



December 7, 2015

Mr. Brett Middleton  
Encana Oil & Gas (USA) Inc.  
143 Diamond Avenue  
Parachute, CO 81635

Via Email Only

**Subject:           Review of Isotopic Analysis from Production, Bradenhead and Surface Samples  
D31 595 Well Pad  
North Parachute Ranch  
Apex Project Number 240.1509.06**

Dear Mr. Middleton:

Apex Companies, LLC (Apex) is pleased to present this letter report to Encana Oil & Gas (USA) Inc., (Encana) summarizing our review of the isotopic data and selected gases for three (3) gas samples collected from a pad site in the North Parachute Ranch area of the Piceance Basin in western Colorado. It is our understanding that these samples were collected from the production casing, bradenhead, and surface casing at the pad site. The purpose of the review was two-fold: (1) to determine whether the sample collected from the surface casing was thermogenic or biogenic; and (2) to attempt to determine if the three gases were from one or more sources.

Provided below is a summary of the basic isotopic principles used in our analysis, review of laboratory isotope analyses, and conclusions.

#### **BASIC ISOTOPE PRINCIPLES**

Hydrocarbon gases (and liquids) contain two naturally occurring stable isotopes of carbon:  $^{12}\text{C}$  and  $^{13}\text{C}$ . The difference between the two carbon isotopes is the presence of an additional neutron in the nucleus of  $^{13}\text{C}$ . Specifically,  $^{12}\text{C}$  has six protons and six neutrons in the nucleus, while  $^{13}\text{C}$  has six protons and seven neutrons in the nucleus.  $^{12}\text{C}$  is the more abundant of the two isotopes, comprising 98.89% of naturally occurring carbon, and  $^{13}\text{C}$  comprises 1.11% of naturally occurring carbon. The small variations between  $^{12}\text{C}$  and  $^{13}\text{C}$  are measured relative to a standard and are expressed in delta ( $\delta$ ) notation as the parts per thousand (‰, per mil) difference of the sample from the standard:

$$\{[(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}]/[(^{13}\text{C}/^{12}\text{C})_{\text{standard}}]\} \times 1000 = \text{delta}(\text{sample} - \text{standard}) = \delta \text{ (‰, per mil)}$$

The standard used for carbon isotopic measurements is the Pee Dee Belemnite (PDB), which is a marine carbonate, and defined as having a carbon isotopic composition ( $\delta^{13}\text{C}$ ) of 0‰. Because natural hydrocarbons are enriched in the lighter isotope,  $^{12}\text{C}$ , they have negative  $\delta^{13}\text{C}$  values. For example, biogenic methane typically has carbon isotopic values of –60‰ or less, while thermogenic methane ranges from about –20‰ to –60‰. When gas is relatively enriched in the lighter  $^{12}\text{C}$  isotope, it is termed isotopically “light”. A gas with a methane carbon isotope value ( $\delta^{13}\text{C}_1$ ) of –55‰ is isotopically lighter than methane with a  $\delta^{13}\text{C}_1$  of –40‰. Conversely, a gas enriched in the heavier  $^{13}\text{C}$  isotope is termed isotopically “heavy” so that a  $\delta^{13}\text{C}_1$  of –40‰ is isotopically heavier than a  $\delta^{13}\text{C}_1$  of –55‰.

Similarly, there are two stable isotopes of hydrogen: protium and deuterium. Protium is the more abundant hydrogen isotope and contains one proton and no neutrons ( $^1\text{H}$ ). Deuterium is the heavy ( $^2\text{H}$ ) isotope of hydrogen with one proton and one neutron. The ratio of  $^2\text{H}$  to  $^1\text{H}$  is measured and reported relative to the international standard, Standard Mean Ocean Water (SMOW). Hydrogen isotopes can also be measured on hydrocarbon gases and are most commonly measured on the hydrogen in methane.

Hydrocarbon gases can be grouped into three categories: 1) bacterial (or biogenic) gas, 2) thermogenic gas, and 3) mixed gases (i.e. mixtures of biogenic and thermogenic gases). Bacterial gases are created when microorganisms consume organic nutrients. During this process, the microorganisms preferentially metabolize the lighter isotope,  $^{12}\text{C}$ , and, consequently, bacterial gases are typically enriched in  $^{12}\text{C}$  relative to  $^{13}\text{C}$  and are therefore isotopically light. Thermogenic gases, on the other hand, are formed by the decomposition of organic matter (kerogen) that occurs in response to thermal stress. Compared to bacterial gases, thermogenic gases are isotopically heavier and their molecular composition is enriched in the wet gas components. Mixtures of bacterial and thermogenic gases are most often recognized by measurement and evaluation of the carbon and deuterium isotopes of methane.

**Figure 1** illustrates how carbon ( $\delta^{13}\text{C}$  methane, ‰) and deuterium ( $\delta\text{D}$  methane, ‰) isotopes measured in methane can be used to determine gas origin. For example, although bacterial gas and post-mature dry gas are both “dry” from a molecular compositional perspective [ $(\text{C}_1)/(\text{C}_1 \text{ to } \text{C}_5) > 95\%$ ], the carbon and deuterium isotopic signatures of bacterial methane and post-mature dry gas are notably different. Specifically, bacterial methane has deuterium isotopes ranging from about –150‰ to –250‰ and methane carbon isotopes less than –60‰. In contrast, methane in post-mature dry gas has deuterium isotopes greater than –150‰ and carbon isotopes greater than –40‰.

In general, the isotopic composition of a gas is a function of the isotopic composition of the organic material in the source rock that generated the gas and the thermal maturity of the organic matter at the time the gas was generated and expelled. For example, as the thermal maturity increases, gases from the same source rock typically become compositionally drier (i.e. enriched in methane) and isotopically heavier ( $\text{C}^{2+}$ ).

## SUMMARY OF ISOTOPIC DATA

VistaGeoScience collected three gas samples from the D31 595 pad site in western Colorado on January 23, 2015. The gas samples were collected in Cali-5 Bond Bags™ and submitted to ISOTECH Laboratories Inc. for analyses of selected gases and stable isotopes. A summary of the laboratory analyses is provided in **Table 1**. A copy of the laboratory report is provided in **Attachment 1**.

Review of the stable carbon and hydrogen isotope compositions of methane ( $\delta^{13}\text{C}_1$  and  $\delta\text{DC}_1$ , respectively) for the three samples shows that the three gas samples are thermogenic in origin. This is supported by the presence of higher chain hydrocarbons (i.e. ethane, propane, butane and pentane) in methane than would ordinarily be detected in microbial gas, which is comprised predominately of methane and carbon dioxide. **Figure 2** is a cross plot of the carbon ( $\delta^{13}\text{C}$  methane) and deuterium ( $\delta\text{D}$  methane) isotopes for the three gas samples and also illustrates the different compositional ranges of different sources of methane (Coleman, 1994). As shown on **Figure 2**, the three gases are thermogenic.

During bacterial oxidation processes,  $^{12}\text{C}$  is oxidized more readily than  $^{13}\text{C}$ . As a result, the residual methane becomes more enriched in  $^{13}\text{C}$ . This is evident for the bradenhead and surface gases, where the  $^{13}\text{C}$  in the methane in these two samples is more enriched than the production gas sample (see **Figure 2**).

As an additional line of evidence of the gas origin, a review of the  $\delta^{13}\text{C}_2$  value of ethane combined with the  $\text{C}_1/\text{C}_2$  ratio was used to assist with identifying the gas origin. Specifically, a  $\text{C}_1/\text{C}_2$  ratio less than 1,000 and  $\delta^{13}\text{C}_2$  value more positive than -45‰ (i.e. less negative) indicates thermogenic gases; a  $\text{C}_1/\text{C}_2$  ratio greater than 1,000 and  $\delta^{13}\text{C}_2$  value less than -45‰ indicates a microbial origin. Similarly, a gas composition with  $\text{C}_1/\text{C}_2$  ratio greater than (>) 1,000 and a  $\delta^{13}\text{C}_1$  less than (<) -50‰ generally indicates microbial gases, whereas a  $\text{C}_1/\text{C}_2$  ratio less than 1,000 and  $\delta^{13}\text{C}_1$  more positive than -50‰ of  $\delta^{13}\text{C}_1$  generally indicates thermogenic gases. The  $\text{C}_1/\text{C}_2$  ratios for the collected gas samples were well below a ratio of 1,000, which is characteristic of a thermogenic gas. The  $\text{C}_1/\text{C}_2$  ratios for the three samples ranged from 14.7 to 23.47.

**Figure 3** depicts the gas isotope profiles for carbon isotopic values ( $\delta^{13}\text{C}_n$  where n = number of carbons) for methane ( $\text{C}_1$ ), ethane ( $\text{C}_2$ ), propane ( $\text{C}_3$ ), isobutane ( $\text{iC}_4$ ) and normal butane ( $\text{nC}_4$ ). The carbon isotopes for each of these five gases was plotted for the three gas samples. As shown on **Figure 3**, two of the gas isotope profiles (surface and bradenhead) are parallel to sub-parallel to each other. In contrast, the profile for the production gas ‘cuts across’ the other two profiles indicating the production gas is from a different source. Furthermore, the parallel to sub-parallel isotope profiles for the surface and bradenhead gases are offset vertically, and the heavier, more thermally mature isotopes plot toward the top. Accordingly, the surface and bradenhead gases are the least thermally mature, and reflect stray gas. The production gas is the most mature of the three gases and is from a separate source.

Cross plots of  $\delta^{13}\text{C}_1$  and  $\delta\text{DC}_1$  can also be used to recognize reservoir ‘compartmentalization’. For example, **Figure 4** shows the separation between surface and bradenhead gas samples, which is indicative that these gases are not in fluid communication and may be from different sources. By

comparing the separation of each data point shown on **Figure 4**, it appears that none of these three gas samples are likely from the same source.

#### SUMMARY OF FINDINGS

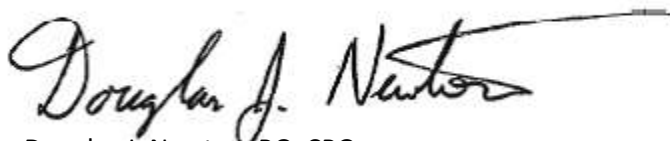
1. Review of the stable carbon and hydrogen isotope compositions of methane ( $\delta^{13}\text{C}_1$  and  $\delta\text{DC}_1$ , respectively) for the three samples shows that the three gases are thermogenic in origin. This is supported by the carbon isotope values that ranged from -37.78‰ to -36.25‰, which is well within the common range for thermogenic methane (i.e. about -20‰ to -60‰). In addition, the  $\text{C}_1/\text{C}_2$  ratios for the collected gas samples ranged from about 14.7 to 23.47, which were well below a ratio of 1,000.
2. Bradenhead and surface gases appear to be a source of stray gas not production gas.
3. The gas collected from the production casing has a notably different isotopic composition than the gases collected from the surface and bradenhead.
4. Bacterial oxidation processes appear to have enriched the  $^{13}\text{C}$  in both the surface and bradenhead gas samples in comparison to the production gas sample.
5. The production gas is the most mature of the three gases and appears to be from a separate source than the gases collected from the bradenhead and surface.
6. The surface and bradenhead gases are the least thermally mature of the three gases and have similar isotopic compositions to one another, which suggests these two gases are from a separate source than the production gas sample.

#### CLOSING

We appreciate the opportunity to assist Encana on this interesting project. If you have any questions or need additional information, please do not hesitate to call.

Sincerely,

**APEX COMPANIES, LLC**



Douglas J. Newton, PG, CPG  
Division Manager

## REFERENCES

1. Baldassare, Fred J., McCaffrey, Mark A., Harper, John A. (2014). A geochemical context for stray gas investigations in the northern Appalachian Basin: Implications of analyses of natural gases from Neogene-through Devonian-age strata. AAPG Bulletin, 2014.
2. Coleman, D., 1994. Advances in the Use of Geochemical Fingerprinting for Gas Identification. American Gas Association – Operations Conference. May 9-11, 1994.
3. Edman, J., 2007. Application of Hydrocarbon Gas Isotopic Data to Tight Gas Sand and Shale Gas Exploration and Production in the Rocky Mountains. August 2007.
4. Revesz, K.M., et al 2010. Carbon and hydrogen isotopic evidence for the origin of combustible gases in water supply wells in north-central Pennsylvania. Applied Geochemistry. 1845-1859.
5. Taylor, S.W., et al. 2000. Bacteriogenic ethane in near surface aquifers: Implications for leaking hydrocarbon well bores. Environ. Sci. Tech. 34. 4727-4732.
6. Whiticar, M.J., and Faber, E. 1986. Methane oxidation in sediment and water column environments – isotope evidence. Org Geochem 10. 759-768.

## TABLES

**Table 1**  
**Summary of the Results of Gas Samples Collected at the D31 595 Pad Site, North Parachute Ranch, Western Colorado.**

Isotech Lab No.	Sample Name	Sample Date	H <sub>2</sub> %	Ar %	O <sub>2</sub> %	CO <sub>2</sub> %	N <sub>2</sub> %	CO %	C <sub>1</sub> %	C <sub>2</sub> %	C <sub>2</sub> H <sub>4</sub> %	C <sub>3</sub> %	C <sub>3</sub> H <sub>6</sub> %	iC <sub>4</sub> %	nC <sub>4</sub> %	iC <sub>5</sub> %
488145	Production	1/23/2015	nd	0.0829	2.47	1.52	9.07	nd	78.91	5.52	0.0002	1.39	nd	0.379	0.193	0.118
488146	Braden	1/23/2015	nd	0.0292	0.79	0.22	3.12	nd	88.43	4.12	0.0002	1.90	nd	0.346	0.546	0.169
488147	Surface	1/23/2015	nd	nd	0.052	0.005	0.041	nd	92.29	3.93	0.00	1.98	nd	0.331	0.58	0.161

**Summary Data (continued)**

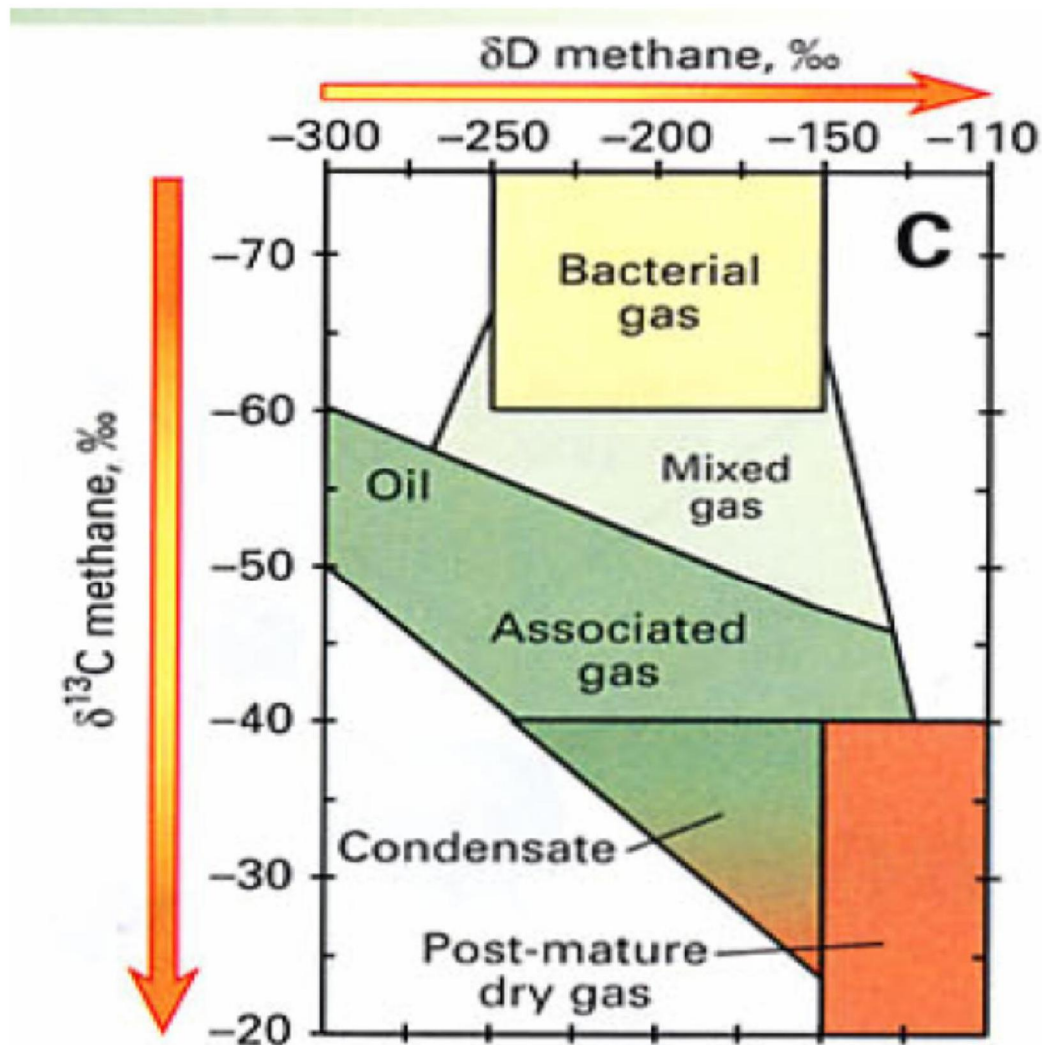
Isotech Lab No.	Sample Name	Sample Date	nC <sub>5</sub> %	C <sub>6</sub> + %	d <sup>13</sup> C <sub>1</sub> ‰	dDC <sub>1</sub> ‰	Specific Gravity	BTU	He %	d <sup>13</sup> C <sub>2</sub> ‰	d <sup>13</sup> C <sub>3</sub> ‰	d <sup>13</sup> iC <sub>4</sub> ‰	d <sup>13</sup> nC <sub>4</sub> ‰
488145	Production	1/23/2015	0.0696	0.277	-37.78	-176.20	0.679	973	nd	-26.46	-23.52	-23.84	-22.43
488146	Braden	1/23/2015	0.136	0.187	-36.37	-176.00	0.635	1069	0.0105	-29.85	-30.14	-28.71	-30.55
488147	Surface	1/23/2015	0.133	0.119	-36.25	-172.00	0.616	1103	0.0118	-30.69	-31.05	-29.64	-31.10

**Notes:**

nd = not detected

## FIGURES





Reference: Edman, 2007

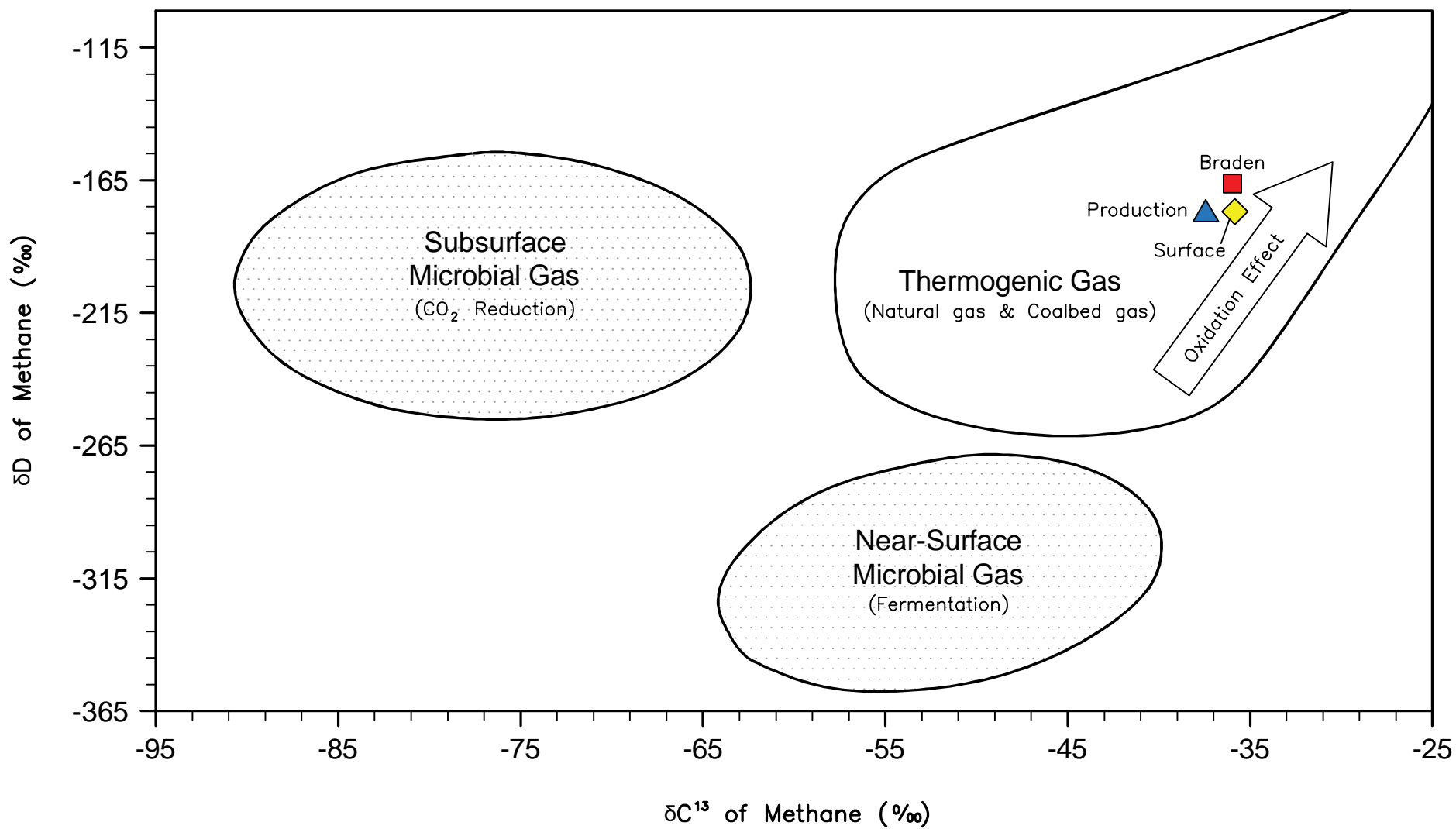
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DATE	11-9-15
SCALE	AS SHOWN
CAD NO.	240.1509.06a
PRJ NO.	240.1509.06

CROSS PLOT OF  $\delta\text{D}$  METHANE  
(DEUTERIUM ISOTOPES) VS.  $\delta^{13}\text{C}$   
METHANE (CARBON ISOTOPES) SHOWING  
FIELDS FOR BACTERIAL GAS, ASSOCIATED  
GAS, POST-MATURE DRY GAS ETC.



FIGURE

1



Reference: Coleman, 1994

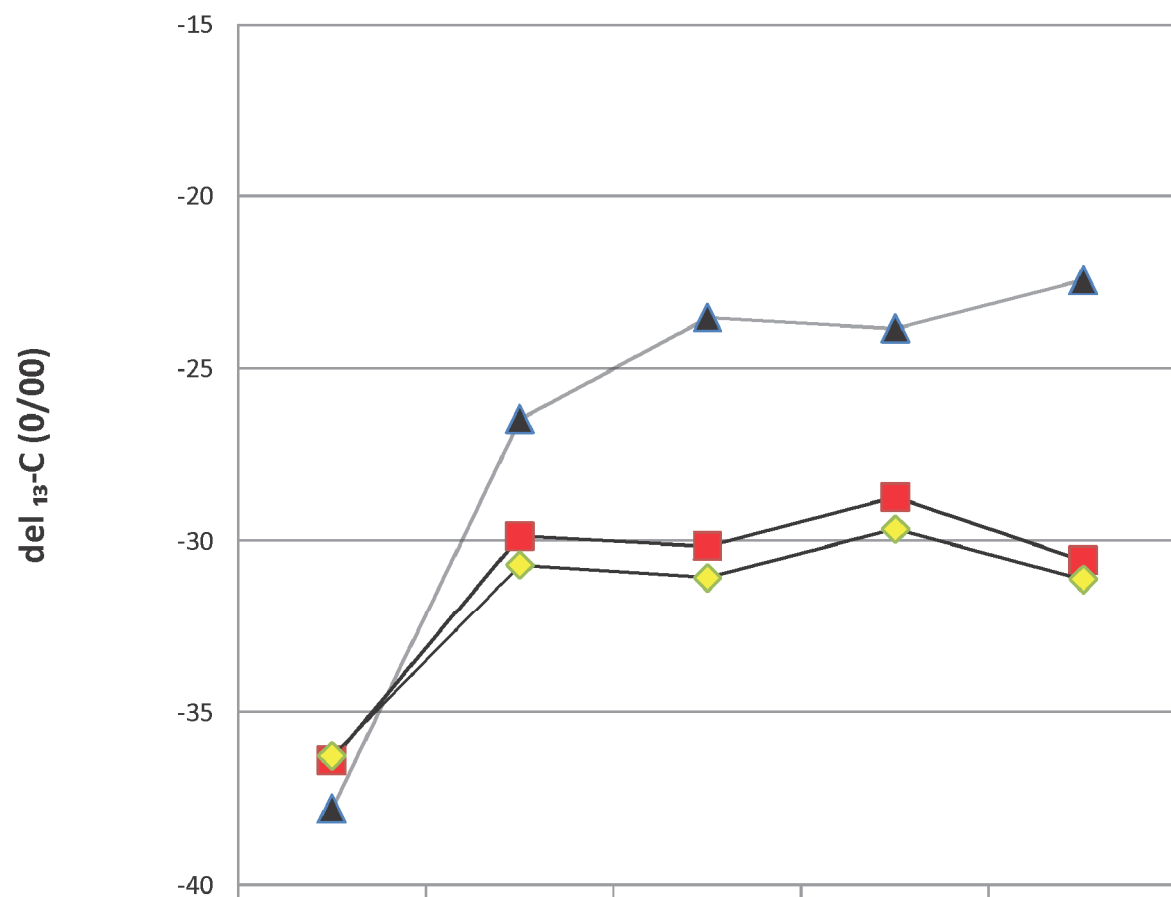
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PRJ NO.	240.1509.06

PLOT OF STABLE ISOTOPES OF CARBON AND  
HYDROGEN FOR METHANE REPORTED IN  
GAS SAMPLES COLLECTED FROM  
PAD D31 1509, NORTH PARACHUTE RANCH



FIGURE

2



**Notes:**

$d_{13}\text{-C}_1 = \delta^{13}\text{C}_1$  (methane)

$d_{13}\text{-C}_2 = \delta^{13}\text{C}_2$  (ethane)

$d_{13}\text{-C}_3 = \delta^{13}\text{C}_3$  (propane)

$d_{13}\text{-C}_4 = \delta^{13}\text{nC}_4$  (n-butane)

$d_{13}\text{-C}_4 = \delta^{13}\text{iC}_4$  (i-butane)

▲ Production	$d_{13}\text{-C}_1$	$d_{13}\text{-C}_2$	$d_{13}\text{-C}_3$	$d_{13}\text{-iC}_4$	$d_{13}\text{-nC}_4$
■ Braden	-37.78	-26.46	-23.52	-23.84	-22.43
◆ Surface	-36.37	-29.85	-30.14	-28.71	-30.55
	-36.25	-30.69	-31.05	-29.64	-31.10

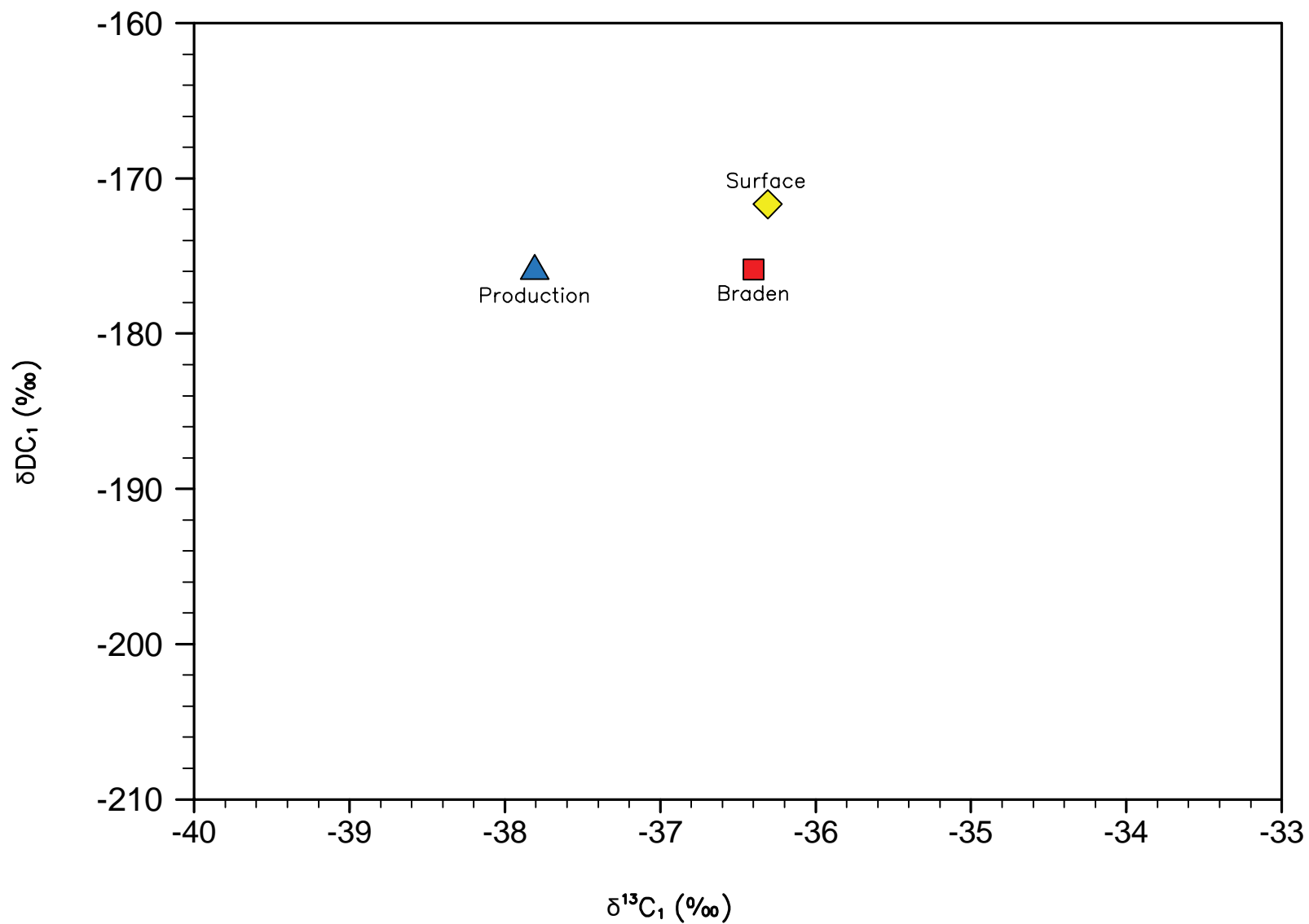
CHK BY	DN
DWN BY	OS
DATE	11-9-15
SCALE	AS SHOWN
CAD NO.	240.1509.06a
PRJ NO.	240.1509.06

PLOT OF CARBON ISOTOPES FOR SELECTED  
GASES OF SAMPLES COLLECTED FROM THE  
PAD D31 1509 SITE, NORTH PARACHUTE RANCH



FIGURE

3



CHK BY	DN
DWN BY	OS
DATE	11-9-15
SCALE	AS SHOWN
CAD NO.	240.1509.06a
PRJ NO.	240.1509.06

PLOT OF STABLE ISOTOPES OF CARBON AND  
HYDROGEN FOR METHANE REPORTED IN  
GAS SAMPLES COLLECTED FROM  
PAD D31 1509, NORTH PARACHUTE RANCH



FIGURE

4