

# THE ORIGIN OF NATURAL GAS IN THE TERTIARY COAL SEAMS ON THE EASTERN MARGIN OF THE POWDER RIVER BASIN

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## ABSTRACT

*The origin of methane being produced from Tertiary coals along the eastern outcrop margin of the Powder River Basin is bacterial. There is no evidence for a thermogenic origin of this gas originating either from Tertiary sediments, or from underlying Cretaceous gas reservoirs. The metabolic pathway used by bacteria to generate methane progressed via the reduction of CO<sub>2</sub>. The extremely dry composition of natural gas in these coals, and the stable isotopic composition of both carbon and deuterium isotopes in co-occurring methane, water, and CO<sub>2</sub> support this conclusion.*

*There are insufficient data to categorically determine the timing of bacterial methane generation in this basin. However, the available information suggests that methane was generated sometime following the onset of basin uplift, 10 to 35 mya., and possibly as recently as during the Pleistocene.*

## CONCEPTS AND TERMINOLOGY

### HYDROCARBON AND NON-HYDROCARBON GAS COMPOSITION

Two techniques are generally used to determine the origin of natural gases in the earth's crust. These are molecular composition, and stable isotopic composition. The most commonly used compositional indexes to be used in this paper are defined here as follows:

#### % wetness

$$\frac{(C_2 + C_3 + nC_4 + iC_4 + nC_5 + iC_5)}{(C_1 + C_2 + C_3 + nC_4 + iC_4 + nC_5 + iC_5)} \text{ Vol.}\%$$

also expressed as,  
 $\frac{\Sigma C_{2+}}{\Sigma C_{1+}} \text{ Vol.}\%$

where the numbers designate the number of carbon atoms in the normal alkanes methane, ethane, propane, normal butane, isobutane, normal pentane, and isopentane, respectively.

#### % dryness

$$C_1 / (C_1 + C_2 + C_3 + nC_4 + iC_4 + nC_5 + iC_5) \text{ Vol.}\%$$

also expressed as

$$C_1 / \Sigma C_{1+} \text{ Vol.}\%$$

#### % non-hydrocarbon fraction

$$\frac{(CO_2 + O_2 + N_2 + Ar + He + H_2)}{(CO_2 + O_2 + N_2 + Ar + He + H_2 + (C_{1+}))} \text{ Vol.}\%$$

## STABLE ISOTOPIC COMPOSITION

There are two types of isotopes in nature, those that are radioactive and decay to daughter products with time, and those that are stable. In this paper, only the stable isotopes will be considered. There are no published data for the radioactive isotopes in the available literature that are pertinent to the gas reservoirs or coalbed aquifers of the Powder River Basin. Stable isotopes of three elements are particularly useful for understanding the origin of water and gas in Powder River Basin coals. These are carbon, oxygen, and hydrogen. For practical reasons, stable isotope data are determined as a ratio, such as the ratio of carbon of molecular weight 13 to carbon of molecular weight 12 (<sup>13</sup>C / <sup>12</sup>C), and not as

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an absolute molecular abundance.

Stable isotopic laboratory analyses are performed using a dual beam mass spectrometer, where one beam of charged ions is obtained from the sample and the other from a known standard. This method provides accurate and repeatable measurements of minute differences in molecular mass. By convention, analytical results are reported as the magnitude, in parts per thousand ( $‰$ ), of the difference between the stable isotope ratio of a sample and that of an NBS standard. The usual  $\delta$  notation used to denote this difference is defined as:

$$\delta R_x (‰) = \left( \frac{R_a / R_b \text{ sample}}{R_a / R_b \text{ standard}} - 1 \right) \times 10^3$$

where  $R_x$  refers to the molecule measured and  $R_a / R_b$  are the isotope ratios of the heavy and light isotopes respectively. In this paper, the symbols used will refer to the stable isotope ratios of following compounds:

$\delta^{13}C_{C_1}$  = isotope ratio  $^{13}C/^{12}C$  of carbon in methane relative to the PDB standard;

$\delta^{13}C_{CO_2}$  = the isotope ratio  $^{13}C/^{12}C$  of carbon in carbon dioxide relative to the PDB standard;

$\delta^{13}C_{DIC}$  = the isotope ratio  $^{13}C/^{12}C$  of carbon in dissolved inorganic carbon relative to the PDB standard;

$\delta^{18}O_{H_2O}$  = the isotope ratio  $^{18}O/^{16}O$  of oxygen in water relative to the SMOW standard;

$\delta D_{H_2O}$  = the isotope ratio  $^2H/H$  of deuterium in water relative to the SMOW standard; and,

$\delta D_{C_1}$  = the isotope ratio  $^2H/H$  of deuterium in methane relative to the SMOW standard;

PDB and SMOW stand for the Pee Dee Belemnite and standard mean ocean water, respectively.

Also by convention, differences in  $\delta$  isotope ratios among samples will be described as being either depleted or enriched in the *heavier* isotope and not as being either depleted or enriched in the *lighter* isotope. For example, a value of  $\delta^{13}C_{C_1}$  of  $-59 ‰$  is heavier and therefore more enriched in  $^{13}C$  than a value of  $-60 ‰$ .

Another term that is frequently used to discuss isotopic data is fractionation. Fractionation results when isotopes are partitioned between products and reactants in a chemical reaction, or when they are partitioned between liquid, gas, and solid phases. The fractionation or separation factor  $\alpha$  is defined as follows:

$$\alpha_{A-B} = (\delta_A + 10^3) / (\delta_B + 10^3)$$

where A refers to the product, and B refers to the reactant. There are numerous references that illustrate how these parameters can be used to

distinguish between various gases, and to interpret their origin (Kaplan, 1994; Loveley and Chapelle, 1995; Smith and Pallaser, 1996; Whiticar et al., 1986; Whiticar, 1994; and Wiese and Kvenvolden, 1993).

## DIFFERENTIATING CRETACEOUS FROM TERTIARY GASES

### Sample Origin:

Non-associated produced gases from the Tertiary Fort Union Formation and associated gases from three fields producing from the Lower Cretaceous Muddy Formation were collected near Gillette, Wyoming, in 1987 and 1988. The Tertiary coalbed gases were mostly collected in townships T50 & T51N-R72W (within and around the Rawhide Butte field), and one Tertiary gas sample was collected from Oedekoven Field in T55N-R73 & 74W. One sample each of gases producing from the Lower Cretaceous Muddy Formation were collected from Kitty Field (T52N- R73W), Mill-Gillette Field (T52N-R73W), and Amos Draw Field (T51N-R75W). There are no other producing horizons in these townships. These townships are located along the eastern margin of the basin where the coal seams dip gently into the subsurface from their outcrops. All samples were analyzed by Global Geochemistry Corporation, Canoga Park, Ca.

### Gas Composition:

Although the non-hydrocarbon gas composition in Cretaceous and Tertiary gases does not help to differentiate them, the hydrocarbon gas composition is diagnostic. Cretaceous gases are wet, whereas Tertiary gases are composed almost completely of methane (Figure 1).

The non-hydrocarbon gases are composed principally of nitrogen and carbon dioxide. In general, the relative amount of nitrogen increases slightly but linearly with an increasing volume percent of non-hydrocarbon gases (Figure 2). A large  $N_2/CO_2$  ratio distinguishes Oedekoven Field gases from all others of this investigation.

### Isotopic Composition:

One plotting method commonly used to discriminate between gases of different origins is based on comparing the isotope composition of carbon in methane with gas dryness (Figure 3). This figure illustrates that carbon isotopes alone are not adequate for differentiating gases of different origin in this area. A more useful diagram for this purpose compares the isotopic ratios of carbon and deuterium in methane (Figure 4). This figure illustrates that the deuterium ratios of methane are diagnostic.

Thus both gas composition and isotopic data are needed to demonstrate that gases found in Cretaceous

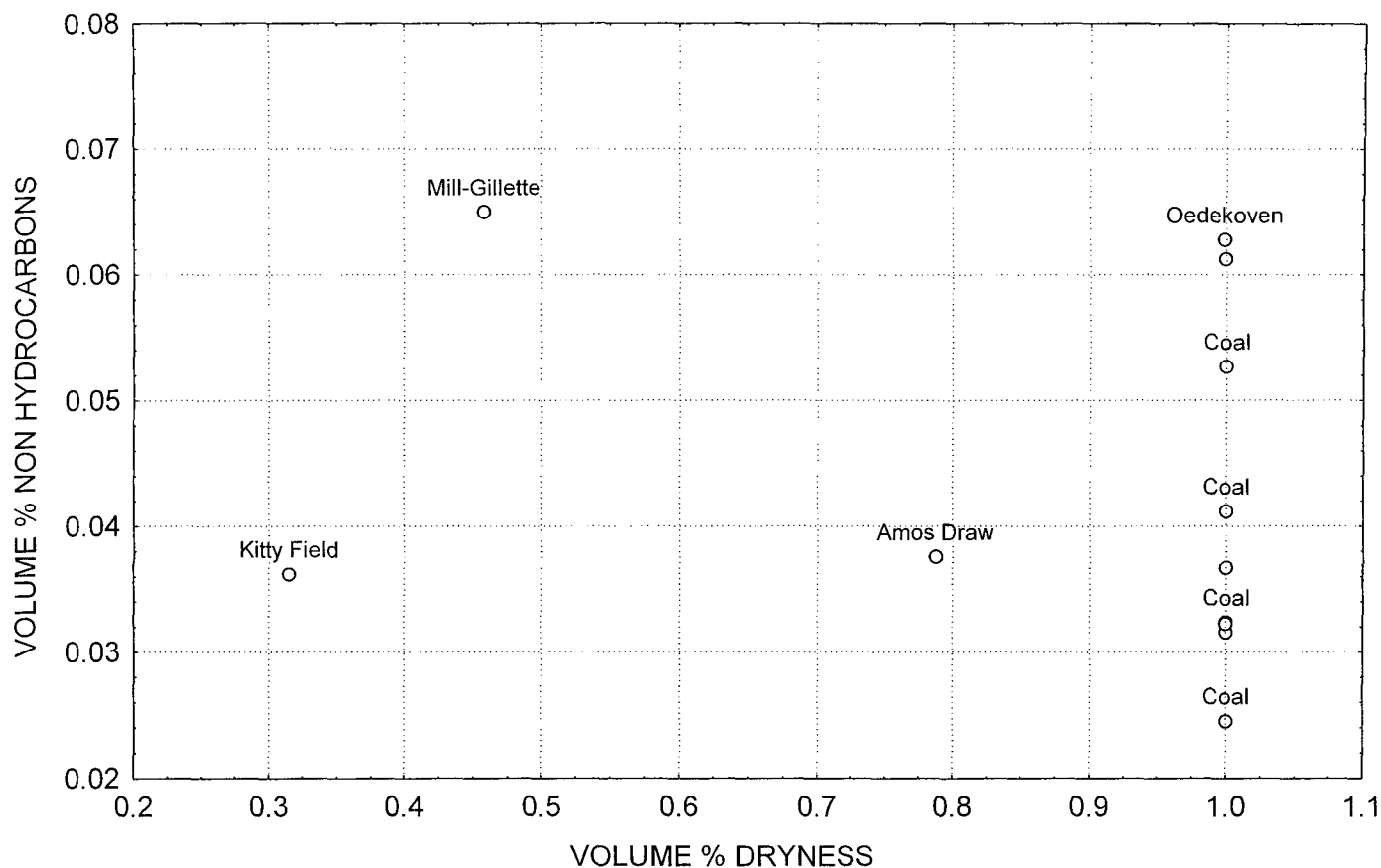


Figure 1. Gas from Cretaceous fields is significantly wetter than those from Tertiary Coals. The volume percent of non hydrocarbons alone is not diagnostic.

reservoirs are distinct from those found in Tertiary sediments. Published empirical evidence and laboratory data have documented that the isotopic composition of gases does not significantly fractionate during migration (Fuex, 1980). Therefore, the observed differences in gas composition indicate that gases in Tertiary sediments did not accumulate as a result of migration from deeper reservoirs, and that they have a different source than that of the gas found in Cretaceous reservoirs.

#### Stable isotopic evidence for a bacterial origin of Tertiary Gas:

An empirical relationship based on global measurements of carbon and deuterium values found in methane is commonly used to distinguish bacterially generated gases from those generated thermogenically by the burial metamorphism of organic-rich sediments (Games, 1978, Schoell, 1984, Whiticar et al, 1986, and Whiticar, 1994). This empiricism is also used to differentiate between bacterial gas originating via fermentation reactions from bacterial gas originating via CO<sub>2</sub> reduction. The composition of Powder River Basin gases relative to the empirically- determined modes of origin is

illustrated in Figure 5, and indicates that Tertiary gases in the Powder River Basin have a bacterial origin. Although the Tertiary data plot in the *methyl-type fermentation* field, a subsequent analysis on the origin of these values in the following sections of this paper demonstrates that these gases originate from the bacterial reduction of CO<sub>2</sub>. The two gas samples plotted in the *mix and transition* field are those collected from the Kitty and Mill-Gillette fields. The single data point within the *early mature thermogenic* field represents the composition of a sample taken from the deepest of the Muddy fields, Amos Draw.

#### CO<sub>2</sub> REDUCTION AS THE BIOCHEMICAL PATHWAY FOR METHANE GENERATION IN TERTIARY COAL SEAMS

##### Metabolic pathways for methanogenesis:

There are two prevalent and volumetrically significant metabolic pathways used by bacteria to generate methane. These are carbon dioxide reduction and acetate fermentation. The simplified equations governing these reactions are as follows:

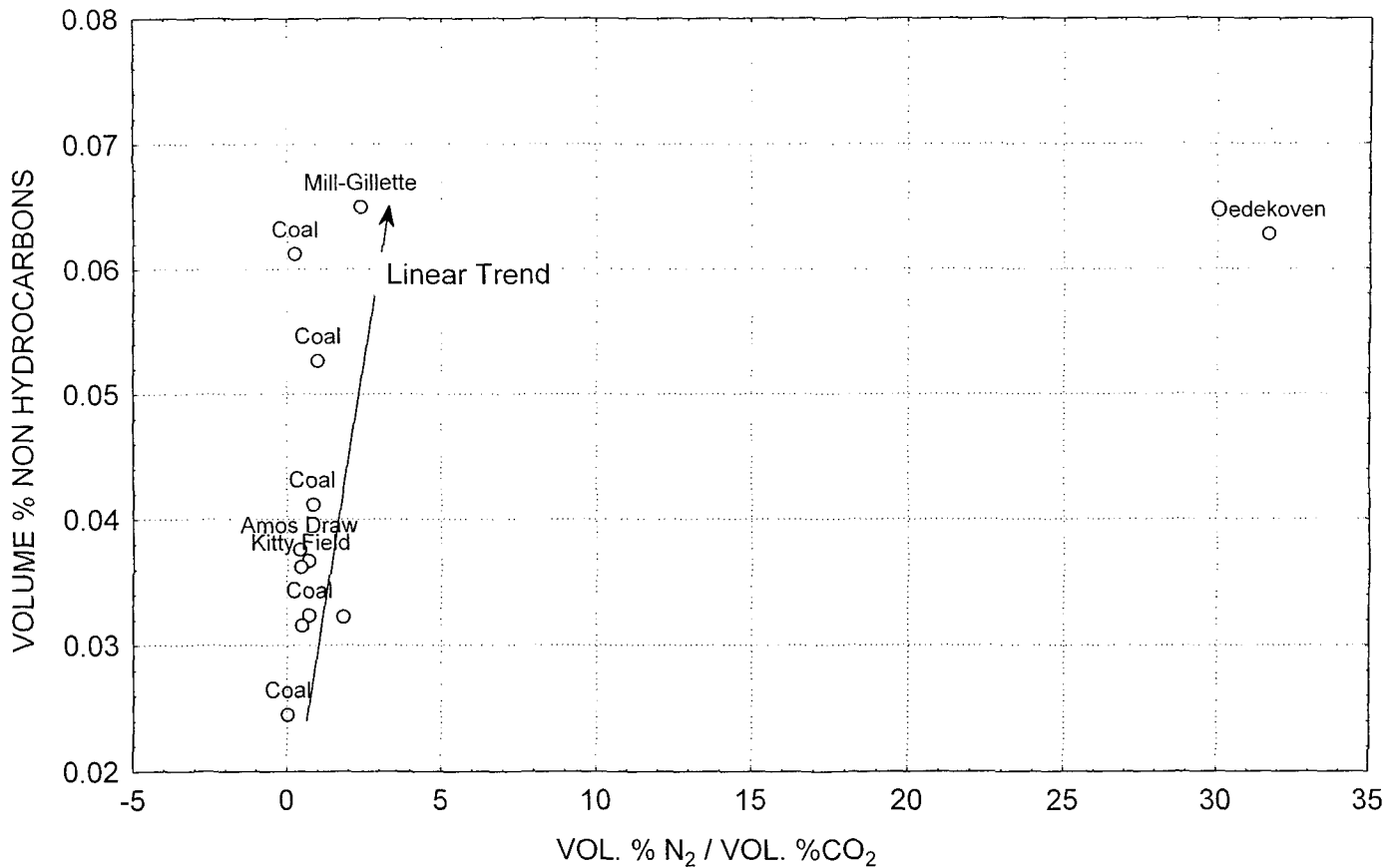
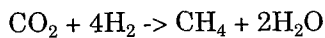
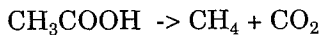


Figure 2.  $N_2 / CO_2$  ratios increase linearly as the volume percent of non-hydrocarbons increases.

Carbon dioxide reduction reaction:



Acetate fermentation reaction:



In this paper, the acetate fermentation reaction is used to represent the most prevalent reaction among the reactions in which bacteria extract the methyl molecule to generate methane. Other common reactants include formate and propionate. Methanogenic bacteria need such simple carbon-based substrates to feed upon.

**Stable Carbon Isotope Analysis:**

The most diagnostic isotopic methods used for differentiating between the two bacterial metabolic pathways take advantage of the fractionation that occurs between the various products and reactants. Carbon isotope fractionation is determined by analyzing the isotopic ratios of carbon in  $CO_2$ ,  $CH_4$ , and the methyl in acetate; deuterium isotope

fractionation is determined by analyzing the isotopic ratios of deuterium in methane and water. No samples of acetate in water were collected for isotopic analysis in this study.

In a system which is closed to the addition of  $CO_2$ , progressive consumption of  $CO_2$  during bacterial reduction leads to a progressive enrichment in  $\delta^{13}C_{CO_2}$ . Such fractionation becomes evident in analytical data once more than 70% of the originally available  $CO_2$  is consumed. Fractionation occurs because bacteria prefer to use the less tightly bound lighter isotope  $^{12}C$  for their cell-building and metabolic processes.

With the exception of a single outlier, the expected relationship between increasing  $\delta^{13}C_{CO_2}$  values and decreasing percentages of  $CO_2$  in gas can be seen in the eastern Powder River Basin coal seam gases plotted on Figure 6. It is significant that the  $\delta^{13}C_{CO_2}$  values of  $CO_2$  associated with methane from the deepest seams are more positive than the values for  $CO_2$  derived from limestone ( $\delta^{13}C_{CO_2} \approx 0.0\text{‰}$ ). Such positive values can only result from bacterial fractionation of  $CO_2$ . Lighter values correspond to gas samples obtained from shallow coal seams (40'-100' deep) and heavier values correspond to the samples

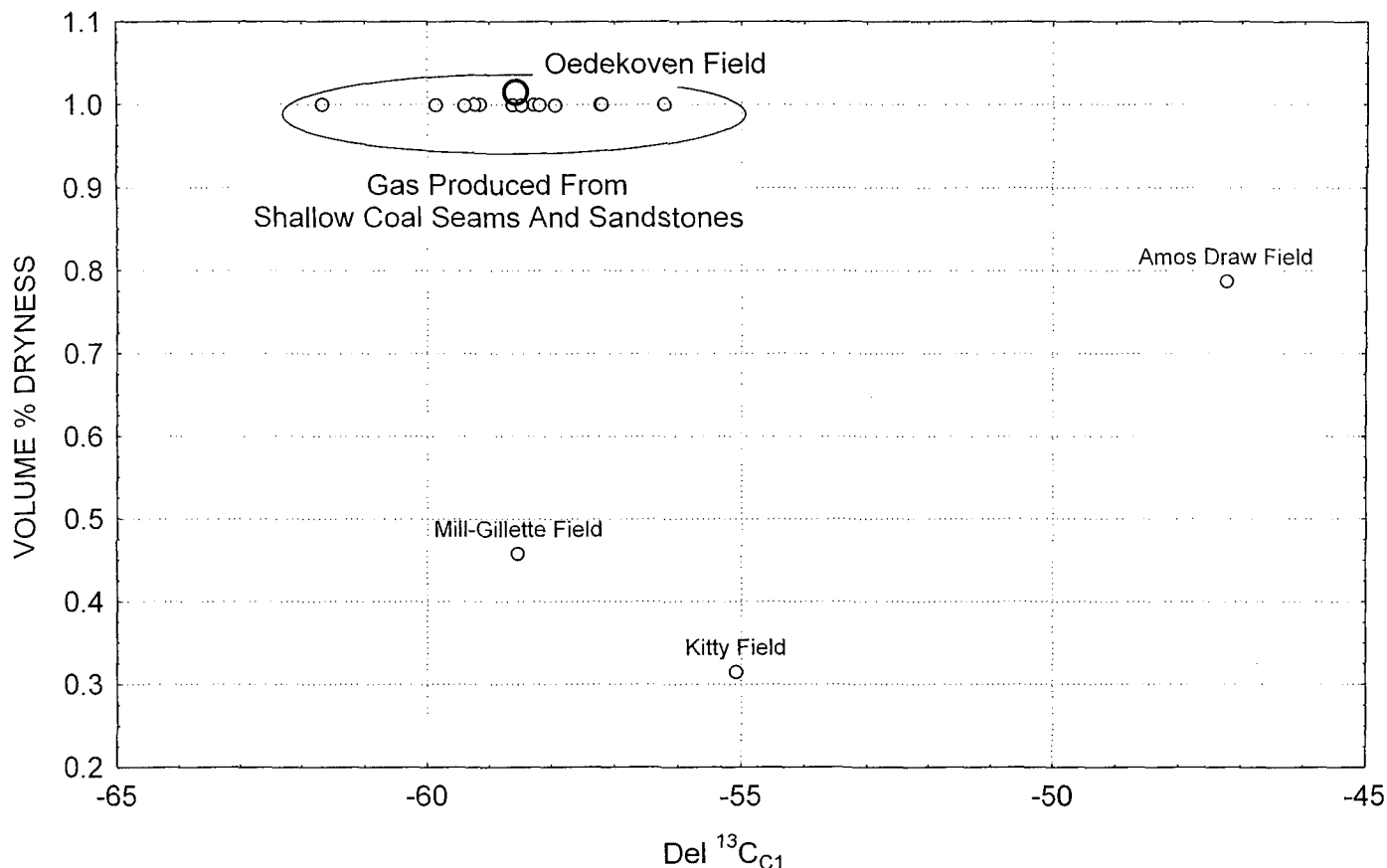


Figure 3. Carbon isotopic ratios alone are not sufficient to differentiate Cretaceous from Tertiary gases.

obtained from deeper coal seams (100'-255' deep). This suggests that deep coal gas migrating to the surface has been mixed with negative  $\delta^{13}\text{C}_{\text{CO}_2}$  values derived from soil gas. Normal values for  $\delta^{13}\text{C}_{\text{CO}_2}$  found in soils from semi-arid climates are on the order of  $-25\text{‰}$ , a value which is diagnostic of root respiration in  $\text{C}_3$  type plants. The most negative value found in this study,  $\delta^{13}\text{C}_{\text{CO}_2} = -23.5\text{‰}$ , corresponds to a gas sample with a high  $\text{CO}_2$  content obtained from a shallow, 43' deep coal seam near the outcrop. This finding is consistent with data indicating the mixing of  $\text{CO}_2$  sources.

Both empirical and laboratory data demonstrate that the fractionation factors between the carbon isotopes of  $\text{CO}_2$  products and  $\text{CH}_4$  reactants can also be used to differentiate between the two bacterial metabolic pathways. Fractionation factors ( $\alpha_{\text{CO}_2\text{-CH}_4}$ ) for  $\text{CO}_2$  reduction should fall in a range between 1.09 and 1.06, whereas those for acetate fermentation should fall in a range between 1.06 and 1.03 (Games, 1978, Kaplan, 1994, Schoell, 1980 and 1988, Whiticar, 1994). Figure 7 illustrates that measured values of gas from Powder River Basin coals fall in the region expected for  $\text{CO}_2$  reduction. Figure 7 also illustrates that there appears to be a linear trend among some of

the coal samples which are in the range between  $\delta^{13}\text{C}_{\text{C}_1} = -60.0$  to  $-57\text{‰}$ . The more negative values correspond to samples taken from shallower coal seams; more positive values correspond to samples taken from deeper seams. This observation further corroborates the results plotted on Figure 6 which indicate mixing of  $\text{CO}_2$  from migrated biogenic coal bed gas with soil gas  $\text{CO}_2$ .

#### Stable Hydrogen Isotope Analysis:

The hydrogen in methane is derived from the catalytic breakdown of water molecules promoted by bacterial enzymes. As evident from the equations presented, the conversion of acetate requires reducing only one molecule of water to provide the hydrogen for one molecule of methane. However, the conversion of  $\text{CO}_2$  requires reducing four molecules of water to provide the hydrogen in one molecule of methane. This difference imparts a predictable fractionation trend in deuterium isotopes. Bacteria also tend to preferentially cleave water molecules containing the lighter hydrogen isotopes. The resulting differences in the fractionation of deuterium between water and methane has been documented as being diagnostic of the different metabolic

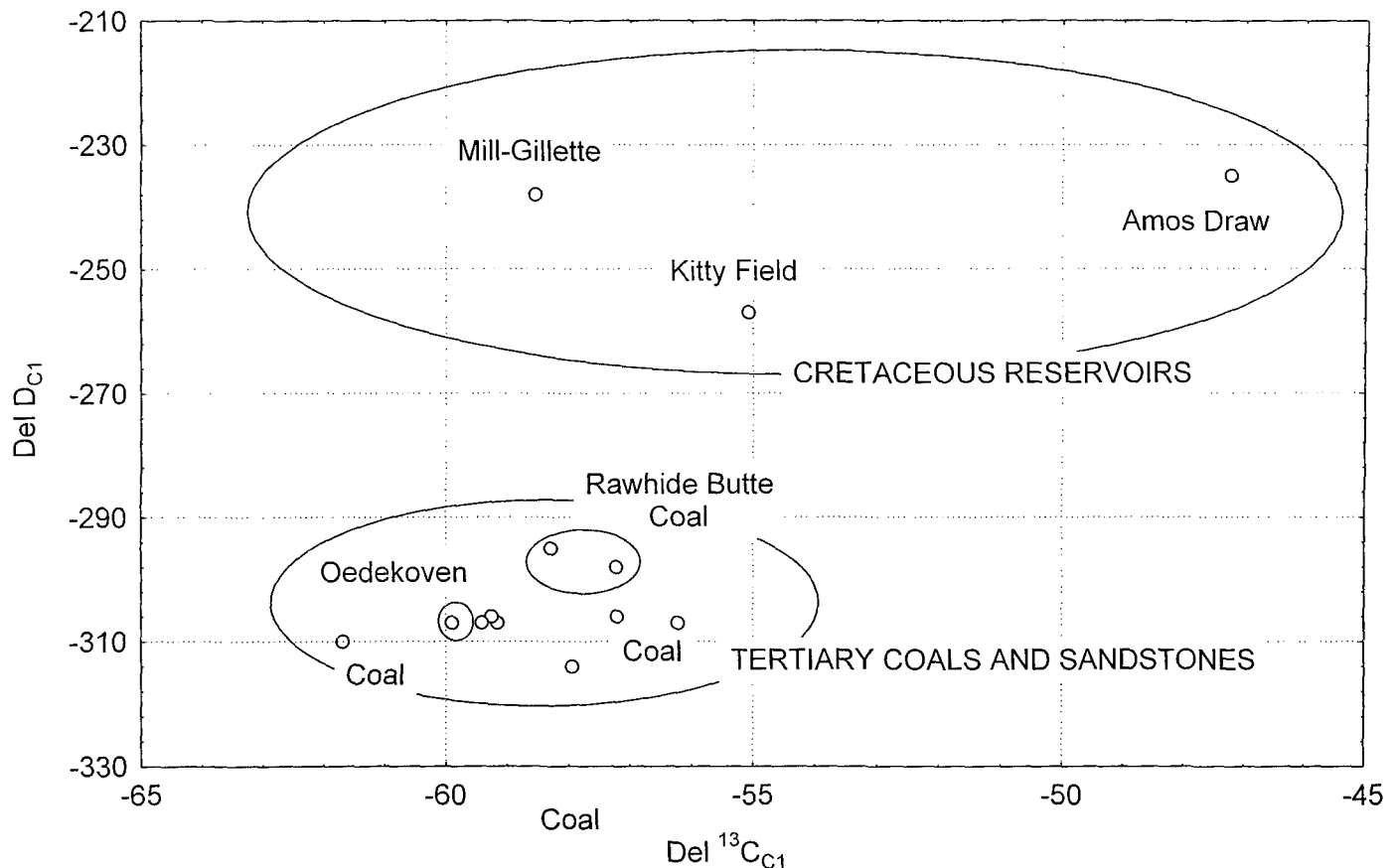


Figure 4. Deuterium isotopes of methane help to clearly differentiate Cretaceous from Tertiary gases.

pathways (Schoell, 1980, 1984, and 1988; Woltemate, et al. 1986).

For acetate fermentation, the currently accepted relationship is as follows:

$$\delta D_{CH_4} = 0.143 \delta D_{H_2O} - 384\text{‰ (SMOW);}$$

And, for carbon dioxide reduction, the currently accepted relationship is as follows:

$$\delta D_{CH_4} = \delta D_{H_2O} - 160 \pm 10\text{‰ (SMOW);}$$

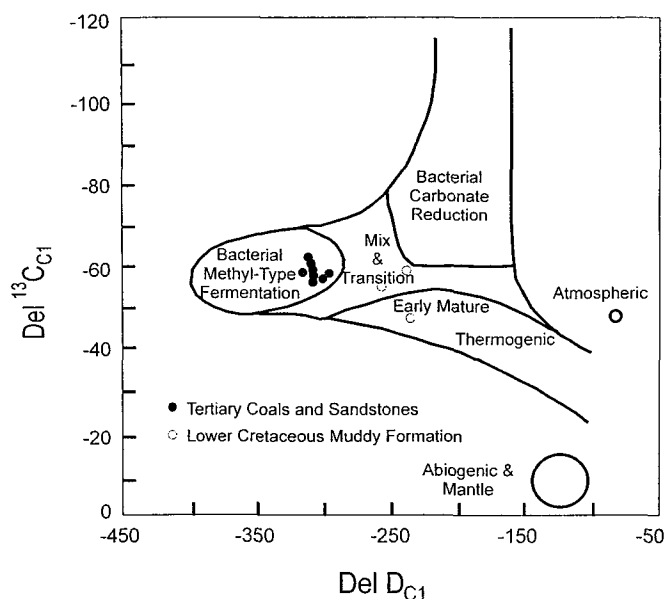
Therefore, in order to predict  $\delta D_{CH_4}$  values using these relationships, it is necessary to determine the stable isotopic ratio of deuterium in water from the study area.

Traditionally, both deuterium and oxygen isotopes are used to characterize the isotopic composition of water. Figure 8 illustrates the values of deuterium and oxygen isotopes in water found among the coal seams and overburden within T50 & 51N-R72W. These indicate that groundwater and surface water samples fall either parallel or close to the global meteoric water line (MWL). An excellent review of the principles governing the stable isotopic values

that define the MWL can be found in Welhan (1987).

Water vapor that migrates from the hot equator to the cold poles across latitudinally-aligned atmospheric circulation belts becomes progressively depleted in deuterium via a Rayleigh distillation process. Accordingly, the slope of the MWL in any given region is fundamentally controlled by the evaporation and condensation physics of water. This slope is relatively constant throughout the world because both hydrogen and oxygen isotopes are proportionally fractionated in response to the constant differences in vapor pressure between water molecules of differing isotopic composition. Lighter isotopes are preferentially fractionated into the vapor phase. Isotopic values along the MWL will vary principally as a function of temperature and/or elevation. The intercept of the MWL, on the other hand, will vary locally depending on differences in local climatic and vegetative conditions.

Surface and aquifer water collected from this area of Wyoming in the Powder River Basin have isotope values that fall predominantly along a slope defining the global meteoric water line. The line of samples which can be observed to deviate from the slope of the MWL are those collected from samples at and closest to the surface. Such a trend is diagnostic of the



**Figure 5. Isotopic ratio plot commonly used to differentiate the different origins of natural gas. Although Powder River data fall in the fermentation field, more detailed analysis indicates a CO<sub>2</sub> reduction mechanism.**

isotopic enrichment in surface waters that results from local evaporation. Another distinctive feature of the data is that the intercept on the deuterium axis is shifted in the negative direction by 2‰ from a value of +10 that is generally accepted to represent the global MWL. This is a consequence of unique local climatic effects imparted by the proximity of this area to the Rockies, the high elevation of the plains in this area, the semi-arid to arid climate, and the poor vegetation. A third trend observable in Figure 8 is that the deeper coal seams contain more negative deuterium and oxygen isotope ratios than the shallower coal seams. This indicates that the deeper reaches of the coal aquifer preserve the isotopic signature of recharge which occurred during significantly cooler, possibly glacial climates.

On the basis of the MWL established for this area of the Powder River basin, it is possible to predict the isotopic ratio of deuterium in bacterial methane. There are only three available analyses reported here of deuterium ratios for both gases and water. All three come from deeper coal seams sampled at depths between 170 and 250 feet below the surface. Figure 9 illustrates that the deuterium data support the interpretation based on the carbon isotopes, that methane originates principally from the bacterial reduction of CO<sub>2</sub>. Many investigators who have previously reported on the origin of Powder River Basin coal gases failed to take into account deuterium fractionation data (Law, et al., 1991; Montgomery, 1999; Rice and Flores, 1991; Scott, 1993).

Jenden and Kaplan (1986) found another empirical relationship that helps determine the

relative proportion of methane generated by the each of the two principal microbial metabolic pathways. The fraction, *f*, of the methane derived from acetate fermentation can be estimated using the following equation:

$$f = (\delta D_{H_2O} - \delta D_{CH_4} - 160) / (0.857 \delta D_{H_2O} + 233‰)$$

Substituting the appropriate values from Figure 9, we find that *f* varies linearly between 0.0 and 0.07. This linear relationship corresponds to the linear relationship of carbon isotopes observed in Figure 6. The most negative values for the carbon isotope in methane have the highest fraction of methane derived from acetate fermentation. It is possible that the oxidative weathering of coal near the surface may locally contribute acetate and other simple methyl compounds to the ground water (Isaacs and Liotta, 1987). These substrates can be used by shallow-dwelling acetate-fermenting methanogens to generate methane. Nevertheless, CO<sub>2</sub> reduction dominates the metabolic pathway for bacterial methane generation in the coal of this area in the Powder River Basin.

#### **Brief arguments against a thermogenic origin of gases derived from coal.**

The available literature indicates that Powder River Basin coals have not been exposed to sufficiently high burial temperatures to have generated methane. Published vitrinite reflectance (%R<sub>o</sub>) values range between 0.20 % and 0.5 % (Hobbs, 1978; Law et al., 1991). Unfortunately, there are no published maps illustrating the distribution of these values in the basin. Presumably, R<sub>o</sub> values are lowest along the eastern margin of the basin and highest along the asymmetric synclinal axis near the western edge of the basin.

Ro values reported for coals around Rawhide Butte Field range from 0.20 % to 0.30 % (Law, et al., 1991). Such low vitrinite reflectance values indicate that these coals can be classified as sub-bituminous C. This classification is supported by average bed moisture contents between 26% and 30%, and calorific values between 6800 and 8200 Btu/lb (Glass, 1975). Coals of this rank have not been buried to sufficient depths to generate thermogenic methane. It is also generally accepted that early thermogenesis in coals does not begin until Ro values increase from between 0.5% to 0.85% (Berner et al. 1992; Law, et al., 1991; Scott, 1994). Published vitrinite reflectance values of 0.45 to 0.50 in Upper Cretaceous sediments along the northeastern margin of the basin indicate that these deeper sediments have not been buried to depths deeper than 5,500 feet (Nuccio, 1988). Given a range of Ro values between 0.20 % and 0.50 %, maximum burial temperatures would have been between 40 and 90 C depending on the time-temperature history of burial (Burnham and Sweeney, 1989). Such low

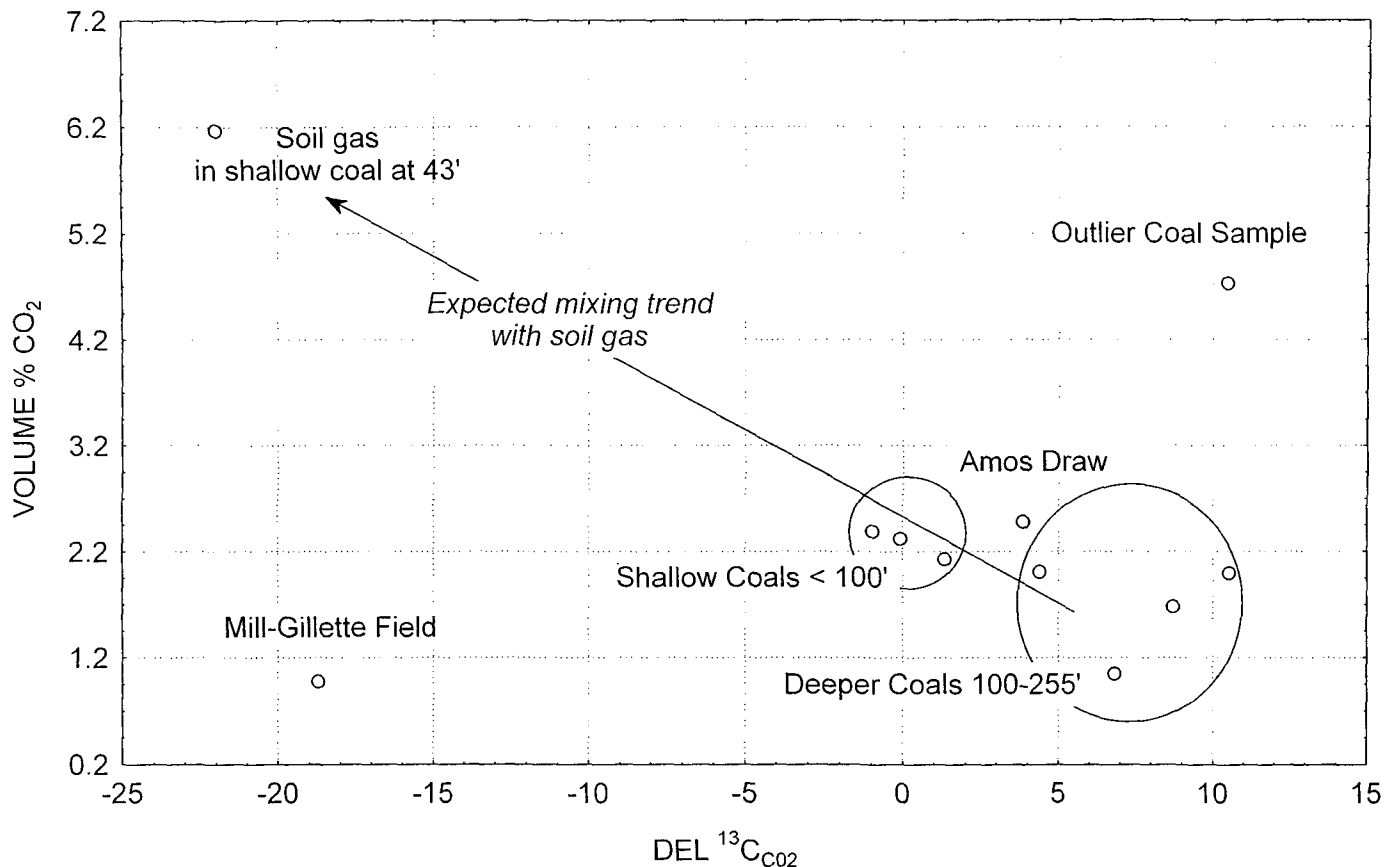


Figure 6. The carbon isotope ratio in CO<sub>2</sub> and relative CO<sub>2</sub> concentrations indicate that gas from the deepest coals mixes with soil gas in coals close to the surface. Heavy carbon isotope values are consistent with an origin from bacterial reduction of CO<sub>2</sub>.

temperatures are not sufficient to generate hydrocarbons.

If it is assumed that thermogenic gas was generated in the deepest coals buried along the western edge of the basin, (possibly having Ro values between 0.5% and 0.85%, then we can predict the isotopic value of methane generated from those coals. Using the fractionation factors published by Berner et al. (1992) for huminitic coals, we can predict the isotopic ratio for carbon in methane using the following equation:

$$\alpha_{\text{coal-CH}_4} = 1.003$$

Substituting average  $\delta C_{\text{coal}}$  values of -24 to -30‰, for the convertible carbon fraction in Powder River coals (Holmes, 1988), we would predict  $\delta C_{\text{CH}_4}$  values between -33‰ and -36‰. Such values are much heavier than those reported here and published elsewhere.

#### DISCUSSION:

The results of analyses conducted for this paper

provide corroborating evidence that the source of methane in Tertiary coals along the eastern margin of the Powder River Basin is derived from the bacterial reduction of CO<sub>2</sub>. The extremely dry composition of these coals and the distribution of both carbon and deuterium isotopes in co-occurring methane, water, and CO<sub>2</sub> all support this conclusion. This interpretation also agrees with other recent interpretations for the source of methane in these coals that are available in the literature (Rice, 1993b and 1993c). The most important remaining issue regards the timing of the generation, migration, and emplacement of this gas. The following discussion addresses this issue.

#### Optimum conditions for bacterial methane generation:

Bacteria living in the upper 1000 m. of the sedimentary column below the oceans and in deep aquifers may account for as much as 10% to 50% of the total biomass of the planet (Cragg et al., 1996; Parkes, et al. 1994; Whitman et al., 1998). Together, they interact to form a gigantic food- web consortium that converts complex organic matter to methane,



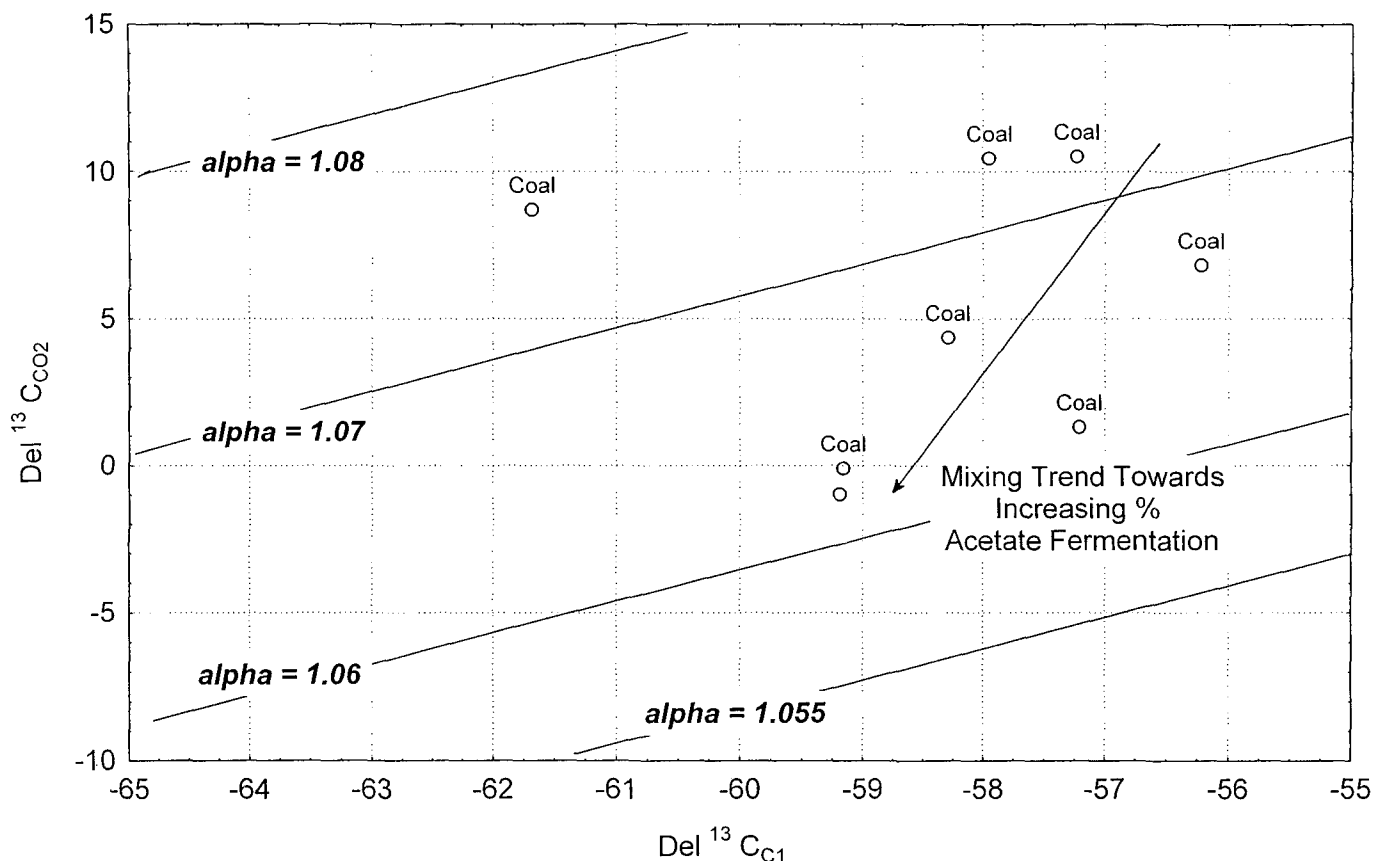


Figure 7. The fractionation of carbon isotopes between  $\text{CO}_2$  and methane is consistent with an origin from bacterial reduction of  $\text{CO}_2$ . Minor mixing with methane derived from fermentation is indicated by the linear trend.

$\text{CO}_2$ , and water at temperatures below  $75^\circ\text{C}$ . Anaerobic digestion of organic material is thought to take place in three stages (Winfrey, 1984). The first stage, hydrolytic and fermentive bacteria breakdown complex organic polymers to organic acids and alcohols. In the second stage, obligate  $\text{H}_2$ -producing acetogenic bacteria convert organic acids and alcohols into acetate,  $\text{H}_2$ , and  $\text{CO}_2$ . These three compounds are principal methanogenic precursors normally found in anaerobic habitats. In the final digestive stage, methanogenic bacteria use the available  $\text{H}_2$  to convert acetate and  $\text{CO}_2$  to methane. Although both reaction pathways can occur simultaneously,  $\text{CO}_2$  reduction usually dominates after acetate fermentation ceases (Mah et al., 1977; Whiticar, 1986). Such a three-stage mechanism readily explains the changes in H/C and O/C ratios that are typically plotted on a Van Kervelen diagram to document the early diagenesis of Type III kerogens in coal-forming deposits. Furthermore, such complex interactions account for the minor discrepancies between empirically-derived carbon and deuterium isotope fractionation factors and those derived on the basis of laboratory cultures (Balabane, et al., 1994; King, et

al., 1997); laboratory cultures can not reproduce the complex interactions among bacterial consortia.

Methanogenic bacteria are a highly specialized and diverse group of organisms which gain energy by converting simple molecules, such as  $\text{H}_2$ ,  $\text{CO}_2$ , CO, formate, acetate, methylamines, and simple alcohols, to methane. Methanogens are obligate anaerobes, meaning they cannot survive in the presence of free or dissolved oxygen. Because both free and bound oxygen are utilized by other bacteria that compete more effectively for nutrients, methanogens cannot flourish until all the free oxygen, nitrates, Mn and Fe oxides, and dissolved sulfates in groundwater have been consumed by competing bacteria. Thus methanogens will flourish in only the most reducing groundwater environments as long as simple substrates are available for their metabolic functions. Methanogenic rates are limited by the availability of these simple substrates. Altogether, methanogens are responsible for producing an estimated 20% of all known commercial gas accumulations (Noble and Henck, 1998; Wiese and Kvenvolden, 1993).

Laboratory culturing techniques for  $\text{CO}_2$ -reducing methanogens indicate that optimum growth rates are

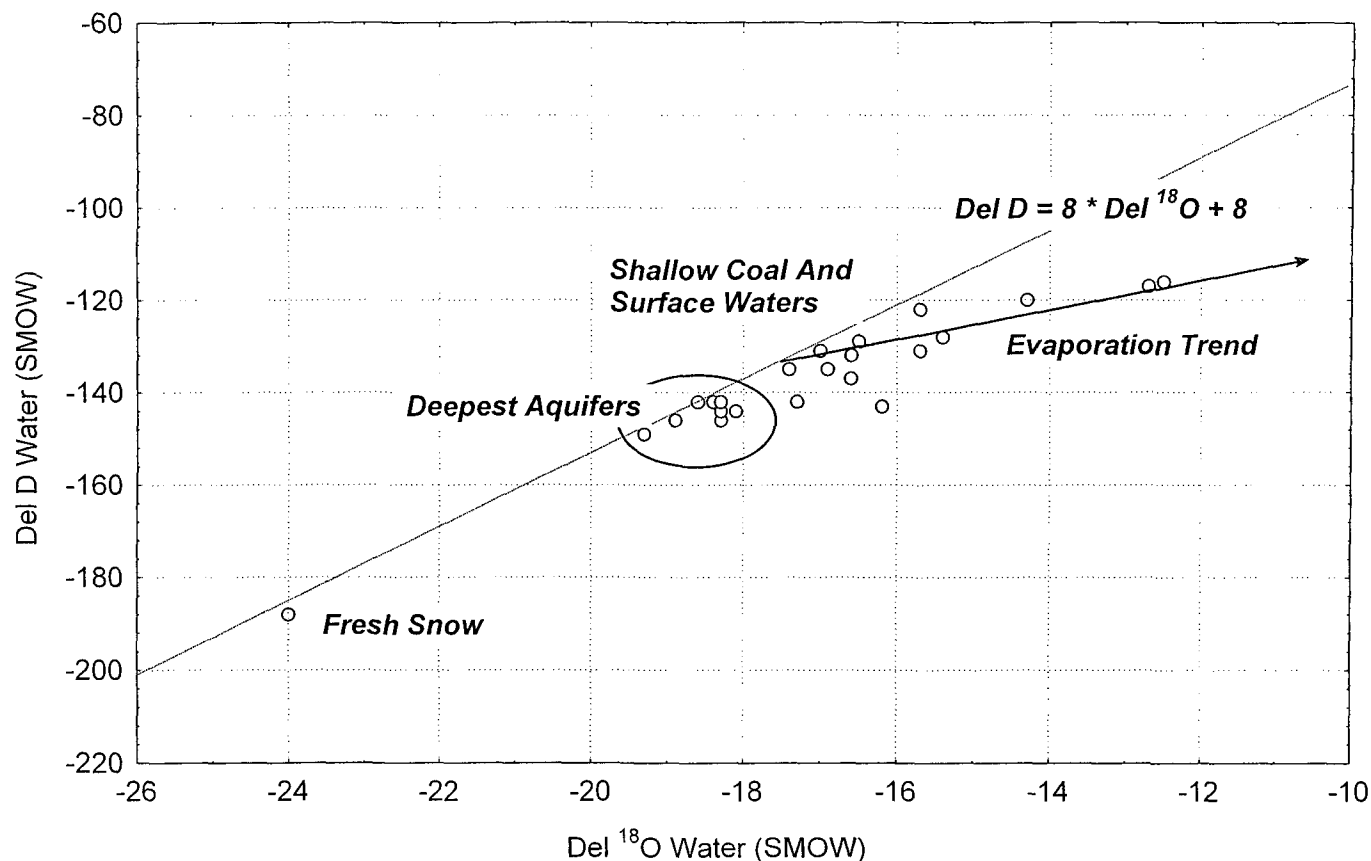


Figure 8. Meteoric water line for this area of the Powder River Basin. The equation corresponding to the global MWL is:  $DeD = 8 * Del^{18}O + 10$ .

achieved at temperatures of 40° C for mesophilic methanogens, and 60° C for thermophilic methanogens, provided that substrates are not limited (Games et al, 1978; Winfrey, 1984). In nature, these methanogens have been observed to generate methane at temperatures between 0° and 100° C. External pressures as high as 1300 psi do not appear to have any affect on growth rates. Optimum growing conditions are also maintained at pH levels between 6 and 8. It has also been determined that although such methanogens can be grown strictly on CO<sub>2</sub> and H<sub>2</sub>, the presence of acetate significantly accelerates the rate at which methane can be produced.

#### Timing of bacterial methane generation and emplacement in Tertiary Powder River Basin coals:

The most ideal conditions for generating bacterial methane in Tertiary Powder River Basin coals would have occurred at the time of maximum burial, sometime between 10 to 35 mya. Maximum estimated burial temperatures between 40° and 90° C would have been well within a range that is ideal for bacterial methane production at that time. Furthermore, this amount of time is sufficient to

account for the vast methane resource in the basin, even at the low conversion rates reported on basis of in-situ observations and culture experiments (Frederickson et al., 1991; Loveley and Chapelle, 1995; McMahon and Chapelle, 1991).

On the other hand, the few available deuterium fractionation data for methane and water in this study area imply a close spatial relationship between the aquifer water and the source of methane. Additional data from deeper portions of the basin are needed to determine whether the deuterium fractionation factors for water and methane remain fairly constant over a wide range of deuterium values. If such a trend could be documented, it would provide *prima facie* evidence that methane generation may be related to the establishment of a regional artesian groundwater system driven by recharge along the basin margins (Scott, 1994; Tyler et al., 1995; Walter, et al., 1995; Walvoord, 1999). Ideal conditions for such an artesian system would have occurred at the onset of basin uplift and would have continued to the present time. On the basis of the deuterium data, it could be argued that a significant amount of methane may have been generated as recently as during the Pleistocene.

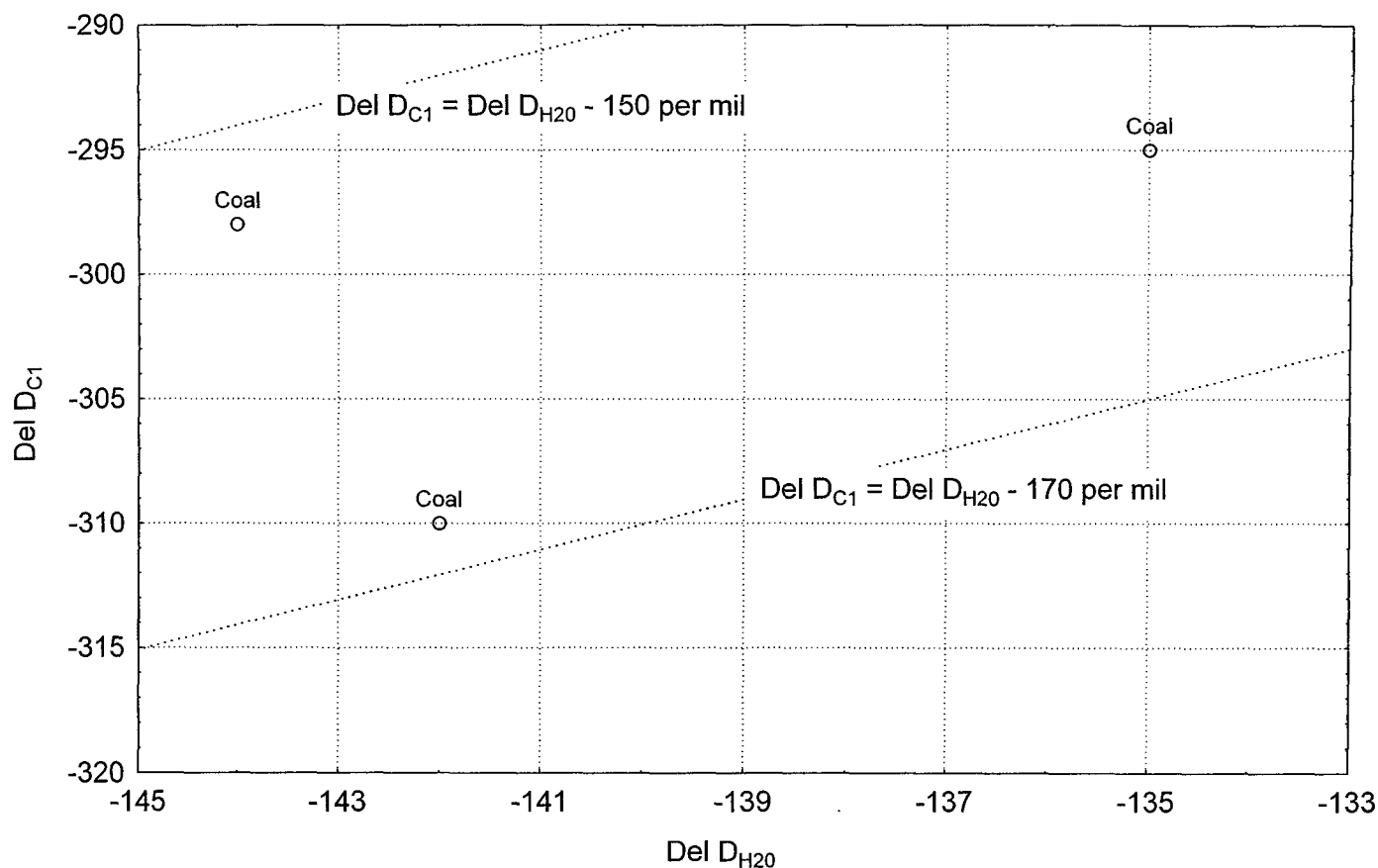


Figure 9. The fractionation of deuterium isotopes between water and methane is also consistent with an origin from bacterial reduction of  $\text{CO}_2$ .

Future studies designed to ascertain the origin of methane in Powder River Basin coal seams should include all of the isotopic analyses presented in this paper. Isotopic fractionation factors of deuterium between water and methane, and of carbon between  $\text{CO}_2$  and methane are absolutely necessary for differentiating biogenic and thermogenic gases of differing origins. Moreover, just as in the San Juan and Black Warrior Basins, we should soon discover that systematic characterization of fluid properties in Powder River Basin coals could help define the most productive exploration fairways.

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