# APPENDIX O

# GEOCHEMISTRY OF NATURAL GAS AND COALBED METHANE

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Primary gases originate from bacterial respiration (biogenic) and thermal alteration of liquid or solid organic precursors (thermogenic) (Schoell, 1983). Four values are found useful in describing variability in natural gases and deducing their origin and processes involved with their origin, including the concentration of $C_2$ through $C_5$ hydrocarbons (i.e. ethane, propane, butane, and pentane) relative to $C_1$(i.e. methane), the carbon and hydrogen isotopic composition of methane, and the carbon isotopic composition of ethane (Schoell, 1983). Additionally, the hydrogen isotope composition of methane and ethane has been found useful for distinguishing between gas sources (Whiticar, 1996).

Coalification involves a series of biochemical and geochemical reactions that transform plant material into a combustible, carbonaceous solid (Kim, 1973). Most coalbed gases are generated during the progressive burial and maturation of the coal (Scott, 1993). Samples of coal collected from various seams by Kim (1973) contained gas that was characterized by generally greater than 90% methane and 1.0-1.5% ethane, with negligible amounts of heavier gaseous hydrocarbons. Similarly, experiments conducted by Kim (1974) involving the collection of gas desorbed from coal samples revealed domination (99.5%) by methane and ethane, with only trace amounts of higher hydrocarbons. Scott (1993) reports that an average coalbed gas will contain 93.2% methane, 3.1% carbon dioxide, 2.6% wet gases (i.e. hydrocarbons $>C_1$) and 1.1% nitrogen.

Isotopes are atoms with the same number of protons but different numbers of neutrons, which results in differing atomic mass for the same element. The difference in properties between two isotopes that may lead to a slight separation in distribution (fractionation) is largely a result of the different vibrational frequencies of heavy and light atoms in a molecular or crystal structure (Krauskopf and Bird, 1995). Atoms of a light isotope vibrate with higher frequencies, hence in general are less strongly bonded to other atoms than atoms of a heavy isotope. It is assumed that migration of gases in most situations does not appreciably change the isotopic composition of the hydrocarbons (Schoell, 1983). The element Carbon includes two stable isotopes, $^{12}C$ and $^{13}C$, as well as the radioactive $^{14}C$. The element Hydrogen includes two stable isotopes, $^{1}H$ and $^{2}H$, the latter being known as Deuterium and referred to with a capital “D.” Hydrogen has a third, radioactive isotope, Tritium ($^{3}H$) with a short half-life of 12.26 years. Three mechanisms of isotope separation can be distinguished, including those depending on physical properties (such as evaporation and precipitation), exchange reactions resulting in equilibrium between two or more substances, and separation depending on reaction rates. The extent of separation between two phases is expressed by a ratio called the fractionation factor, which compares the ratio of concentrations of heavy to light isotope in one phase to the same ratio in another phase. The comparison ratio is reported in concentrations of per mil, or parts per thousand, relative to the heavier isotope. Carbon isotope ratios are expressed as δ$^{13}$C in parts per thousand (per mil or ‰) deviations from the Pee Dee Belemnite marine carbonate standard, for which the internationally accepted standard for the ratio of $^{13}$C/$^{12}$C is equal to 0.0112372. A positive value of the fractionation ratio indicates relative enrichment of the heavier isotope, whereas a negative value represents a relative depletion of the heavier isotope compared to the lighter isotope. In practice, the Peedee Belemnite has a very high $^{13}$C content, so virtually all terrestrial samples will exhibit a negative value of δ$^{13}$C‰ in comparison such that a relative enrichment will be expressed.

Natural gas is generated from organic matter throughout the burial history of sedimentary rocks. Three principal episodes of gas generation are recognized: 1) biogenic gas is formed during the early, low temperature (<60-100° C) phase of sediment burial history at shallow (< 3 km) depths, by anaerobic bacteria, characterized by isotopically light methane of δ$^{13}$C< -60‰; 2) early thermogenic gas is produced along with liquid hydrocarbons during the intermediate phase of burial history; 3) late thermogenic gas is produced during the high temperature phase of burial history, which is destructive to earlier formed liquid hydrocarbons. Jenden et al. (1993) state that at greater depths and temperatures, thermal degradation of kerogen yields thermogenic gases, in addition to hydrocarbon liquids, and that although geochemistry is strongly dependent on source rock and maturity, they are generally characterized by ethane contents greater than 1% and δ$^{13}$C values for methane of greater than -50‰. In general the amount of natural gas formed increases as a sedimentary unit progresses through the various stages of gas generation (Claypool et al., 1978; Jenden et al., 1993). The gas formed during each of these stages has a characteristic chemical composition and stable carbon isotope ratio for methane. Biogenic gas is predominantly methane that is isotopically light (δ$^{13}$C = -90 to -55‰). Methane originating during the thermal generation of petroleum is always accompanied by ethane and heavier hydrocarbons, and is isotopically heavier (δ$^{13}$C = -55 to -35‰). Data from samples compiled by Scott (1993) for the San Juan, Piceance, and Black Warrior Basins, for coal classified as high-volatile C bituminous rank, indicates δ$^{13}$C values for methane of -49.3 to -60.2‰, δD values for methane of -223 to -256‰, and δ$^{13}$C values for ethane of -29.2 to -30.8‰. Data for samples compiled by Laughrey and Baldassare (1998) for coalbed methane in the central Appalachian Basin indicate δ$^{13}$C values for methane of -39.9to -55.1‰ and values of δD for methane of -194 to -219‰.

The accident investigation team collected gas samples from UBB, another longwall mine in the Eagle seam located 14 miles away, and from separate gas wells producing from the Greenbrier Formation and Marcellus Shale within seven miles of the 1 North Panel. The hydrocarbon contents and stable isotope ratios were compared and plotted on discrimination diagrams to determine the sources of gas entering the mine, and to understand the role of gas in the geologic model. Samples from the other Eagle seam longwall mine were collected from gas feeders that were discovered on June 7, and October 25, 2010. The gas content (by mole) of the June 7 event contained 90.141% methane, 4.188% ethane, 1.496% propane, 0.838% combined butanes, 0.458% combined pentanes, 0.264% hexanes, 0.127% heptanes, and 0.203% hydrogen. The gas content from the October 25 event contained 98.27% methane, 1.23% ethane, 0.3% propane, 0.11% combined butanes, 0.03% combined pentanes, and 0.01% $C_{6+}$ hydrocarbons. Therefore, the relatively high ethane content (>4%), and presence of propane, butane, pentane, hexane, and heptane (i.e. a "wet" composition) is an indication that the floor gas represents natural gas derived from a source other than a coal seam. Plots of stable isotope values indicate that the gas was derived from a Type II kerogen, such as expected for organic-rich shale. This suggests a source in the Devonian-aged black shale such as the Marcellus/Millboro/Lower Huron. Plots of stable isotope values on discrimination diagrams developed by Jenden et al. (1993) indicate a vitrinite reflectance value of approximately 0.7-0.8% for the source rock, which is at the lower range of vitrinite reflectance reported for the Lower Huron of western West Virginia, a source of Type II kerogen.

Several samples of gas were collected at different times by MSHA, WVOMHST, and company investigators from floor feeders located behind the shield pontoons on the longwall face at shield 160 and shield 170. The immediate vicinity of the floor feeders were characterized by a distinctive smell similar to that noted at the other Eagle seam longwall mine, and registered high values of methane and CO. The samples were characterized by gas contents of 40.61% (90.15% normalized to 100% hydrocarbons) methane, 2.7% (5.99%) ethane and 1.21% (2.68%) propane, as well as 0.135% (0.3%) and 0.188% (0.41%) iso-butane and n-butane, respectively; 0.04% (0.08%) and 0.0202% (0.04%) iso-pentane and n-pentane, respectively, and; 0.018% (0.04%) hydrocarbons including or heavier than hexane. The sample also contained 0.279% hydrogen, and no CO, despite a hand-held methane detector indicating several hundred parts per million CO. These samples are chemically and isotopically very similar to those collected from the other Eagle seam longwall mine, and are representative of organic shale-derived thermogenic gas, rather than biogenic gas derived from humic coal.

Numerous samples were collected by MSHA and company investigators from small feeders emanating from the floor throughout the HG 22 and 'new' TG 22 sections. Analysis results indicate a different kind of gas than that sampled at shield 160-170 or the other Eagle seam longwall mine. In contrast to those samples, which contained significant ethane and other heavier hydrocarbons, the HG 22 and TG 22 samples were characterized by methane content of 75-78%, with only 0.01-0.02% ethane and insignificant or nondetectable contents of $C_{2+}$ hydrocarbons. Furthermore, the samples contained no hydrogen, and during the sampling process the hand-held gas detector indicated no CO. Although subsequent analyses indicated that no CO is actually present in any of the samples, a CO reading of several hundred parts per million is simply a proxy for hydrogen, which the hand-held detector is incapable of registering. These samples were also subjected to determination of stable isotope contents, and plotted on discrimination diagrams for comparison with other collected samples, where they represent a distinct and separate sample population The source of coalbed methane bubblers may be the Lower (Little) Eagle seam, based on an absence of hydrocarbons higher than methane, although isotopes suggest some mixing with a deeper thermogenic source.

A sample of Eagle seam coal was collected from the longwall face on August 31, 2010 in an aluminum desorption canister for determination of hydrocarbon content. After a prolonged period of desorption, five 15-cc test tubes of gas were obtained from the sample, and sent for analysis. Because the desorbed samples were highly diluted with air, chemical analysis indicated only 0.580% (mole) methane but failed to detect any $C_{2+}$ hydrocarbons in the sample. This is an indication that the gas is typical of coalbed methane, but may also represent that last residual gas to desorb from the coal. Nitrogen and oxygen contents were similar to expected for ambient air, at 77.55% and 20.85%, respectively. Because of the very low sample volume and high dilution, the results may not be conclusive, since ethane occurs at such a small ratio to methane even in samples of natural gas. However, stable isotope contents for methane indicated a $\delta^{13}C$ value of -61.68‰ and a δD value of -247‰, which is indicative of microbial gas. Thus, it appears that gas derived from the Eagle seam itself is different from the coalbed methane gas emanating from floor bubblers, as well as the natural gas emanating from floor fractures.

A chemical analysis was obtained from Equitable Resources for well no. 7645 (API 005-00810) developed to the Greenbrier Formation, indicating over 89% methane, 4.8% ethane, 1.7% propane, 0.3% iso-butane, 0.6% n-butane, 0.2% iso-pentane, 0.2% n-pentane, and 0.4% content of hexane and longer hydrocarbons. This composition is very similar, in terms of the presence of longer-chain hydrocarbons, to the samples collected from the floor feeders at the other Eagle seam longwall mine, and from the floor fractures at Shields 160-170.

Chemical analyses were obtained from samples of gas from two EXCO Resources wells producing from the Devonian-aged Marcellus Shale, located 6.25-7 miles ESE of the 1 North Panel face (API No.'s 4708101435 and 4708101436). Data from these samples were plotted on discrimination diagrams together with other samples collected from the mine, and are considered the basis for comparison with natural gas (Figures O-1 to O-4). The samples plot very close to those collected from the other Eagle seam longwall mine and from shields 160-170, confirming previous interpretations that those samples represent natural gas rather than coalbed methane.

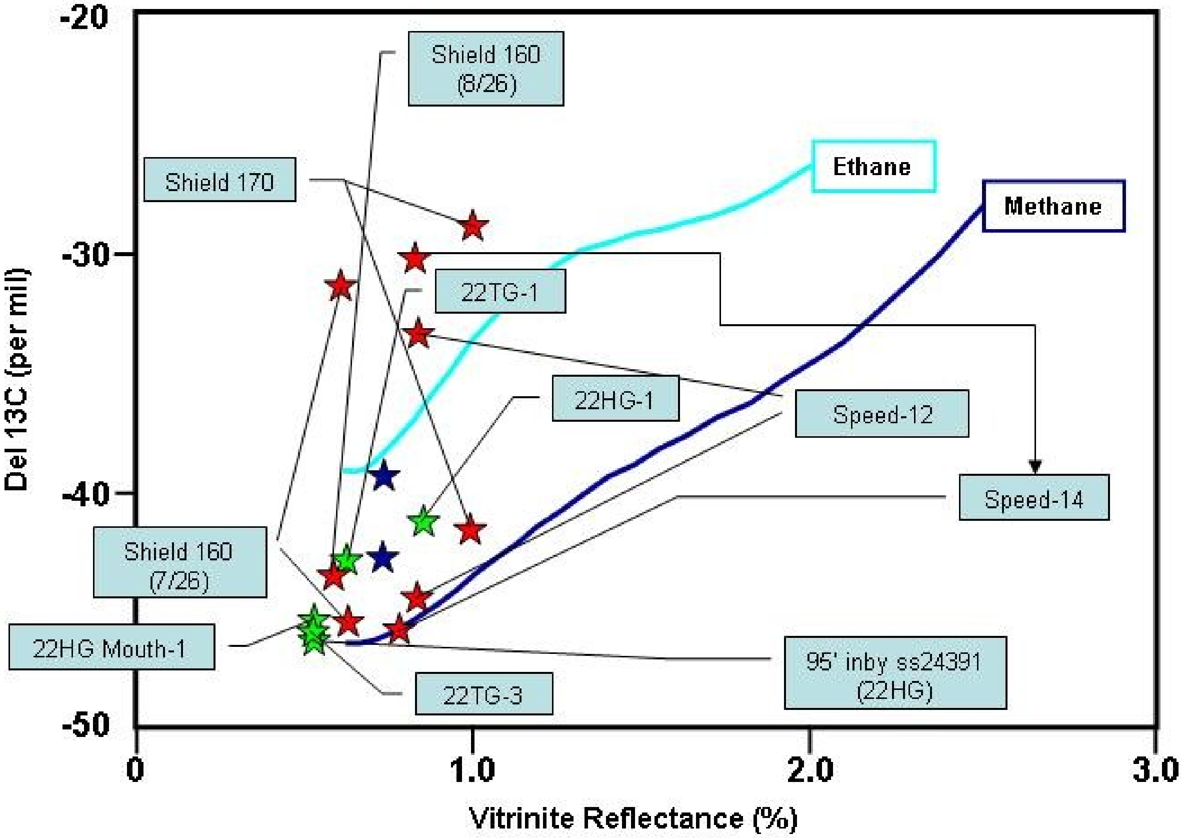

Figure O-1. Plot of collected gas samples for δ $^{13}$C for methane (‰) and ethane versus vitrinite reflectance, after Berner and Faber (1996), indicating derivation from Type II kerogen, such as expected for organic shale. Vitrinite reflectance is unknown for Marcellus Shale beneath UBB, but values of 0.8% and 0.6% for samples collected from the American Eagle Mine and UBB, respectively, are based on Figure 46. Published data for area coal seams in the southern Appalachian Basin suggest that vitrinite reflectance may be as high as 0.9%. For both samples, values lie along the curve defined for methane, but diverge significantly from the curve defined for ethane. Red stars indicate samples that contain $C_{2+}$ hydrocarbons; green stars indicate samples with little or no $C_{2+}$ hydrocarbons. Blue stars indicate composition of natural gas produced from the Marcellus Shale.

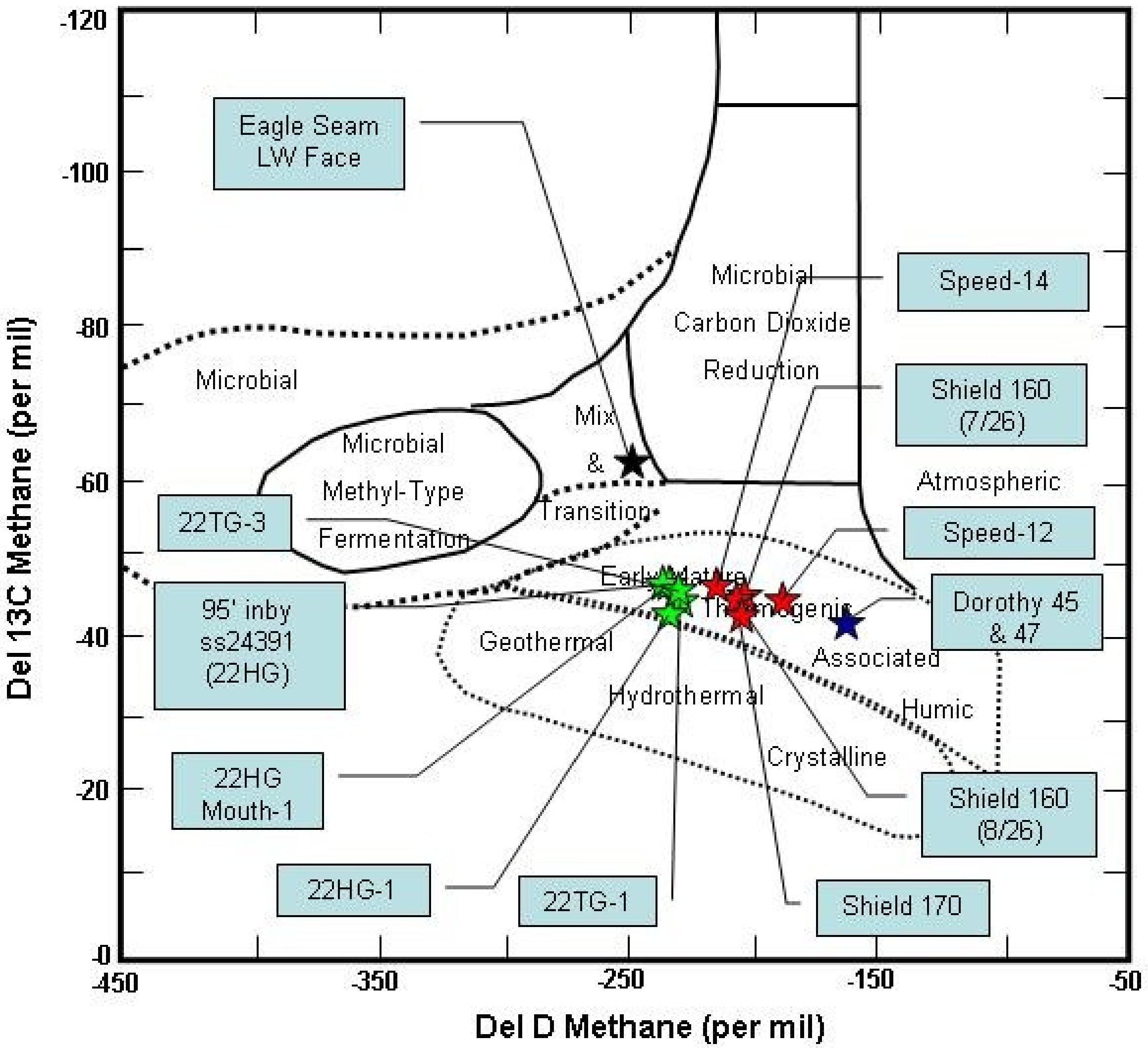

Figure O-2. Discrimination diagram from Whiticar (1996) showing gas fields based on plotting δ $^{13}$C for methane (‰) versus δ D for methane (‰). Red stars indicate samples that contain $C_{2+}$ hydrocarbons; green stars indicate samples with little or no $C_{2+}$ hydrocarbons. Blue star indicates samples that were obtained from the Dorothy 45 and Dorothy 47 wells, which produce natural gas from the Marcellus Shale.

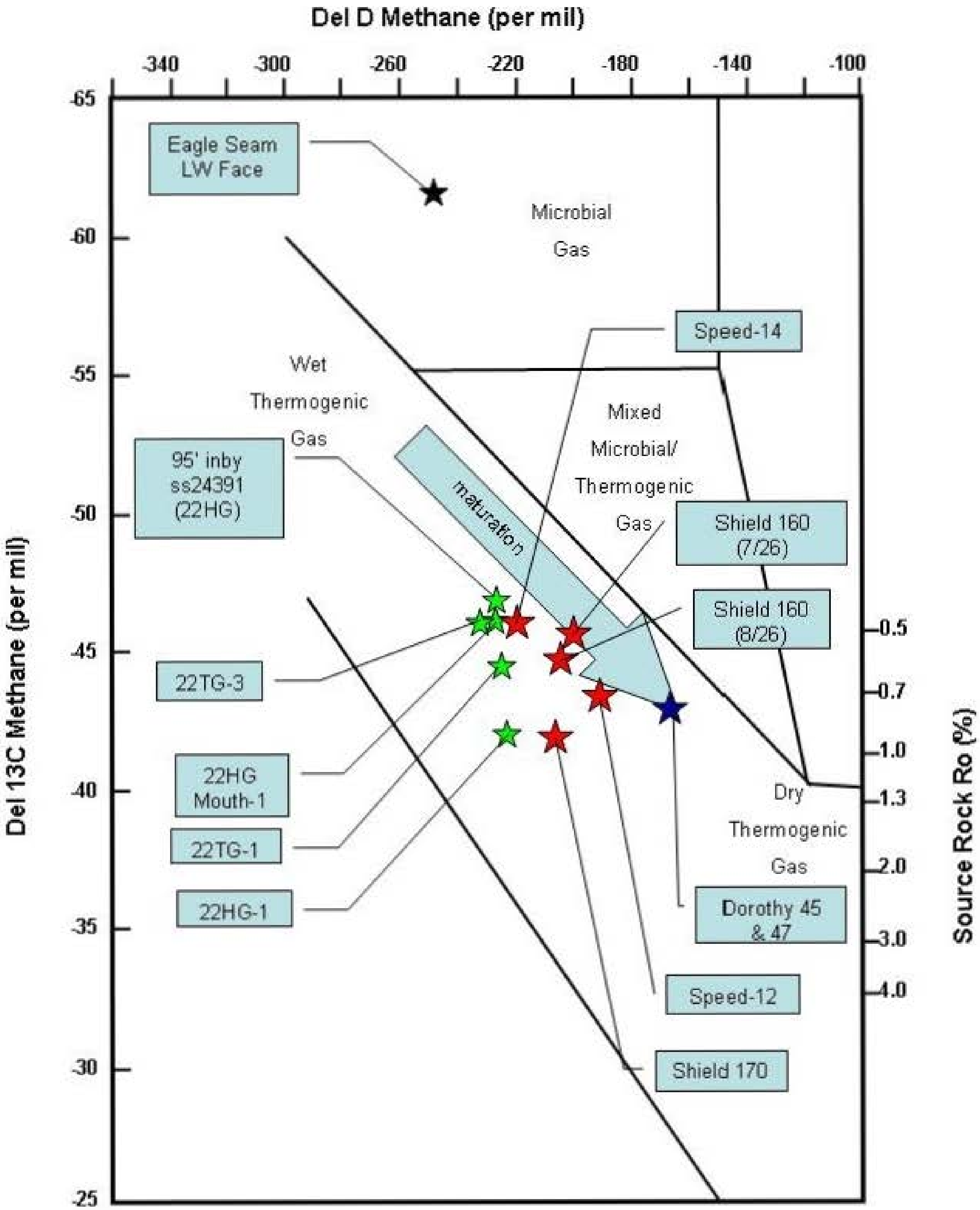

Figure O-3. Discrimination diagram after Jenden et al. (1993) showing fields of microbial and thermogenic gas based on plotting values of δ $^{13}$C for methane (‰) and δ D for methane (‰). Values for vitrinite reflectance are shown for comparison. Red stars indicate samples that contain $C_{2+}$ hydrocarbons; green stars indicate samples with little or no $C_{2+}$ hydrocarbons. Blue star indicates samples that were obtained from the Dorothy 45 and Dorothy 47 wells, which produce natural gas from the Marcellus Shale.

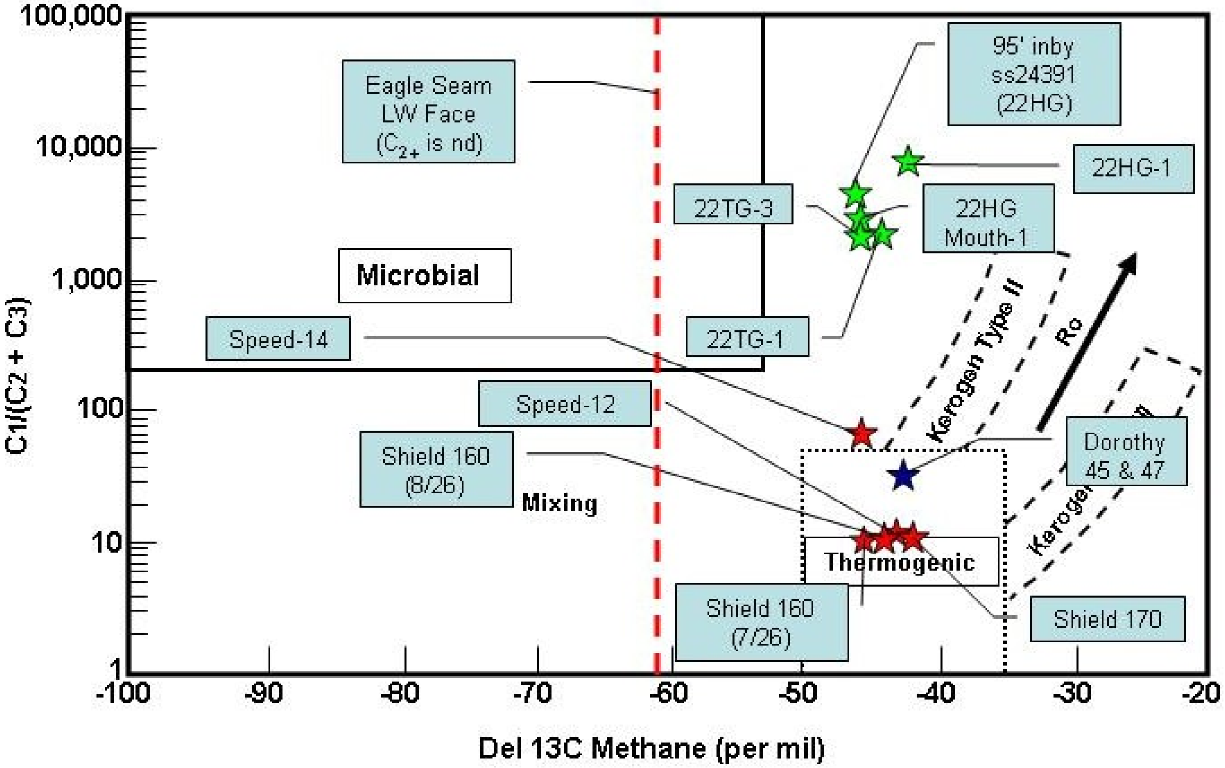

Figure O-4. Discrimination diagram showing fields of gas from microbial and thermogenic sources, based on comparison of $C_1$, $C_2$, and $C_3$ hydrocarbons (ratio of methane to combined ethane and propane), compared to $\delta^{13}C$ for methane (‰). Diagram modified from Whiticar, 1996). Red stars indicate samples that contain $C_{2+}$ hydrocarbons; green stars indicate samples with little or no $C_{2+}$ hydrocarbons. Blue star represents samples obtained from the Dorothy 45 and Dorothy 47 wells, which produce natural gas from the Marcellus Shale.

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# APPENDIX P

# RECONSTRUCTION OF VENTILATION MAP

CAN BE FOUND IN THE BACK OF THE BINDER