeast Alberta gas field spanned at least 15 m.y. from the time of sediment deposition (about 81 Ma) until about 65 Ma.

In summary, the results of this study preclude late-stage methanogenesis and better fit the model of early-stage methanogenesis as proposed by previous studies (Rice, 1980; Rice and Shurr, 1980; Gautier, 1981; Rice and Claypool, 1981; Rice et al., 1990; Gautier and Rice, 1982; Fishman et al., 2001; Shurr and Ridgley, 2002). Methanogenesis likely began soon after the deposition of the source sediments (Cenomanian to Campanian), and continued until

the food supply (CO₂ and hydrogen) was depleted, or the pore size was compacted to below tolerance levels of the methanogens (Fig. 11). The water data suggests that one or more episodes of mixing of meteoric water may have occurred in the Paleogene that may have sustained or rejuvenated methanogenesis until the source sediments were fully compacted and lithified. This process (episodic or rejuvenated methanogenesis) introduces a terminology problem in terms of early-stage versus late-stage methanogenesis. Perhaps the term "secondary methanogenesis" could be used to describe this process where fluid migration through less indurated sediments provides more nutrients to sustain or rejuvenate methanogenesis.

Trapping Mechanism

Microbial methane generated in unconsolidated sediments goes into solution until saturation is reached. Subsequent methane generated will bubble up through the sediments as a free gas and be recycled as food for methane-oxidizing bacteria or be lost to the atmosphere. However, methane can be trapped and accumulate under certain conditions depending on the physical state of the gas (dissolved, free, hydrate), sedimentation rate, and the timing of the formation of reservoir, seal and trap (Rice and Claypool, 1981; Rice 1993a). Previous studies of the gas accumulations in north-central Montana have proposed that most of the gas charge was originally dissolved in the pore waters, and a later reduction in hydrostatic pressure from lowering of sea level, uplift and erosion, or upward

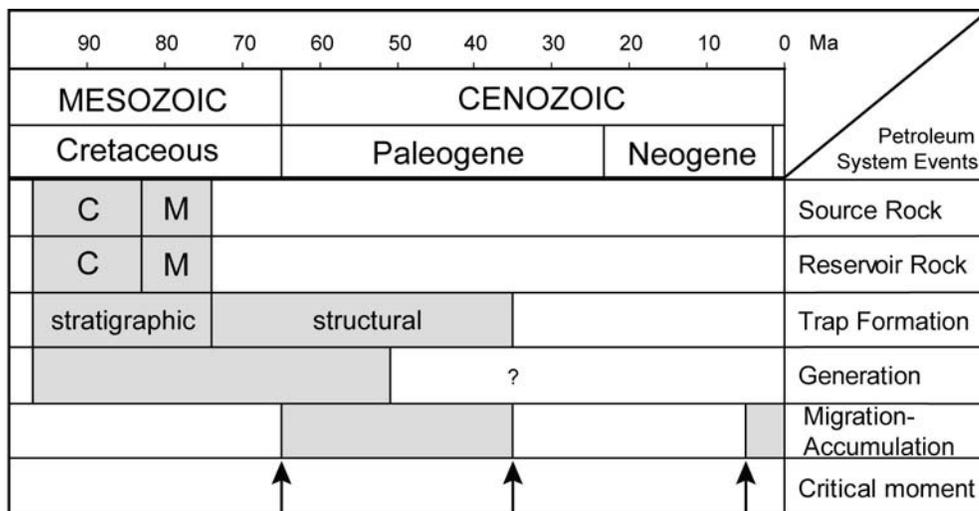


Figure 11. Events chart for the Colorado Group and Montana Group microbial petroleum systems (modified from Magoon and Dow, 1994).

migration of gas-bearing waters caused the gas to exsolve and migrate into local traps (Rice and Claypool, 1981). In this area, underpressured gas fields and lack of free gas below 2000 ft (Rice et al., 1990) are consistent with this scenario.

The Colorado Group gas accumulations of this study are concentrated along a broad structural high (Bowdoin field area) in numerous small stratigraphic traps consisting of thin discontinuous lenses and layers of siltstone, sandstone and carbonate reservoirs encased in impermeable muds (Rice, 1975b; Rice and Claypool, 1981; Rice et al., 1990; Rice and Spencer, 1996). There is evidence that early authigenic calcite and siderite precipitation prior to and during methanogenesis may locally provide diagenetic seals for gas accumulations (Gautier, 1981; Rice and Claypool, 1981; Gautier and Rice, 1982; Gautier and Claypool, 1984; Fishman et al., 2001). Some free methane may have been trapped in these early-formed stratigraphic traps with later exsolved methane adding to the charge (Fig. 11). The Montana Group gas accumulations in the Tiger Ridge field area are conventional fault traps with coastal/nonmarine sandstone reservoirs (Rice, 1980; Gautier and Rice, 1982; Rice and Claypool, 1981). These traps probably did not form until after methanogenesis so they were probably charged by exsolved methane (Fig. 11).

Can sufficient methane be sequestered in solution to charge economic gas accumulations? Using Bowdoin field data of Rice et al. (1990) and methane solubility data of Duan et al. (1992), an approximate calculation suggests that there is sufficient storage capacity for dissolved methane in the pore water alone to supply the gas reserves at Bowdoin field (Appendix II). For example, uplift of pore water from about 5000 ft at 60°C to about 1700 ft at 30°C will release 0.0446 moles methane per kg

water or about 1 cubic foot methane per cubic foot water. Given 15% porosity, 380,000 acres, and 450 ft of source rock, the calculated methane charge is 1117 BCF, similar to the in-place total reserves of Bowdoin field given by Rice et al. (1990). The calculation ignores several factors that would reduce or increase the charge number such as the effects of salinity, pore volume reduction, diffusion, and capillary pressure. As was stated before, however, some of the methane charge was likely trapped as free gas by early-formed stratigraphic traps. The relative importance of syndepositional gas charge versus a postdepositional charge by the exsolution of methane in pore water is unknown.

Critical Moment

The critical moment is defined as the point in time selected by the investigator that best depicts the generation, migration, and accumulation of most hydrocarbons in a petroleum system (Magoon and Dow, 1994). For most systems, generation, migration and accumulation occur in a geologically short time span and are considered to be a single geologic event. However, in the case of the microbial gas system in north-central Montana, a significant geologic time period may separate the generation (methanogenesis) and the migration-accumulation (exsolution of methane) events. Thus the critical moment becomes the timing of exsolution and migration of gas into previously formed traps. Determining the timing of exsolution for the Colorado and Montana gas systems requires burial history modeling, and is beyond the scope of this study. Rice (1980) proposed that gas in the Tiger Ridge area migrated into traps as result of early to middle Eocene

uplift. Rice et al. (1990) proposed that gas in the Bowdoin dome exsolved from formation water from uplift and erosion during Late Cretaceous and (or) early Tertiary time. Toth and Corbet (1986) proposed that gas in southeast Alberta came out of solution in response to about 700 meters of erosional unloading beginning about 5 Ma. Thus the critical moment of the Colorado and Montana gas systems may be a combination of geologic events including the lowering of sea level in the Late Cretaceous, and subsequent uplift and erosion events (Fig. 11).

CONCLUSIONS

The Cenomanian to Campanian rocks of north-central Montana contain economic accumulations of shallow dry natural gas derived from microbial methanogenesis. The methanogens utilized carbon dioxide derived from organic matter in the marginal marine sediments and hydrogen from *in situ* pore water to generate methane (carbon dioxide reduction pathway). Methanogens also produced small quantities of ethane.

Two microbial gas families are identified based on stable carbon isotope and gas composition. The Montana Group gas family has heavier $\delta^{13}\text{C}$ methane values, slightly lighter δD methane values, and has a lower carbon dioxide and nitrogen content than the Colorado Group gas family. The two gas families may reflect, in part, the source rock depositional environments, with the Colorado Group rocks representing a more offshore marine depositional environment and the Montana Group rocks representing proximal marine, deltaic and nonmarine depositional environments.

Assuming the gas families reflect only source rock characteristics, two microbial petroleum systems can be defined. The first petroleum system, called the Colorado Group microbial gas system, consists of Colorado Group rocks with shale beds in the Belle Fourche Formation, Greenhorn Formation, and the Carlile Shale as the presumed source rocks and the interbedded Phillips and Bowdoin sandstones and Greenhorn Formation carbonate rocks as reservoirs. The second petroleum system, called the Montana Group microbial gas system, consists of the Montana Group rocks that include the Gammon Shale and possibly the Claggett Shale as source rocks and the Eagle Sandstone and the Judith River Formation as reservoirs. The Niobrara Formation is tentatively assigned to the Colorado Group gas system based on a single gas analysis, whereas in southeast Alberta the unit is assigned to the Montana Group gas system based on reported gas and source rock compositions.

The pod of active source rock of the two systems includes the entire geographic extent of the Colorado and Montana Group source rocks because they could support methanogenesis at the time of deposition as long as optimal

conditions existed (low temperatures, and adequate food supply and porosity). The geographic extent of the two systems is much larger than the study area and includes an area at least from the Alberta basin to the northwest to the Powder River basin to the southeast. However, Upper Cretaceous microbial gas accumulations have not been recognized within the surrounding basins because methanogenesis ends with increasing burial and the subsequent charge of thermogenic oil and gas masks the pre-existing microbial gas accumulations.

Methanogenesis began soon after the deposition of the Cenomanian to Campanian source sediments (early-stage methanogenesis), and was either sustained or rejuvenated by episodic meteoric water influx until sometime in the Paleogene. Methanogenesis probably continued until CO_2 and hydrogen was depleted or the pore size was compacted to below tolerance levels of the methanogens. The composition of the Montana and Colorado Group gases and coproduced formation water precludes a scenario of late-stage methanogenesis like the Antrim gas system in the Michigan basin.

Because some of the current traps of the microbial gas fields of north-central Montana may not have existed at the time of methanogenesis, a model has been proposed that the methane charge was originally dissolved in the pore waters, and subsequent uplift and erosion caused the methane to exsolve and migrate into local traps. In the study area, underpressured gas fields and lack of free gas below 2000 ft are consistent with this scenario. An approximate calculation using published gas field data and methane solubility data shows that sufficient methane can be sequestered in solution to charge economic gas accumulations.

Because a significant geologic time period may separate the generation (methanogenesis) and the migration-accumulation (exsolution of methane) events, the critical moment of these microbial gas systems becomes the timing of exsolution and migration of gas into previously formed traps. Determining the timing of exsolution for the Colorado and Montana gas systems requires burial history modeling, and is beyond the scope of this study. Based on other studies, the critical moment may be a combination of geologic events including the lowering of sea level in the Late Cretaceous, and subsequent uplift and erosion events, the youngest of which began about 5 Ma.

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Appendix I.

Natural gas data from north-central Montana analyzed by the U.S. Bureau of Mines (Threlkeld, 2004).

No.	Field	API Number	Well Name	Depth (ft)	Producing Zone	Location
1	Badlands	25041218920000	Milam 25-2	1000-1015	Eagle	25-33N-14E
2	Badlands	25041217810000	Papillo 28-1	1000-1028	Eagle	28-33N-15E
3	Black Coulee	25005221260000	State 14-36	1148-1172	Eagle	36-32N-18E
4	Bowdoin	25071062870000	515	668-775	Big Shale	8-31N-34E
5	Bowdoin	25105062710000	Hoham 521	755-755	Bowdoin	10-31N-34E
6	Bowdoin	25105050430000	Government 959	701-780	Bowdoin	20-31N-35E
7	Bowdoin	25071063020000	845	1010-1130	Bowdoin	19-32N-32E
8	Bowdoin	25071063140000	State 504	712-780	Bowdoin	36-32N-32E
9	Bowdoin	25071063130000	State 501	740-800	Bowdoin	36-32N-32E
10	Bowdoin	25071219010000	Federal 2451 2	1290-1333	Bowdoin	24-35N-31E
11	Bowdoin	25071213170000	Federal-2061 1	1461-1498	Bowdoin	20-36N-31E
12	Bowdoin	25071214420000	Federal-223631 1	1336-1412	Bowdoin	22-36N-31E
13	Bowdoin	25071214390000	Fee-2970 1	1397-1509	Bowdoin	29-37N-30E
14	Bowdoin	25071219000000	Federal 1221 2	1191-1223	Phillips	12-32N-31E
15	Bowes	25005050370000	Hobson 1	1026-1026	Eagle	9-31N-19E
16	Bowes	25005051210000	6	1060-1130	Eagle	9-31N-19E
17	Bowes	25005051620000	O R Stevens 1	735-770	Eagle	26-32N-19E
18	Boxelder	25005051760000	Stranahan 1	1272-1272	Eagle	14-32N-17E
19	Browns Coulee E.	25041214160000	Grant 12-22	602-626	Eagle	22-34N-15E
20	Fresno	25041222710000	State 2-36	1000-1006	Eagle	36-33N-13E
21	Loring	25071221470000	Loring 0461-4	1474-1739	Bowdoin	4-36N-31E
22	Loring E	25071215630000	Anderson 0161-1	1355-1397	Bowdoin	1-36N-31E
23	Loring E	25071218890000	Federal 2971-2	1556-1624	Bowdoin	29-37N-31E
24	Red Rock	25041218040000	Cunningham 1-14	670-691	Eagle	14-34N-16E
25	Red Rock	25041213810000	Wltr E Paulsen EtA 1	1140-1151	Eagle	32-34N-17E
26	Red Rock	25041218050000	Miller 1-29	1489-1501	Virgelle	29-34N-16E
27	Tiger Ridge	25041224870000	Hillbrant 3-12	1332-1350	Eagle	3-30N-15E
28	Tiger Ridge	25005210200000	Dehlbom 3-2	1204-1418	Eagle	3-30N-18E
29	Tiger Ridge	25005225610000	S-B 26-9	1397-1432	Eagle	26-31N-18E
30	Tiger Ridge	25041210560000	Sands 15-1	1010-1010	Eagle	15-32N-15E
31	Tiger Ridge	25041210770000	Lumpkin 23-1	1071-1076	Eagle	23-32N-15E

Appendix I (continued)

Natural gas data from north-central Montana analyzed by the U.S. Bureau of Mines (Threlkeld, 2004).

No.	N ₂	O ₂	Ar	CO ₂	H ₂	He	C ₁	C ₂	C ₃	n-C ₄	i-C ₄	n-C ₅	i-C ₅	C ₆	C ₂₊ %
1	2.7	0	0	0	0	0.08	96.7	0.4	0.1	0	0	0	0	0	0.51
2	5.1	0.4	0	0.2	0	0.08	93.5	0.4	0.1	0	0.1	0	0	0	0.64
3	3.6	0	0	0.1	0	0.08	95.6	0.5	0.1	0	0	0	0	0	0.62
4	4.5	0.1	0	0.2	0	0.07	95.2	0.0	0.0	0	0	0	0	0	0.00
5	6.8	0	0	0.3	0	0.07	91.2	1.7	0.0	0	0	0	0	0	1.83
6	6.4	0	0	0.1	0	0.10	93.2	0.2	0.0	0	0	0	0	0	0.21
7	6.5	0	0	0	0	0.10	93.0	0.2	0.1	0	0	0	0	0	0.32
8	7.4	0	0	0.2	0	0.07	92.4	0.0	0.0	0	0	0	0	0	0.00
9	4.3	0.3	0	0.3	0	0.07	95.1	0.0	0.0	0	0	0	0	0	0.00
10	6.4	0	0	0.2	0	0.07	92.9	0.3	0.1	0	0	0	0	0	0.43
11	6.3	0	0	0.2	0	0.08	93.0	0.3	0.0	0	0	0	0	0	0.32
12	6.5	0	0	0.1	0	0.08	92.9	0.3	0.1	0	0	0	0	0	0.43
13	6.4	0	0	0.3	0	0.09	92.8	0.3	0.1	0	0	0	0	0	0.43
14	6	0	0	0.2	0.1	0.07	93.2	0.2	0.0	0	0	0	0	0	0.21
15	3.1	0.4	0	0.5	0	0.10	95.7	0.3	0.0	0	0	0	0	0	0.31
16	11	0.1	0	0	0	0.11	89.0	0.2	0.0	0	0	0	0	0	0.22
17	5.4	0	0	0.1	0	0.10	94.0	0.3	0.1	0	0	0	0	0	0.42
18	4.3	0.2	0	0.1	0	0.04	93.7	1.7	0.0	0	0	0	0	0	1.78
19	3	0	0	0.1	0	0.09	96.4	0.2	0.1	0	0	0	0	0	0.31
20	2.8	0	0	0	0	0.08	96.6	0.4	0.0	0	0	0	0	0	0.41
21	7	0.1	0	0.3	0	0.07	92.2	0.3	0.0	0	0	0	0	0	0.32
22	7.6	0	0	0	0.2	0.09	91.6	0.3	0.1	0	0	0	0	0	0.44
23	6.2	0	0	0.1	0	0.07	93.1	0.3	0.0	0	0	0	0	0	0.32
24	2.6	0	0	0	0	0.08	97.0	0.3	0.0	0	0	0	0	0	0.31
25	3.2	0	0	0	0	0.09	96.2	0.4	0.0	0	0	0	0	0	0.41
26	3.2	0	0	0	0	0.09	96.3	0.3	0.0	0	0	0	0	0	0.31
27	4.5	0	0	0.1	0	0.08	94.9	0.4	0.1	0	0	0	0	0	0.52
28	3.1	0	0	0	0.1	0.09	94.0	1.5	0.6	0.2	0	0.1	0	0.1	2.59
29	6.7	0.8	0.1	0.2	0	0.12	91.4	0.5	0.1	0	0.1	0	0.1	0	0.87
30	3.2	0	0	0	0.1	0.09	96.4	0.3	0.0	0	0	0	0	0	0.31
31	8.1	1.2	0.1	0.1	0.1	0.08	90.0	0.3	0.0	0	0	0	0	0	0.33

Appendix II.

Calculation of dissolved methane released from removal of overburden.

Input Data

Methane solubility at various pressures (depth) and temperatures (Duan et al., 1992).

bars (ft)	moles methane/kg water (fresh)	
	30°C	60°C
200 (6,699)	0.1481	0.1202
150 (5,024)	0.1249	0.0993
100 (3,350)	0.0949	0.0736
50 (1,675)	0.0547	0.0412

15% porosity, 450 ft thickness of source rock, 380,000 acres of drainage area for Bowdoin field area (Rice et al., 1990).

Calculations

Scenario 1 — change in solubility from removal of 100 bars (3,349 ft) of overburden and temperature reduction from 60 to 30°C

$$0.0993 \text{ (150 bars 5,024 ft 60°C)} - 0.0547 \text{ (50 bars or 1,675 ft at 30°C)} = 0.0446 \text{ moles/kg water}$$

$$0.0446 \text{ moles/kg water} \times 22.41383 \text{ lit/mole} \times 1 \text{ liter/kg} = 1.0 \text{ cu ft methane/ cu ft water at STP}$$

$$1.0 \text{ cu ft methane/cu ft water} \times 0.15 \text{ water/rock} \times 43,560 \text{ ft/acre} \times 450 \text{ ft} \times 380,000 \text{ acres} = 1,117 \text{ BCF}$$

Scenario 2 — change in solubility from removal of 50 bars (1,675 ft) of overburden at a temperature of 30°C

$$0.0949 \text{ (100 bars or 3,350 ft at 30°C)} - 0.0547 \text{ (50 bars or 1,675 ft at 30°C)} = 0.0402 \text{ moles/kg water}$$

$$0.0402 \text{ moles/kg water} \times 22.41383 \text{ lit/mole} \times 1 \text{ liter/kg} = 0.901 \text{ cu ft methane/ cu ft water at STP}$$

$$0.901 \text{ cu ft methane/cu ft water} \times 0.15 \text{ water/rock} \times 43,560 \text{ ft/acre} \times 450 \text{ ft} \times 380,000 \text{ acres} = 1,007 \text{ BCF}$$

In-place total reserves for Bowdoin field = 1,120 BCF (Rice et al., 1990)