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Oil-Source Rock Correlation in the Late Paleozoic,
Denver Basin, Nebraska -The Search for a Negative $\delta^{13}\text{C}$
Anomaly in Pennsylvanian-Permian Cyclothems

By

John P. Still

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Oil-Source Rock Correlation in the Late Paleozoic, Denver Basin, Nebraska -The Search for a Negative $\delta^{13}\text{C}$ Anomaly in Pennsylvanian-Permian Cyclothems

John P. Still, M.S.

University of Nebraska, 2013

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Late Paleozoic sedimentation in the Denver basin occurred in two environmentally distinct depocenters. The northern-most Alliance Basin has been interpreted to have a restricted character: anhydrite-bearing mudstones are present in cyclothems comprising wackestone, packstone and mudstone. The source of petroleum produced from these intervals is considered to be organic-rich units within these cyclothems. Oil recovered from late Paleozoic reservoirs has $\delta^{13}\text{C}$ values that range from -30.8‰ to -28.8‰: values that are lower than those reported previously for prospective source rocks from this interval. Cores from seven wells that penetrate upper Pennsylvanian to lower Permian rocks have been chosen for analysis. The top unit in many of these cyclothems consists of thin (~1 ft) organic-rich marlstone, mudstone or microbial laminites. Geophysical log correlation is used to identify rocks that have not been tested previously as potential sources for the petroleum recovered from Paleozoic

reservoirs. Facies relationships indicate that these rocks were deposited in a hypersaline environment. Burial history plots show that these intervals were subjected to subsurface conditions conducive to the release of hydrocarbons. Analysis of kerogen samples reveals $\delta^{13}\text{C}$ values that are lower than seen in prior work. Two anomalies are noted (Pennsylvanian and Missourian) that contain prospective source rocks with $\delta^{13}\text{C}$ values approaching -31.0‰. Burial history, TOC values, lithologic relationships and $\delta^{13}\text{C}$ data all indicate that organic-rich strata deposited during the two negative $\delta^{13}\text{C}$ anomalies are the sources for some of the Paleozoic oils.

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1. Introduction

Although the Denver basin (Figure 1) is a mature petroleum province, the source of some of the oils produced from Paleozoic reservoirs remains enigmatic. This study tests the hypothesis that microbial laminite, mudstone, and marlstone within Pennsylvanian and Permian cyclic sedimentary rocks are the sources for some of these oils.

Oils produced from Paleozoic reservoirs in the northern Denver basin (northeastern Colorado and southwestern Nebraska; Figure 1) have been grouped into two families based on their geochemical characteristics (Clayton et al., 1987; Sulistyo, 1994). The first group of oils is produced from the Lyons Sandstone, Missourian Group, Cherokee Group and Marmaton Group. These oils have pristane:phytane ratios less than 1.0, abundant branched alkanes and aryl isoprenoids (Clayton et al., 1992), exhibit a predominance of even-number n-alkanes over odd-numbered n-alkanes in the C₂₂ to C₃₂ fraction (Clayton et al., 1987) and contain abundant gammacerane (Sulistyo, 1994). This family of oils is interpreted to have been derived from source rocks deposited in a hypersaline environment. The second group of oils is produced from the Virgil, Admire, Wykert and Morrow Groups. These oils have pristane:phytane ratios that exceed unity and a higher concentration of n-alkanes relative to the abundance of branched and cyclic alkanes.

Gilleland (2011) interpreted the late Paleozoic depositional environment in the northern Denver basin (Figure 1) as a shallowly-dipping carbonate ramp with successive

sub-, intra- and supratidal facies. The Pennsylvanian and Permian strata were deposited as a succession of upward-shallowing cycles in a climate that became more arid through time (Gilleland, 2011). Organic-rich rocks from hypersaline facies in these cyclothems have been postulated to be the source for some Paleozoic oils (Clayton, 1989; Clayton and Swetland, 1977; Clayton et al., 1987; Clayton et al. 1992; Sulistyo, 1994). No source interval, however, has been clearly identified.

Although most production in the Denver basin is derived from Cretaceous reservoirs [1.05 BBO and 3.67 TCFG (Higley and Cox, 2007)], Paleozoic plays still represent attractive targets [Pierce Field – 11.5 MMBO; Black Hollow Field – 10.8 MMBO (Higley and Cox, 2007)]. In order to fully evaluate the hydrocarbon potential of Paleozoic reservoirs, it is necessary to understand the processes that controlled the distribution of oil. Accurate identification of a source helps to characterize the behavior of the petroleum system and predict the location of future prospects charged by that source.

This study examines oil and core samples from the Pennsylvanian and Permian on the eastern slope of the northern Denver basin. An existing framework will be used to interpret the stratigraphy in the study area and to inform correlation of wells. Carbon isotope geochemistry will be utilized as the primary tool to correlate oils to potential source rocks. Carbon isotope geochemistry is among the most powerful tools for oil-source rock correlation in this environment. The oils examined to date have relatively restricted $\delta^{13}\text{C}$ values, whereas the $\delta^{13}\text{C}$ values obtained from kerogen, have been quite variable (-30.5‰ to -22.6‰) (Figure 2). Primary $\delta^{13}\text{C}$ values of organic matter reflect, in

large part, global atmospheric CO₂ levels and $\delta^{13}\text{C}$ values (Hayes et. al., 1999), but local environmental conditions also play a role in regulating $\delta^{13}\text{C}$ values. The fractionation of carbon isotopes during petroleum generation is small and the amount of carbon in the expelled oil relative to the kerogen remaining in the rock is also small. Oils therefore, will have $\delta^{13}\text{C}$ values that are similar to the kerogen in their respective source rocks. Attempts to identify a source that has the level of ^{12}C enrichment seen in many of the oils recovered from Paleozoic reservoirs has been unsuccessful. This situation may exist because of the presence of significant variations in the $\delta^{13}\text{C}$ value of organic matter over short stratigraphic intervals. This thesis is an attempt to search for such $\delta^{13}\text{C}$ anomalies.

2. Geologic Setting

The Denver basin is an asymmetric cratonic foreland basin that spans an area of 155,000 km² (Tainter, 1984) (Figure 1). It extends north into Wyoming, covers much of the Colorado and thins into western Nebraska. A combination of early and late Paleozoic positive structures controlled the basin boundaries (McCoy III, 1953). These include the Cambridge and Chadron Arches to the northeast; the Hartville uplift, Laramie and Front Ranges along the west; and the Las Animas Arch, Sierra Grande and Apishipa Uplifts in the south (Martin, 1965) (Figure 3). Two depocenters, referred to as the Alliance and Sterling sub-basins, formed during the Pennsylvanian. These sub-basins were separated by the Transcontinental Arch (Montgomery et al., 1998), which created a barrier shoal complex. The northern Alliance sub-basin developed a restricted environment, whereas

the southern Sterling sub-basin experienced an open marine shelf environment (Garfield et al., 1988). This study focuses on the northern Alliance basin.

The stratigraphy of the late Paleozoic in the Denver basin is summarized in Figure 4. Pre-Pennsylvanian deposition was restricted to a narrow belt of sediment from southeast to west-central Colorado, controlled by the Siouxia and Sierra Grande uplifts (McCoy III, 1953) (Figure 3). Deposition of Pennsylvanian carbonates began with the transgression of Morrowan seas from the Anadarko basin. Near the basin axis, these carbonates interfinger with clastic sediment from the west (derived from erosion of the growing Ancestral Rocky Mountains) (Garfield et al., 1988; Martin, 1965). Permian strata comprise cyclic carbonates and evaporites deposited in response to fluctuating sea level (Goolsby and Goolsby, 1994), but with the addition of clastic rocks in the east rather than the west. Triassic sedimentation was characterized by fluvial deposition. The rocks deposited by these rivers are absent in much of the eastern limb of the basin. Jurassic strata reflected a greater marine influence and are continuous across the basin (Martin, 1965). Seas again invaded the basin during the Cretaceous. Rock deposited in this era comprises ~60% of the present basin fill (Miller, 1963).

3. Stratigraphic Context

A stratigraphic analysis of the intervals of interest was performed to inform sample selection. This is important because variations in $\delta^{13}\text{C}$ typically occur over narrow stratigraphic intervals. Two important previous works are by Gilleland (2011) and

Sulistyo (1994). The description of cyclothems in this area (Gilleland, 2011) provides the framework for assignment of depositional environments and systems tracts that would most likely preserve petroleum source rocks. Sulistyo (1994) geochemically evaluated late Paleozoic strata for source rock potential. Aided by wells used in Sulistyo (1994), potential source intervals examined in this study can be compared stratigraphically with samples from previous workers.

3.1. Lithostratigraphy

Gilleland (2011) identified nine shallowing upward cycles in the Virgilian and Wolfcampian through the use of well logs, core, thin sections and biostratigraphic data. Although the cycles vary from well to well, the base of each cycle comprises wackestone or packstone, whereas the uppermost units in each cycle are anhydrite, microbial laminite or red to green siltstones interpreted to be a paleosol (Gilleland, 2011) with very little siliciclastic input (Montgomery et al., 1998) (Figure 5). Progressing up the depositional cycle, the concentration of allochems decreases, and evaporitic minerals representative of the supratidal environment, increase (Gilleland, 2011).

Cores used in this study have been resolved into cycles based on facies relationships. Rocks interpreted to be prospective sources occur in association with anhydrite or are microbial laminites. The association of lithologies in which most prospective source rocks occur is overlain by wackestone and packstone; units with a higher concentration of allochems. An example of the use of this relationship to identify a

cycle transition is observed in Figure 6. The juxtaposition of wackestone on anhydritic mudstone is considered to be evidence for a rapid transgression (beginning a new cycle). Transgressive deposits are often absent in this part of the basin, presumably because sea level rise was often rapid (Gilleland, 2011).

Graphic logs from all available cores are plotted together in Figure 7. The lowermost interval in the Brauer 14-1, Livingston 1-33, Mathewson 1-20, Pahl 3 and Beyer 1 wells was not cored. Based on lithologies observed in the Michaels 1 and Bird 4-1 wells, coupled with well log response, the missing interval was interpreted to contain the deeper-water facies (wackestone and packstone). The thickness of anhydrite beds increases in younger parts of the section, particularly the Admire (Figure 7). This observation is consistent with the findings of previous workers (Gilleland, 2011; Montgomery et al, 1998; Olszewski and Patzkowsky, 2003) in which the thickening of evaporitic facies is attributed to increasing aridity and a shift from an open marine environment to a restricted environment through time.

Intervals sampled in this study are denoted by red circles (Figure 7). These samples provide good coverage temporally from the lowermost Wolfcampian to the uppermost Missourian, with the exception of the lower Virgilian.

Rock samples described as intertidal, microbial laminites and marlstone with high organic matter contents (Table 1) occur at the top of cycles when water depths were minimized and when environmental conditions facilitated the deposition and preservation of organic matter. Seawater salinity would have increased as sediment accumulated and water depth decreased in this restricted part of the basin. Hypersaline environments are

considered to have restricted biota and limited grazing fauna (Kerker, 2004); these conditions would allow microbial mats to flourish. Organic matter derived from these microbes would then have accumulated in greater concentrations. Black shales, representing deposition in the deepest relative water depths, are rarer than other potential source rock lithologies, as sea level rise was not substantial enough for their deposition in many sequences. These black shales, when they do occur, are at the bottommost part of a cyclothem following a rapid transgression.

3.2. Geophysical Log Correlation

All wells in this study area are correlated in a South to North direction using well logs (Figure 8). Correlations are made based on the responses of the gamma ray and deep vs. shallow resistivity tools. Formation tops from the Nebraska Oil and Gas Conservation Commission were considered during correlation but were not used as absolute datums.

Three cross sections were produced utilizing wells sampled by Sulistyo (1994) along with wells examined in this study (Figure 9). These cross sections were generated in order to place the previous sampling from this region into the modern stratigraphic framework and to correlate data published previously, with those samples collected in this study. After correlating wells from this study to wells from previous work, horizons containing potential source rocks were cross referenced to identify duplicates. Figure 10 shows wells used in this study that exhibit lateral equivalents in samples from Sulistyo (1994). The 32-9 Spear Diamond Ranch well was chosen because it has the most

continuous coverage in samples through the Pennsylvanian and Permian and has the greatest number of samples. This exercise establishes that there are only seven samples from this study which may be from similar stratigraphic horizons as those of the 32-9 Spear Diamond Ranch well.

4. Burial History

The burial history of the sediments from the study area was reconstructed (Figure 11). The isotherms, compaction factors and time-temperature indices were calculated by Higley and Cox (2007) using Cretaceous data from the G.W. Steiber Unit No. 1 well. The depth and thickness of the Paleozoic Lyons Sandstone was added using the Pierce Unit No. 3 well. The Pierce Unit No. 3 well is within half a degree latitude of the G.W. Steiber Unit No. 1 well. A constant geothermal gradient of 2.55 F°/100-foot burial depth is assumed as fluid movement transported heat upward and created a geothermal hot spot in this area (Meyer and McGee, 1985). The diagram includes an estimate of 1,400 feet of deposition and erosion of Tertiary sediments (Higley and Cox, 2007).

The burial history diagram (Figure 11) does not account for compaction of the Paleozoic Lyons Sandstone. The lithology of the unit is medium-grained, well-sorted quartz sandstone (Nering, 1963). The well-sorted nature will limit compaction as quartz grains are undeformable under most conditions and little input from ductile rock fragments is observed (Blatt et al., 1980). Because the grain size is medium sand, compaction from fracture closure will be minimal due to lesser stress per grain contact

than coarser-grained rock (Bjørlykke et al., 2009). It is assumed therefore, that the compaction rate is negligible for the Lyons Sandstone and observed thickness at depth is projected through time.

The major increase in depth at Point “A” is caused by rapid deposition of sediment during the Cretaceous and the uplift at Point “B” represents the final adjustments of the Laramide Orogeny during the Tertiary (McCoy III, 1953).

Hydrocarbon generation is both a time and temperature dependent process (Waples, 1980). The standard values of Time-Temperature Indices (TTI) for the onset, peak and end of oil generation (Lopatin, 1971) are used. TTI of 15 represents the onset of oil generation and 160 marks the passage into the wet gas window. The Wolfcampian Lyons Sandstone entered the oil window at about 70 million years ago and passed through to the wet gas window at 40 million years ago. Although wells in this area do not reach the rest of the upper Paleozoic (targeting the Lyons Sandstone), samples from this study are situated stratigraphically adjacent to the confirmed Lyons Sandstone. The TTI model therefore, supports the interpretation that source rocks present in the Pennsylvanian and Permian were subjected to burial conditions sufficient for generating hydrocarbons.

5. Analytical Methods

Cores used in this study penetrate Pennsylvanian or Permian strata and are located within the Nebraska portion of the Denver basin. All available cores from wells that met these requirements were examined for the presence of dark marlstone, mudstone or microbial laminites that could be potential source rocks. Cores from seven wells were examined (Beyer 1, Bird 4-1, Brauer 14-1, Livingston 1-33, Mathewson 1-20, Michaels 1 and Pahl 3).

Core was sampled using a hand-powered rock splitter. After each split, the faces of the splitter were washed with water and rinsed with acetone to remove soluble and particulate organic matter. Lengths of core were then broken into smaller intervals to provide a finer resolution for testing. Those intervals were powdered using an Angstrom mill, producing 59 samples from seven wells (Table 1). The mill and puck were cleaned with fine sand and washed with water and acetone between each run. All samples were stored in new glass jars. Various analyses require different compositions of material to be sampled. Samples for elemental analysis were prepared by:

- 1) One gram aliquots of powdered rock were removed from the total sample
- 2) The spatulas used in partitioning the samples were cleaned using acetone after each use.
- 3) These aliquots of sample were sent to the School of Biological Sciences at the University of Nebraska-Lincoln.

Analyses were performed by Cathleen McFadden using dry combustion GC analysis on a Costech ECS 4010 Elemental Analyzer. The precision of results from elemental analysis are reported to one tenth of one percent for carbon and one thousandth of one percent for nitrogen.

Kerogen samples for isotope analysis were prepared in a 9 step process:

- 1) Solvent-soluble organic matter was extracted from the total sample using a Soxhlet apparatus. All components were first washed with methanol (Fisher HPLC grade) and dichloromethane (Fisher pesticide grade).
- 2) Cellulose extraction thimbles were cleaned in the Soxhlet apparatus during an 18 hour dichloromethane reflux.
- 3) The powdered rock was extracted overnight with dichloromethane to recover the solvent-soluble organic matter.
- 4) The dichloromethane was then evaporated from the solvent-soluble organic matter using a Büchi RE 111 Rotovapor coupled with a Büchi 461 Water Bath.
- 5) The resultant bitumen was refrigerated in solvent-washed glass containers with PFTE-lined lids to prevent bacterial degradation.
- 6) Inorganic carbon was removed from the extracted rock by reaction with hydrochloric acid (6 N).
- 7) The hydrochloric acid was then removed by vacuum filtration and rinsing of the filtered residue with three aliquots (40 ml each) of deionized water.

- 8) The aliphatic fraction of the oil samples and carbonate-free residue of the extracted rock samples were sent to the Keck Paleoenvironmental & Environmental Stable Isotope Laboratory at the University of Kansas for $\delta^{13}\text{C}$ analysis. The carbonate-free residue consisted of material that was insoluble in organic solvents and HCl and thus was a mixture of kerogen and silicate minerals.
- 9) Samples were combusted at 1800°C in a Costech ECS 4010 Elemental Analyzer and resultant CO and CO₂ were detected and measured on a MAT253 Isotope Ratio Mass Spectrometer. Combustion of the mixture of kerogen and silicates should yield carbon dioxide from the kerogen, thus, those data are referred to hereafter as kerogen $\delta^{13}\text{C}$ values. The precision of $\delta^{13}\text{C}$ is reported at 1 part per 10,000.

Carbon isotope data were retrieved from 30 kerogen samples and the aliphatic fraction of 11 oil samples. Stable carbon isotopes of the kerogen and oil samples are presented in the standard delta notation relative to VPDB:

$$\delta^{13}\text{C}_{\text{VPDB}}(\text{‰}) = 1000 \left\{ \left[\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{SAMPLE}} / \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}} \right] - 1 \right\} \quad \text{Eq.1}$$

6. Results

The $\delta^{13}\text{C}$ values of the kerogen samples range from -22.6‰ to -30.5‰ (Table 2) with a mode at < -30.0 ‰. These $\delta^{13}\text{C}$ values are among the lowest reported from kerogen in this part of the Denver basin. The $\delta^{13}\text{C}$ values of oil samples range from -28.3‰ to -30.9‰ (Table 2). These values are consistent with $\delta^{13}\text{C}$ values that have been obtained previously from oils produced from Paleozoic reservoirs (Clayton et al., 1987; Sulistyo, 1994) (Figure 2).

If the $\delta^{13}\text{C}$ values of the kerogen are projected to a single well, the variation in the kerogen $\delta^{13}\text{C}$ values as a function of stratigraphic position can be examined (Figure 12). The Michaels 1 well was chosen for this purpose as it is located centrally with respect to the other wells in this study and because the gamma ray and resistivity responses can be correlated easily to all other wells in this study. Two intervals have $\delta^{13}\text{C}$ values that are significantly lower than the rest of the section. These two negative $\delta^{13}\text{C}$ anomalies are denoted by rocks with $\delta^{13}\text{C}$ values that more closely approximate those obtained from many of the oil samples from Paleozoic reservoirs.

The total organic carbon (TOC) concentrations reported here reflect the organic carbon of both kerogen and the solvent-soluble fractions. Total inorganic carbon (TIC) concentrations were obtained by comparing mass before and after dissolution. TOC concentrations range from 0.2% to 28.2% by weight (Table 2). Exceedingly high TOC values (28.2% and 27.9%) were obtained from the Livingston 1-33 6641'1" and Pahl 3 6383'5" samples, respectively. These two samples also display some of the lowest values

of total inorganic carbon (1.7% and 2.4%). The TOC values measured on the kerogen-silicate residues were 34.5% and 30.9%, respectively. These values are evidence that the organic matter in these samples consists largely of kerogen and are not predominantly migrated oil. The $\delta^{13}\text{C}$ values of these two samples are -27.4‰ and -27.2‰, respectively: more positive than the values observed in the strongest Paleozoic kerogen negative $\delta^{13}\text{C}$ anomalies.

TOC values are projected stratigraphically to the Michaels 1 well log (Figure 13). All samples have total organic carbon values above an arbitrary 1% by weight threshold for the expulsion of hydrocarbons (Jones, 1984) with the exception of two samples from the Pahl 3 well (0.2%). If a >1.5% threshold is used, only two other samples have insufficient TOC concentrations. The average value for the 59 samples is 4.6% total organic carbon.

7. Discussion

7.1. Elemental Analysis

TOC concentrations display distinctive patterns as a function of depositional environment. Compared to the average TOC concentration from all the samples (4.6%), black shales (deepest water) contain above average TOC (8.8%) (Table 2). Marlstones average 3.0% TOC and microbial laminites average 3.9% TOC (Table 2). Although the values for marlstones and microbial laminites are below the average TOC for all the

samples, when evaluated with regards to hydrocarbon generation, TOC concentrations are well above an accepted organic richness ($>1.0\%$) to be productive source rocks.

The black shale rock samples (Table 1) are interpreted to be deep water deposits from brief periods of more pronounced inundation. These rocks represent the very bottom of a new cycle of deposition and are analogous of the core shales in the “Kansas-type cyclothem” of the Midcontinent (Heckel, 1986). The high TOC concentrations observed in black shales from this study are consistent with those of other core shales from Midcontinent cyclothems (Algeo and Maynard, 2004). Core shales typical of the Kansas-type cyclothem are not widely recognized in the northern Denver basin (Gilleland, 2011). Very thin black shales observed in this study are deposited during “major cycles” (Heckel, 1986), where the transgressive phase was substantial enough for deep-water shale deposition. These black shales are often thin; they represent a short segment of the depositional system [$\sim \leq 10^5$ years (Heckel, 1986; Watney et al., 1989).

Nearly all samples from this study contain a very high concentration of TOC (4.6% by weight on average) (Table 2). The beds from which these samples were obtained, however, are all less than 2.0 feet thick and average 1.0 foot. Significant amounts of oil can be generated from thin beds that have very high TOC values. This relationship is a component of “The Charge Equation” where TOC is multiplied by area and thickness, along with other factors, to achieve a value of hydrocarbon generation (Cornford, 2000). If thickness is low, total hydrocarbon generation can still be high as long as TOC content is also high. The very high concentrations of TOC observed in rock

samples from the Denver basin suggests that thin units could have produced significant amounts of hydrocarbons.

Black shales that have been interpreted as productive source rocks in the northern Denver and Powder River basins (Clayton et al., 1992) are only 0.5 m thick. Clayton et al. (1992) suggests that slow rates of sedimentation created favorable conditions for sulfate reducers. These conditions provided for high preservation of organic matter in a thin interval of rock. Although sample beds from this study are thin (~0.5 to 2.0 feet), previous workers concluded that such intervals exhibit very high TOC preservation, thus, the necessary characteristics for petroleum generation.

Carbon/Nitrogen ratios (C/N) are useful in that they examine bulk properties and represent the entire organic fraction. Biomarker molecules on the other hand, yield very precise information but are representative of a very small fraction of the total mixture. Nitrogen occurs in amino acids in organic matter and is selectively altered more readily than refractory molecules. Algal-derived organic matter contains a higher concentration of nitrogen-bearing compounds than plant-derived organic matter. This distinction is attributed to the absence of cellulose in algae and the abundance in vascular plants (Premuzic et al., 1982). After synthesizing, the nitrogen-bearing organic matter will be consumed at faster rates than other organic compounds, driving C/N ratios up (Meyers, 1994). Although many mechanisms effectively change the C/N ratio after synthesis, relative comparison of rock type with C/N ratio can be useful (Figure 14).

Black shales from this study have the lowest C/N ratios (Figure 14). This supports the conclusion that the organic matter in these rocks is primarily algal and deposited in the deepest water, far from coastal sources of terrestrial organic matter. Microbial laminites have C/N ratios that are slightly higher and marlstone C/N ratios vary greatly (~100 to 600) (Figure 14; Table 2).

Two samples show extremely high TOC concentrations (Livingston 1-33, 6641'1" = 28.2%; Pahl 3, 6383'5" = 27.9%) (Table 2). These samples are both black shales. Despite the very high TOC concentration, the percent nitrogen is also very high (0.427% and 0.517%, respectively) keeping the C/N ratio relatively low (Table 2), suggesting an algal source of organic matter and deep water deposition.

7.2. Geochemistry

The oils analyzed herein are of two distinct varieties (Clayton et al., 1987). The first family has pristane (2,6,10,14-tetramethylpentadecane) to phytane (2,6,10,14-tetramethylhexadecane) ratios approaching 1.5. There is a relatively low abundance of branched and cyclic alkanes and Pr/nC₁₇:Ph/nC₁₈ ratios that are slightly greater than one. Pristane and phytane are created by the reaction of phytol with differing environments. Phytanic acid (derived from a side chain in chlorophylls) decarboxylates to form pristane in oxidizing conditions (Peters et al., 2005). Under reducing conditions on the other hand; the carboxylic acid functional group is reduced and phytane is generated after sufficient dehydration (Peters et al., 2005). The low concentration of isoalkanes is an indicator of

minimal biodegradation and the absence of organisms that require a higher salinity (Jones et al., 2008). These characteristics type these oils as having some organic matter contribution from higher land plants (Peters et al., 2005).

The second family has pristane to phytane ratios that are less than one, abundant branched and cyclic alkanes relative to n-alkanes and Pr/nC₁₇:Ph/nC₁₈ ratios that are less than one. The low pristane to phytane ratio suggests a reducing environment and the relative abundance of isoalkanes indicates the presence of organisms that have adapted to specific salinity and nutrient conditions during deposition (Schreiber et al., 2001). There is a strong even over odd predominance in response intensity over the C₂₂ to C₃₂ fraction, which is considered to be evidence for a source rock deposited in a hypersaline environment (Clayton et al., 1992; Kettler, 2011-Personal Communication; Schreiber et al., 2001). The R₂₂ values,

$$R_{22} = \frac{2 \times nC_{22}}{nC_{21} + nC_{23}} \quad \text{Eq. 2}$$

for these samples are greater than 1.0. These R₂₂ values are evidence that oil was derived from organic matter deposited in a hypersaline environment (ten Haven et al., 1985).

The Aloha Mula 1, Aloha Mula 9, Black Hollow and Pierce Lyons oils in the second family contain significant amounts of aryl isoprenoids. These aryl isoprenoids have been linked with the presence of green sulfur bacteria (Summons and Powell, 1987). This explains the high TOC concentrations (average 4.6%) (Table 2); green sulfur

bacteria can contribute appreciable amounts of organic matter in a short period (Takahashi and Ichimura, 1968). Green sulfur bacteria are photoautotrophic obligate anaerobes that require saline waters and abundant sunlight (Vila et al., 2002). These organisms fix carbon by anoxygenic photosynthesis, using reduced sulfur compounds (Overmann and Garcia-Pichel, 2013). All of these observations are consistent with the conclusion that source rocks from the second family of oils were deposited in a restricted setting under reducing conditions.

The preservation of the organic matter is enhanced by stratification of the brines in the area of deposition, much like the circumstances in the present day Arabian Gulf (Butler, 1969). Sulistyo (1994) noted the presence of the compound gammacerane ($C_{30}H_{52}$ pentacyclic triterpane) in nearly all oil samples. Gammacerane is derived from bacterivorous ciliates which feed, in part, on green sulfur bacteria (Sinninghe Damsté et al., 1995). Anaerobic ciliates live at or below the chemocline. Ciliates will biosynthesize tetrahymanol only if their diet is deprived of sterols. Upon diagenesis, gammacerane is released through selective cleavages of C-S bonds within the tetrahymanol. The presence of gammacerane is, therefore, considered to be evidence of water column stratification. The presence of obligate anaerobes suggests stratification in the water column during deposition and would provide an environment (anoxic and reducing conditions) in which organic matter can be preserved.

7.3. Stable Carbon Isotopes

The $\delta^{13}\text{C}$ value of organic matter changes in response to the overall global carbon cycle as it exchanges between sources and sinks, creating a quasi-steady-state system (Sharp, 2007). However, variations in $\delta^{13}\text{C}$ may also occur on a local scale and be the result of diagenesis (Houghton, 2007).

Kerogen $\delta^{13}\text{C}$ values are all plotted together on the Michaels 1 well log according to their stratigraphic horizons (Figure 11). The isotope data show a range of values not reported previously in source rocks of the late Paleozoic of the northern Denver Basin. Two zones of relative ^{12}C enrichment are observed. The uppermost is seen in the Michaels 1 and Mathewson 1-20 samples (Figure 11). This grouping of strongly negative $\delta^{13}\text{C}$ values is termed the “Pennsylvanian anomaly.” It occurs at the top of the Virgilian just before the Pennsylvanian to Permian transition.

Kűspert (1982) attributes enrichment of ^{12}C in an anoxic environment to recycling of organic matter-respired CO_2 . Organic matter is mineralized to aqueous carbon dioxide which is again fixed as organic carbon. The stratification of the water column, as inferred by the presence of gammacerane (Sulistyo, 1994), would allow for the gradual buildup of CO_2 below the chemocline (Kűspert, 1982). This CO_2 , depleted in ^{13}C , would be used by anaerobic photoautotrophic organisms such as green sulfur bacteria [existence inferred by the presence of aryl isoprenoids (Clayton et al., 1992)] and produce $\delta^{13}\text{C}$ values that are more negative than that of the atmosphere. This model is consistent with the mechanism that produced other highly negative $\delta^{13}\text{C}$ values seen in other Pennsylvanian formations,

such as the Marmaton, Paradox and Tyler (Lewan, 1986). The occurrence of $\delta^{13}\text{C}$ values around -30.0 and lower in this part of the basin are the product of localized control by anoxic organic matter recycling.

The lowermost anomaly, termed “Missourian anomaly” is seen in the Bird 4-1 samples. These values occur in the Lansing Group of the Missourian series, which has not been examined in previous research in the basin, just below the base of strata from the Virgilian series.

As was the case with the Pennsylvanian anomaly, environmental conditions (anoxia) prompted the reworking of organic matter within the system and further enriched ^{12}C . The $\delta^{13}\text{C}$ values from the Missourian anomaly are more negative than those seen in the Pennsylvanian anomaly (averaging -30.5‰ and -30.0‰ respectively). Again, as was the case with the Pennsylvanian anomaly, this negative anomaly was triggered by local phenomena (anoxic organic matter recycling). In this latter case, the $\delta^{13}\text{C}$ values may have been driven to more negative values by a slightly more negative global atmospheric $\delta^{13}\text{C}$ signature or longer periods of ^{12}C enrichment by recycling of organic matter. Based on these data, the Missourian anomaly is also a candidate for producing the relatively low $\delta^{13}\text{C}$ values of the oils in Paleozoic reservoirs.

Although the $\delta^{13}\text{C}$ values of the black shale and microbial laminite samples overlap completely (Figure 14), some generalizations can be made. The microbial laminites tend to have higher $\delta^{13}\text{C}$ values. Four of the five microbial laminite samples have $\delta^{13}\text{C}$ values that are higher than -24‰, whereas six of the nine black shale samples

have $\delta^{13}\text{C}$ values that are lower than -25‰ (Table 2). The marlstones, however, exhibit particularly low $\delta^{13}\text{C}$ values relative to the other rock types.

All isotope data from this study and from previous studies are plotted together in Figure 15. The kerogen from samples from within the Pennsylvanian and Missourian anomalies display $\delta^{13}\text{C}$ values that are lower than -29.5‰, whereas the values reported in previous research are all greater than -29.5‰. Although oils show a bimodal distribution, the highest frequency of $\delta^{13}\text{C}$ values is at -29.0‰ to -31.0‰. Kerogen samples from the Pennsylvanian and Missourian anomalies are within a reasonable range to be matches for some oils from Paleozoic reservoirs.

8. Charge

After analyzing which sources match the characteristics of oils in which reservoirs, a generalized charge regime is inferred by the evaluating isopach thickness maps and reservoir location, from each series (Figure 16).

8.1. Morrowan (Figure 16a)

There are two oil samples from reservoirs of Morrowan age (Vick A1-9 and Braukmann Farms). The Morrowan section thickens to the south and is absent in much of the north. Both samples have very negative $\delta^{13}\text{C}$ values (-30.0‰ and -30.7‰, respectively) and are within a reasonable range to be matches with the $\delta^{13}\text{C}$ values of

rocks from the Pennsylvanian and Missourian anomalies (Table 2). It is unlikely, however, that these reservoirs were charged by source rocks from either of the anomalies. After generation, the oils would have to migrate down stratigraphically through the Desmoinesian and Atokan before being captured in Morrowan reservoirs. Though this is not impossible, a simpler explanation is that deeper source rocks within stratigraphically lower units, such as the Mississippian, expelled these hydrocarbons. The Mississippian section in this area contains marlstone which could have organic carbon contents high enough for the production of hydrocarbons (Martin, 1965). This study has no core samples from the Desmoinesian, Atokan, or Morrowan to cross-reference for oil staining from migration.

8.2. Desmoinesian (Figure 16b)

Oil samples from Desmoinesian reservoirs are sourced from a rock deposited in a hypersaline setting and have $\delta^{13}\text{C}$ values that are more positive than values from other fields in this study. The depositional environment may have been anoxic, but with limited carbon recycling. These oils were probably derived from rocks that were deposited at times other than the two noted negative anomalies. The $\delta^{13}\text{C}$ values observed in the oils from Desmoinesian reservoirs are consistent with Desmoinesian-age oil (-27.69) from Clayton et al. (1987). Sulistyo (1994) notes lower $\delta^{13}\text{C}$ values of kerogen samples from the Desmoinesian as well, supporting the conclusion that the oils in these reservoirs were sourced locally.

8.3. *Missourian and Virgilian (Figure 16c)*

The oils in Missourian- and Virgilian-age reservoirs were probably sourced directly from the organic-rich intervals within the $\delta^{13}\text{C}$ anomalies as the oils themselves are also strongly negative (-30.6 to -30.7) (Table 2). The McMillian oil from the Bird Field was collected from perforations at 6672'-6857' in the Upper, Middle, and Lower Missouri Formation. The Bird Field reservoir is more shallow than the rocks of the Missourian anomaly (6867-77') and was probably charged by source rocks with abnormal carbon isotope compositions from either the Pennsylvanian or Missourian anomalies by means of standard migration toward the surface. The isopach map shows a thickening of this section in a basinward direction. This strengthens the theory that source intervals could be thicker in a basinward direction because of the increased accommodation space and potential volume for source intervals to fill.

8.4. *Wolfcampian (Figure 16d)*

The Permian isopach map displays a separation in thicknesses of the two depocenters as the Transcontinental Arch was more strongly pronounced. Wolfcampian reservoirs contain both families of oils: The hypersaline family (Black Hollow and Pierce Lyons) and the terrestrial family (Wykert and Admire). Clayton et al. (1987) also notes this distinction in the Lyons Sandstone and some Wolfcampian reservoirs in southwest Nebraska. The $\delta^{13}\text{C}$ values from oils of Wolfcampian age vary greatly (-30.8 to -28.8)

(Table 2) which suggests that these two oil families were sourced by two genetically diverse source rocks. The Wykert and Admire oils were probably generated by source rocks deposited in either the Pennsylvanian or Missourian anomalies, whereas the Black Hollow and Pierce Lyons are from unidentified sources (likely of Wolfcampian or Virgilian age because of the wide variation in kerogen $\delta^{13}\text{C}$ values).

9. Conclusions

Potential source rocks comprising the uppermost (microbial laminites and marlstones) to bottommost (black shales) sections of limestone-shale cycles from the upper Pennsylvanian and lower Permian occur in the Denver basin. Two $\delta^{13}\text{C}$ anomalies were identified. In the case of the Pennsylvanian anomaly, strongly negative $\delta^{13}\text{C}$ values of Paleozoic oils and prospective sources were caused by ^{12}C enrichment by recycling of organic matter in anoxic conditions. The $\delta^{13}\text{C}$ values from the Missourian anomaly are also a product of anoxic organic matter recycling, but may be coupled with an already more negative atmospheric $\delta^{13}\text{C}$ value or longer periods of anoxic recycling conditions.

The prospective source rocks identified in this study have TOC values that are high enough to be considered sufficient for the expulsion of hydrocarbons (Figure 13) and were subjected to subsurface conditions conducive to the release of hydrocarbons (Figure 11).

To date, the two negative $\delta^{13}\text{C}$ anomalies of kerogen samples from the late Paleozoic from this study are the only zones in which source rock $\delta^{13}\text{C}$ values equal those seen in

some oils from Paleozoic reservoirs. Although prospective source intervals are thin, previous workers conclude that other exceedingly thin source rocks from the Denver basin have been productive (Clayton, 1992). Depositional conditions were conducive to the accumulation and preservation of high concentrations of TOC, compensating for the lack of thickness and allowing for significant hydrocarbon expulsion.

Stratigraphic and geochemical evidence suggests that Morrowan oils (Braukmann Farms and Vick A1-9), Desmoinesian oils (Aloha Mula 1 and Aloha Mula 9) and some Wolfcampian oils (Black Hollow and Pierce Lyons) from this study were sourced by rocks other than those from the Pennsylvanian and Missourian anomalies. Virgilian oils (Bird 4-2 and Mathewson 1-20), Missourian oil (McMillian 3-1) and other Wolfcampian oils (Admire and Wykert) were likely sourced by rocks with anomalous $\delta^{13}\text{C}$ values from the Missourian or Virgilian series.

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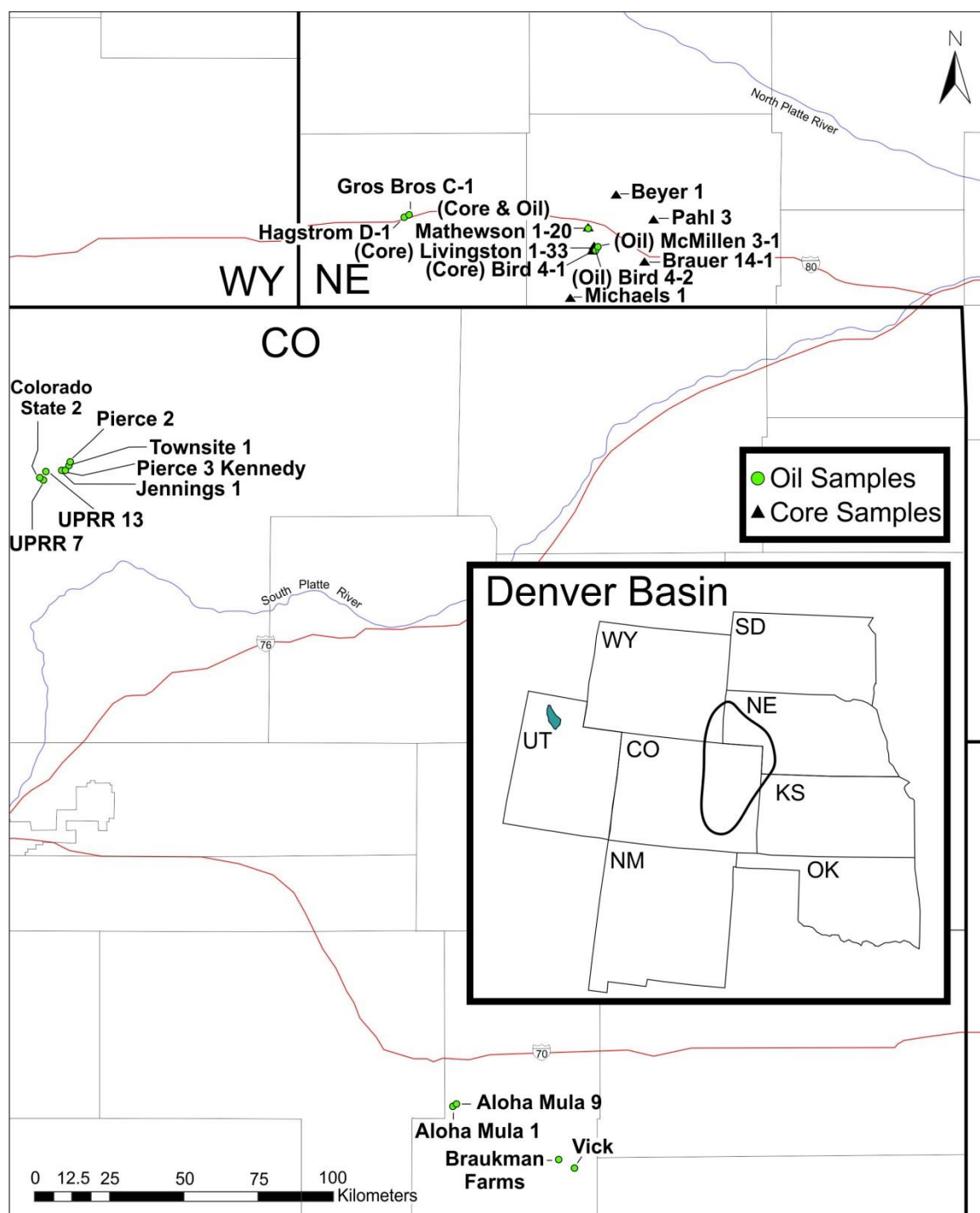


Figure 1. Study Area – Denver Basin, U.S.A. Larger white box shows positioning of the Denver Basin in its surrounding states. Larger map shows locations of cored wells (black triangles) and oil samples (green circles).

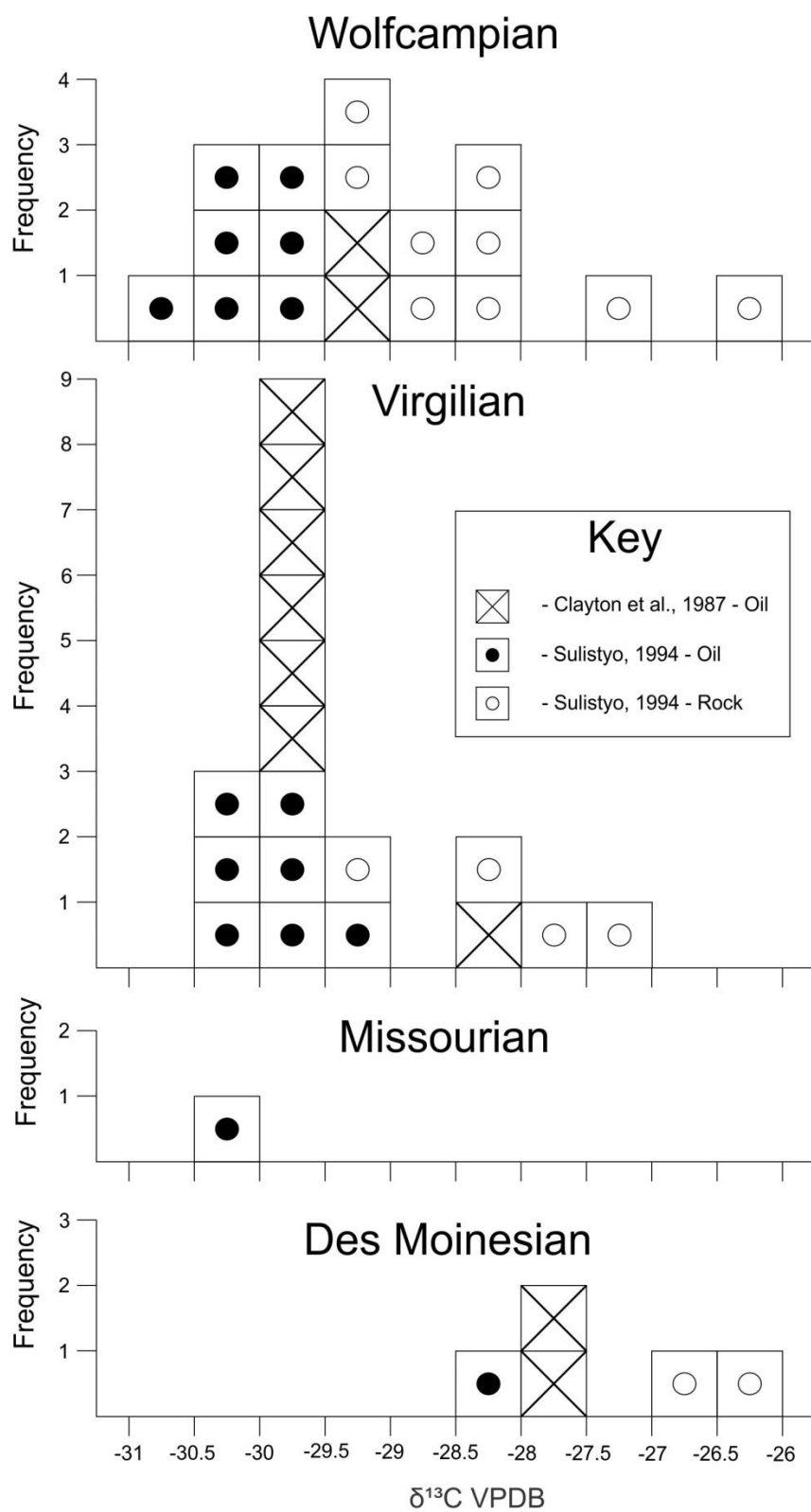


Figure 2. Late Paleozoic $\delta^{13}\text{C}$ Values. Diagram shows $\delta^{13}\text{C}$ values from work by Sulistyo (1994) and Clayton et al. (1987). Note that core samples are consistently more positive than oil samples.

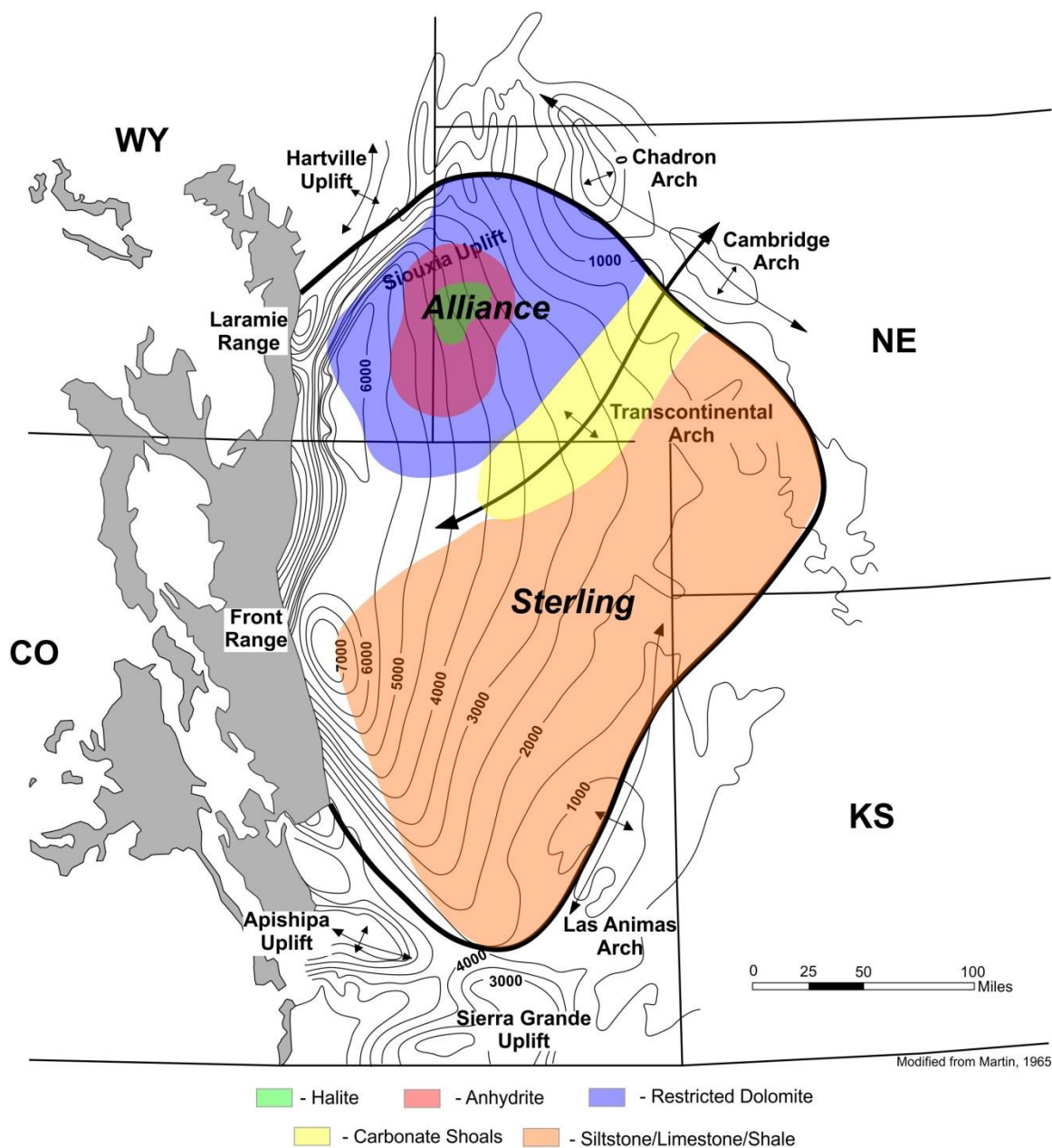
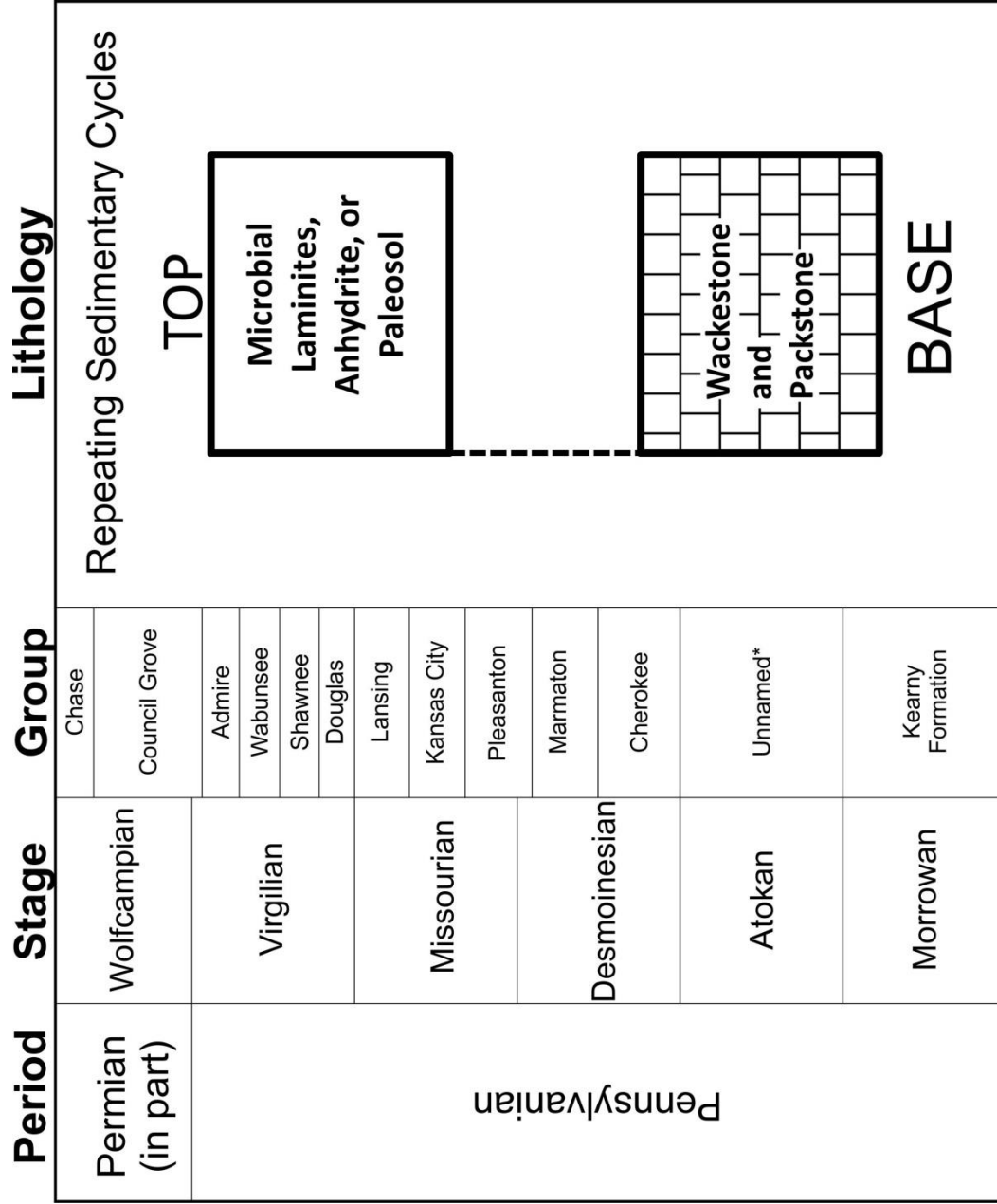


Figure 3. Structural map of the Denver basin. The Transcontinental Arch separates the Alliance and Sterling sub-basins. Datum is the base of the Pennsylvanian. Contour interval is 500 feet. Depositional facies by Garfield (1988).



* Kansas Geological Survey Bulletin 252, pt. 2

Figure 4. Stratigraphic column showing the series and units of the Pennsylvanian and Permian considered in this study. The lithology of the Virgilian and Wolfcampian have been interpreted to be nine repeating sedimentary cycles (Gilleland, 2011).

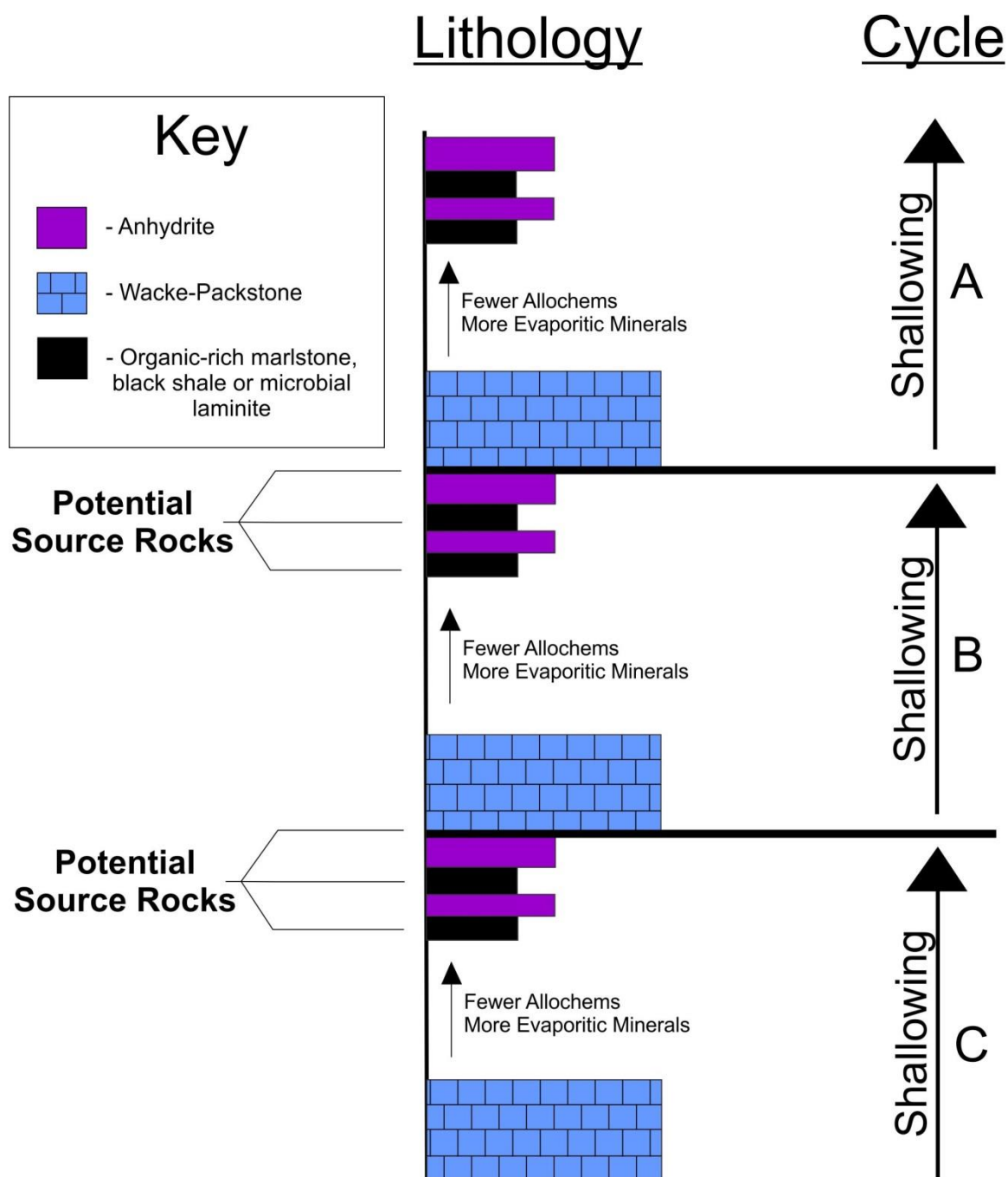


Figure 5. Three theoretical cyclothems. Each cycle shows wackestone and packstone near the base and anhydrite with potential source rocks at the top (Gilleland, 2011). Black shales occur at the very bottom of new cycles

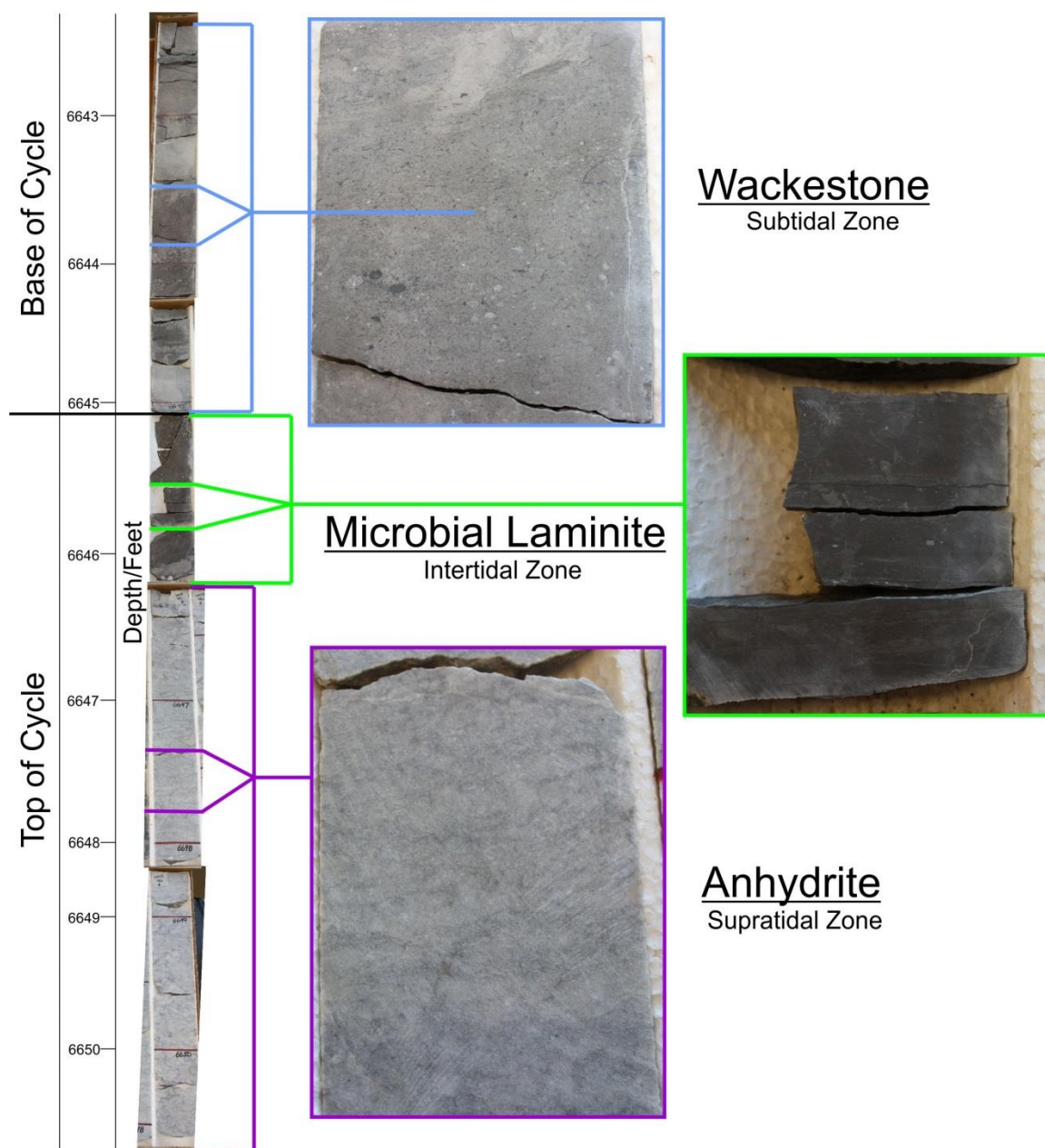


Figure 6. Core Evaluation – Cycle Boundary. Photos from Beyer 1 well core, displaying part of the Wolfcampian Council Grove Group. Anhydrite and microbial laminites are found together at the top of a cycle. Skeletal wackestone is seen in the base of the overlying cycle.

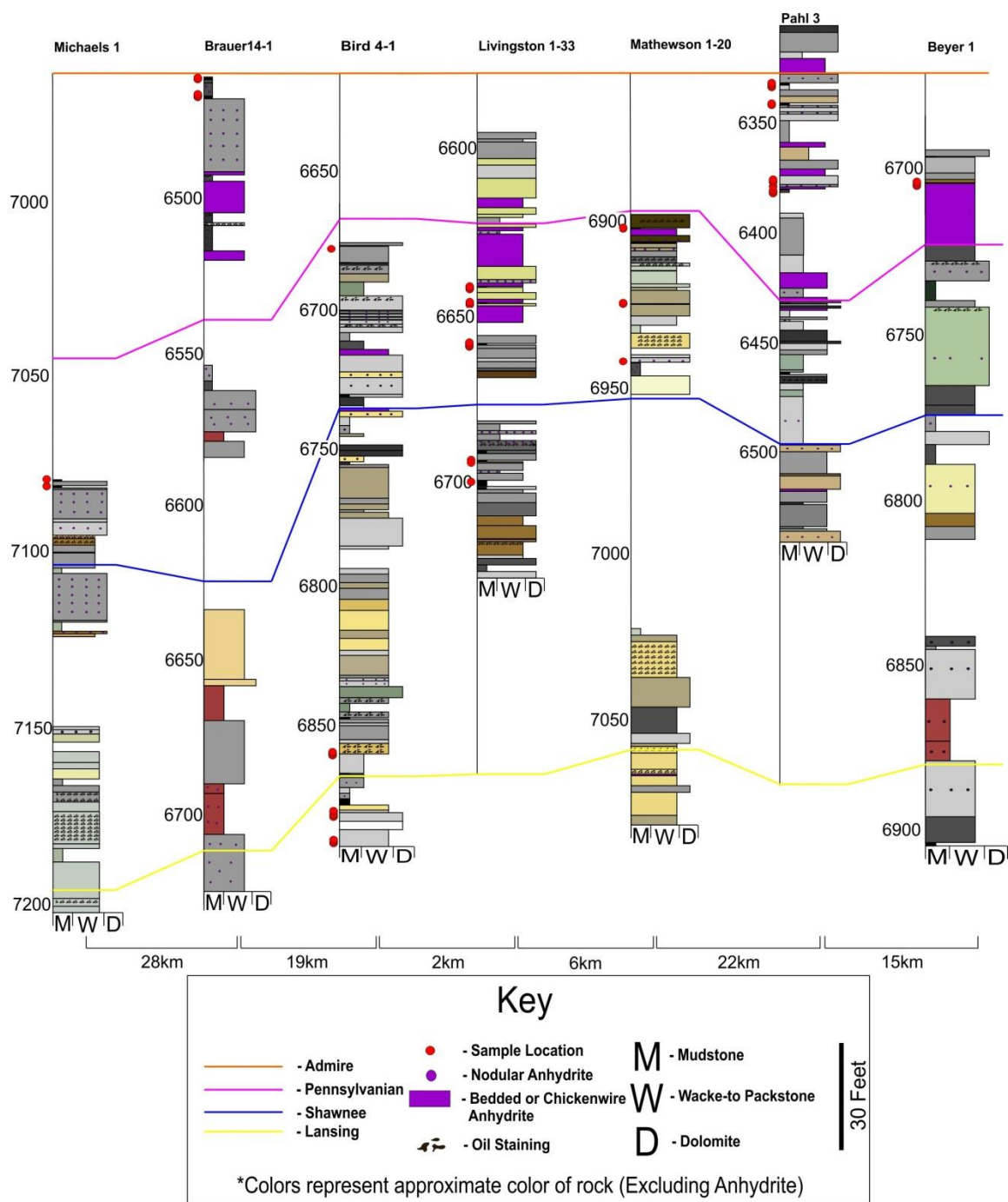


Figure 7. Graphic logs from all core evaluated in this study. Location of potential source rocks to be sampled are plotted as red circles. All wells are hung on the Admire. Well spacing not to scale. Depth of the Admire is labeled to the left of the log, in feet.

Table 1
List of all samples used in this study

Well	Depth/ft	API Number	Latitude	Longitude	Sample Type	Age
Bird 4-2	6672	26-033-22307	41.1294	-103.16682	Oil	Virgil
Gros Bros C-1	8142	26-105-22443	41.2093	-103.72819	Oil	Wolfcamp
Hagstrom D-1	8296	26-105-22389	41.2042	-103.74343	Oil	Wolfcamp
Mathewson 1-20	6809	26-033-22268	41.176	-103.1919	Oil	Virgil
McMillian 3-1	6672	26-033-22289	41.1328	-103.16279	Oil	Missouri
Aloha Mula 1	7110	05-073-06371	39.1587	-103.596305	Oil	Desmoines
Aloha Mula 9	7014	05-073-06390	39.1626	-103.58917	Oil	Desmoines
Braukman Farms	6854	05-073-06106	39.0323	-103.27727	Oil	Morrow
Townsite 1	9160	05-123-05520	40.6385	-104.75179	Oil	Wolfcamp
Jennings 1	9190	05-123-05508	40.6311	-104.76109	Oil	Wolfcamp
Pierce 2	9144	05-123-07596	40.6418	-104.75151	Oil	Wolfcamp
Pierce Kennedy 3	9214	05-123-12952	40.6312	-104.76583	Oil	Wolfcamp
Colorado State 2	8952	05-123-05454	40.6123	-104.83504	Oil	Wolfcamp
UPRR 7	8952	05-123-05445	40.6089	-104.83406	Oil	Wolfcamp
UPRR 13	9012	05-123-05482	40.6234	-104.8291	Oil	Wolfcamp
Vick A1-9	6754	05-073-06304	39.0107	-103.23166	Oil	Morrow
Beyer 1	6645' 2"	26-033-22309	41.2557	-103.1056	Micro-Lam	Virgil
	6645' 4"				Micro-Lam	Virgil
	6645' 8"				Micro-Lam	Virgil
	6645' 9"				Micro-Lam	Virgil
Bird 4-1	6679' 1"	26-033-22248	41.1328	-103.1722	Marlstone	Virgil
	6847' 3"				Marlstone	Virgil
	6847' 6"				Marlstone	Virgil
	6847' 10"				Marlstone	Virgil
	6848'				Marlstone	Virgil
	6866' 4"				Marlstone	Virgil
	6866' 6"				Marlstone	Virgil
	6867' 1"				Marlstone	Missouri
	6867' 3"				Marlstone	Missouri
	6867' 4"				Marlstone	Missouri
	6868' 2"				Marlstone	Missouri
	6868' 4"				Marlstone	Missouri
	6868' 6"				Marlstone	Missouri
	6876' 2"				Marlstone	Missouri
	6876' 8"				Marlstone	Missouri
	6876' 10"				Marlstone	Missouri
	6877' 2"				Marlstone	Missouri
Brauer 14-1	6383' 6"	26-033-22329	41.1048	-103.0203	Marlstone	Wolfcamp
	6383' 7"				Marlstone	Wolfcamp
	6389' 6"				Black Shale	Virgil
	6389' 7"				Black Shale	Virgil

Micro-Lam = Microbial Laminite

Table 1 cont.

List of all samples used in this study

Well	Depth/ft	API Number	Latitude	Longitude	Sample Type	Age
Livingston 1-33	6641' 1"	26-033-22241	41.13657	-103.1682	Black Shale	Virgil
	6641' 2"				Black Shale	Virgil
	6641' 3"				Black Shale	Virgil
	6646' 7"				Black Shale	Virgil
	6646' 8"				Black Shale	Virgil
	6646' 9"				Black Shale	Virgil
	6658' 7"				Micro-Lam	Virgil
	6658' 8"				Micro-Lam	Virgil
	6658' 9"				Micro-Lam	Virgil
	6694' 3"				Marlstone	Virgil
	6694' 4"				Marlstone	Virgil
	6700' 9"				Marlstone	Virgil
Mathewson 1-20	6842' 9"	26-033-22268	41.17607	-103.1919	Marlstone	Virgil
	6842' 11"				Marlstone	Virgil
	6867' 9"				Marlstone	Virgil
	6867' 11"				Marlstone	Virgil
	6884' 11"				Marlstone	Virgil
Michaels 1	6966' 2"	26-033-22276	41.01663	-103.2435	Marlstone	Virgil
	6968' 1"				Marlstone	Virgil
Pahl 3	6332' 1"	26-033-05680	41.20213	-102.9914	Black Shale	Wolfcamp
	6332' 3"				Black Shale	Wolfcamp
	6332' 4"				Black Shale	Wolfcamp
	6341' 1"				Micro-Lam	Wolfcamp
	6341' 3"				Micro-Lam	Wolfcamp
	6380' 1"				Micro-Lam	Virgil
	6380' 2"				Micro-Lam	Virgil
	6380' 3"				Micro-Lam	Virgil
	6383' 5"				Black Shale	Virgil
	6384'				Black Shale	Virgil
	6384' 1"				Black Shale	Virgil
	6384' 2"				Black Shale	Virgil
	6384' 3"				Black Shale	Virgil

Micro-Lam = Microbial Laminite

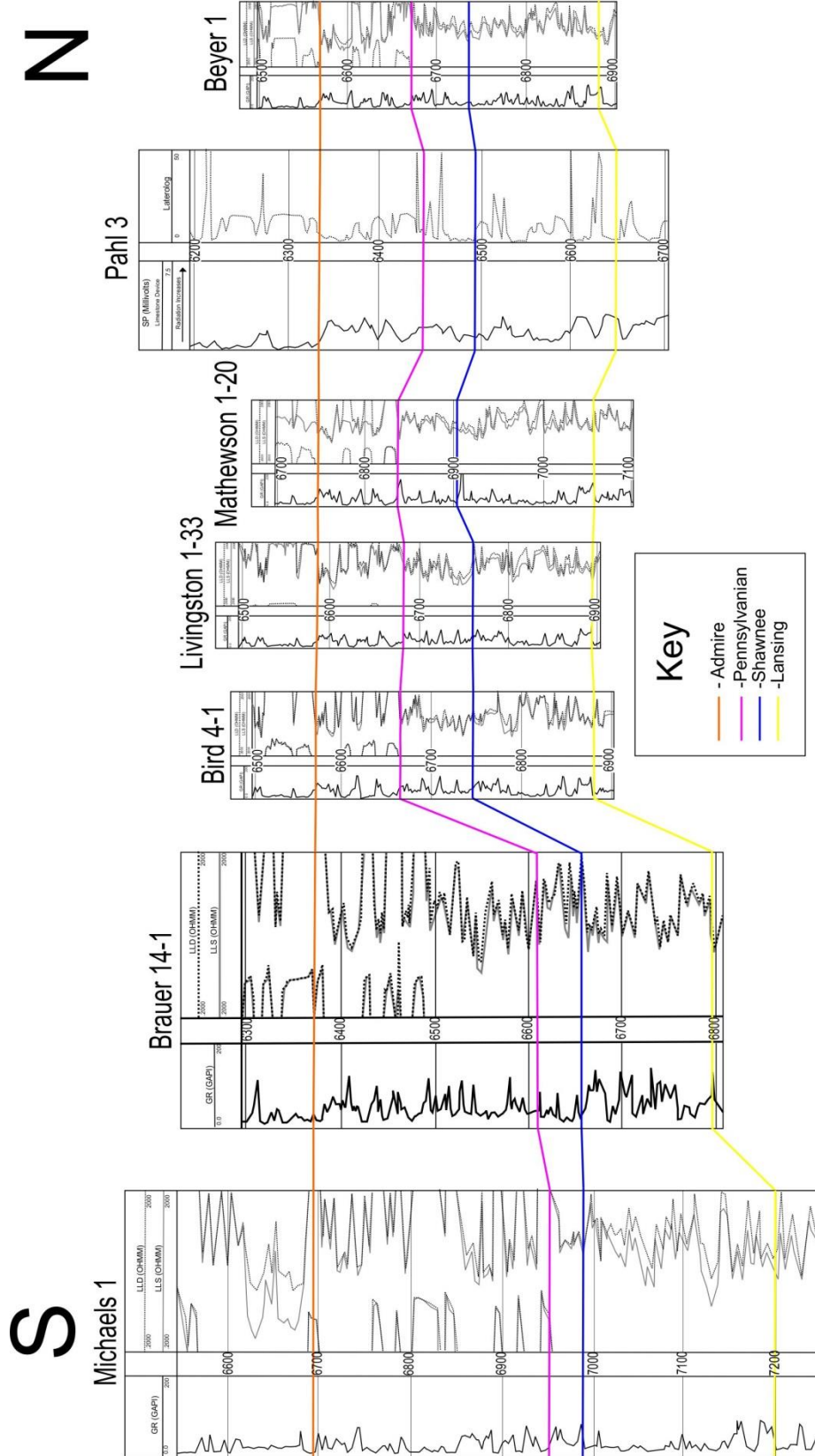


Figure 8. Well log correlation of available core – south to north. Major formation tops are from adjusted from data available at the Nebraska Oil and Gas Conservation Commission. All wells are hung on the Admire.

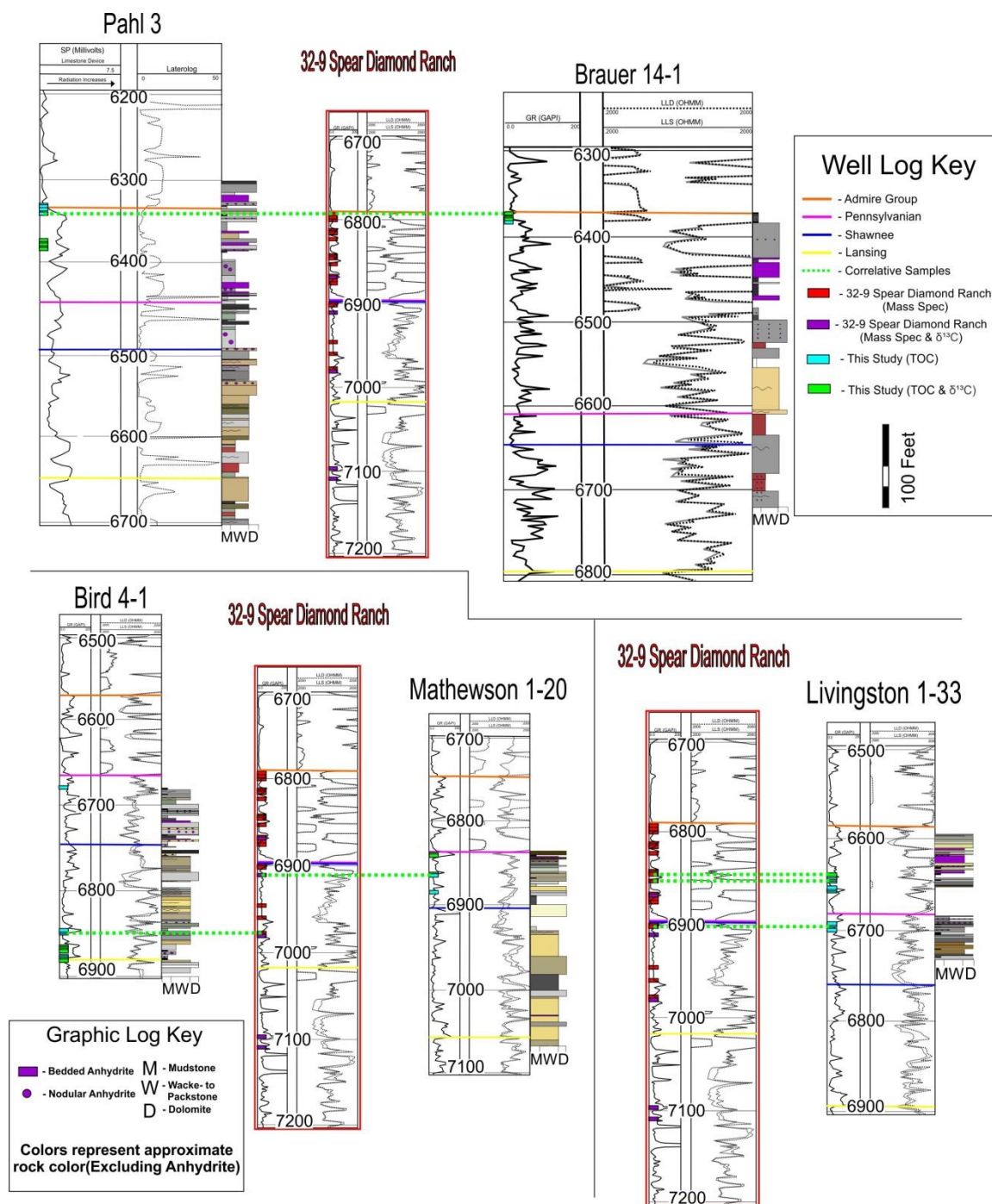


Figure 10. 32-9 Spear Diamond Ranch Sample Correlation: This Study. All wells from this study plotted along with the 32-9 Spear Diamond Ranch well from Sulistyo (1994). The 32-9 Spear Diamond Ranch shows the best spread of samples and has the highest volume of sample points. The hashed green lines connect possible duplicates. Notice that there are only seven possible matches of the 59 samples from this study. Depths at beginning of reading is at the left of log, in feet.

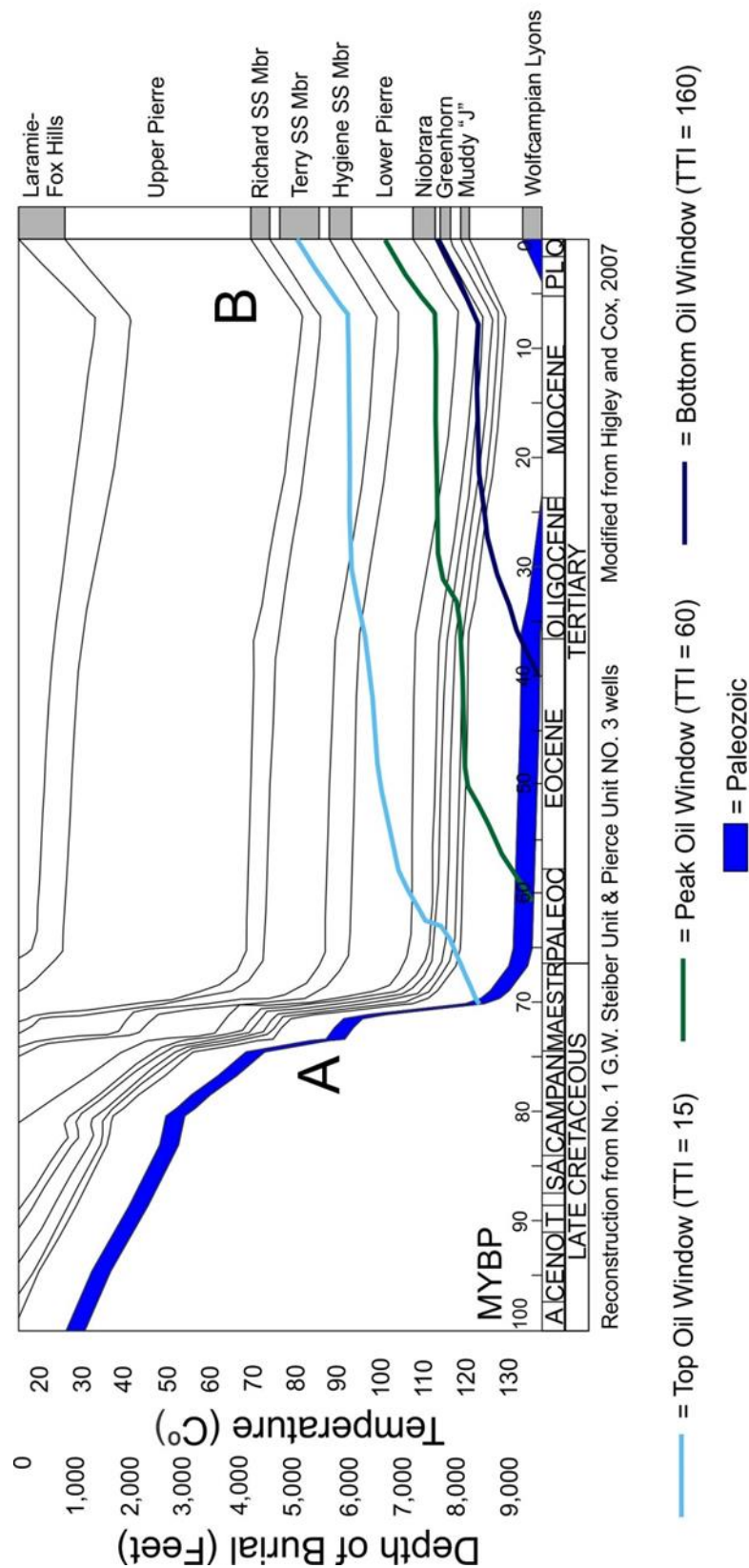


Figure 11. Burial History – Denver Basin. Light and dark blue lines indicate the upper and lower thresholds for the oil generating zones. Point “A” represents rapid deepening of sediments from deposition by Cretaceous seas. Point “B” indicates a zone of uplift and tilt from the final adjustments of the Laramide Orogeny during the Tertiary period. Note that extension of the oil window thresholds put Pennsylvanian and Permian rocks in the oil producing zone between 70 and 40 mya.

Table 2
List of TOC and $\delta^{13}\text{C}$ Results

Well	Depth/ft	Sample Type	$\delta^{13}\text{C}$ VPDB	TOC%* ¹	TIC%* ²	TN%* ³	C/N* ⁴
Bird 4-2	6672	Oil	-30.7				
Gros Bros C-1	8142	Oil	-30.8				
Hagstrom D-1	8296	Oil	-30.7				
Mathewson 1-20	6809	Oil	-30.6				
McMillian 3-1	6672	Oil	-30.6				
Aloha Mula 1	7110	Oil	-28.2				
Aloha Mula 9	7014	Oil	-28.3				
Braukman Farms	6854	Oil	-30.7				
Townsite 1	9160	Oil	-28.8				
Jennings 1	9190	Oil					
Pierce 2	9144	Oil					
Pierce Kennedy 3	9214	Oil					
Colorado State 2	8952	Oil	-28.9				
UPRR 7	8952	Oil					
UPRR 13	9012	Oil					
Vick A1-9	6754	Oil	-30.0				
Beyer 1	6645' 2"	Micro-Lam	-22.6	3.3	8.2	0.016	208.4
	6645' 4"	Micro-Lam	-23.4	3.2	8.6	0.016	200.2
	6645' 8"	Micro-Lam	-23.4	3.4	8.3	0.021	162.1
	6645' 9"	Micro-Lam	-23.1	2.7	9.0	0.022	121.3
Bird 4-1	6679' 1"	Marlstone		2.1	10.7	0.011	190.1
	6847' 3"	Marlstone		2.7	9.7	0.010	266.8
	6847' 6"	Marlstone		1.2	10.2	0.013	95.8
	6847' 10"	Marlstone		3.4	8.6	0.007	483.0
	6848'	Marlstone		2.8	9.6	0.012	235.9
	6866' 4"	Marlstone	-30.1	1.8	1.3	0.018	100.5
	6866' 6"	Marlstone	-30.1	1.9	1.5	0.018	105.4
	6867' 1"	Marlstone	-30.2	2.0	1.4	0.019	105.9
	6867' 3"	Marlstone	-30.1	2.1	1.4	0.018	114.9
	6867' 4"	Marlstone	-30.2	1.9	1.4	0.019	100.3
	6868' 2"	Marlstone	-30.5	1.9	1.6	0.018	102.9
	6868' 4"	Marlstone		1.9	2.0	0.019	97.6
	6868' 6"	Marlstone		1.7	2.6	0.016	105.8
	6876' 2"	Marlstone	-30.3	1.6	11.3	0.012	134.8
	6876' 8"	Marlstone		2.4	10.5	0.015	157.2
	6876' 10"	Marlstone		3.0	11.2	0.023	130.5
	6877' 2"	Marlstone	-30.4	2.6	11.4	0.017	151.4
Brauer 14-1	6383' 6"	Marlstone	-26.1	6.0	7.9	0.101	59.4
	6383' 7"	Marlstone	-25.8	5.7	6.7	0.073	78.1
	6389' 6"	Black Shale	-26.8	4.6	0.9	0.157	29.1
	6389' 7"	Black Shale	-26.9	8.2	0.4	0.196	42.0

*¹ TOC = Total Organic Carbon; *² TIC = Total Inorganic Carbon; *³ TN = Total Nitrogen

*⁴ C/N = Carbon/Nitrogen Ratio

Table 2 cont.

List of TOC and $\delta^{13}\text{C}$ Results

Well	Depth/ft	Sample Type	$\delta^{13}\text{C}$ VPDB	TOC/% ^{*1}	TIC/% ^{*2}	TN% ^{*3}	C/N ^{*4}
Livingston 1-33	6641' 1"	Black Shale	-27.4	28.2	1.7	0.427	66.0
	6641' 2"	Black Shale		7.3	7.7	0.061	119.4
	6641' 3"	Black Shale		9.2	6.1	0.073	126.0
	6646' 7"	Black Shale		3.9	5.7	0.036	108.5
	6646' 8"	Black Shale		2.8	0.4	0.094	29.8
	6646' 9"	Black Shale	-27.8	4.2	0.6	0.120	34.8
	6658' 7"	Micro-Lam		5.4	7.5	0.046	116.5
	6658' 8"	Micro-Lam		2.2	6.3	0.020	109.8
	6658' 9"	Micro-Lam		4.7	6.7	0.057	82.3
	6694' 3"	Marlstone		3.3	9.0	0.011	300.5
	6694' 4"	Marlstone		1.6	10.9	0.014	114.8
	6700' 9"	Marlstone		2.7	9.2	0.009	295.8
Mathewson 1-20	6842' 9"	Marlstone	-29.4	2.7	5.9	0.015	179.3
	6842' 11"	Marlstone	-29.6	3.4	6.3	0.010	344.2
	6867' 9"	Marlstone	-29.9	4.0	9.2	0.008	503.5
	6867' 11"	Marlstone	-30.0	6.0	7.6	0.010	598.6
	6884' 11"	Marlstone		5.8	7.7	0.009	646.2
Michaels 1	6966' 2"	Marlstone	-30.0	3.5	6.7	0.006	581.3
	6968' 1"	Marlstone	-29.7	6.0	6.7	0.013	458.9
Pahl 3	6332' 1"	Black Shale		6.2	6.4	0.033	187.3
	6332' 3"	Black Shale		5.9	6.6	0.034	173.5
	6332' 4"	Black Shale		6.1	6.4	0.037	165.6
	6341' 1"	Micro-Lam		0.2	2.7	0.039	5.2
	6341' 3"	Micro-Lam		0.2	2.5	0.038	5.4
	6380' 1"	Micro-Lam		5.5	7.4	0.025	220.9
	6380' 2"	Micro-Lam		7.1	7.3	0.065	109.1
	6380' 3"	Micro-Lam	-27.2	8.6	6.2	0.062	138.6
	6383' 5"	Black Shale	-27.2	27.9	2.4	0.517	54.0
	6384'	Black Shale	-25.5	10.8	4.8	0.154	70.0
	6384' 1"	Black Shale	-24.8	6.4	8.7	0.105	60.6
	6384' 2"	Black Shale	-23.1	7.4	7.6	0.125	58.9
	6384' 3"	Black Shale	-23.5	1.5	10.1	0.115	13.0

^{*1} TOC = Total Organic Carbon; ^{*2} TIC = Total Inorganic Carbon; ^{*3} TN = Total Nitrogen^{*4} C/N = Carbon/Nitrogen Ratio

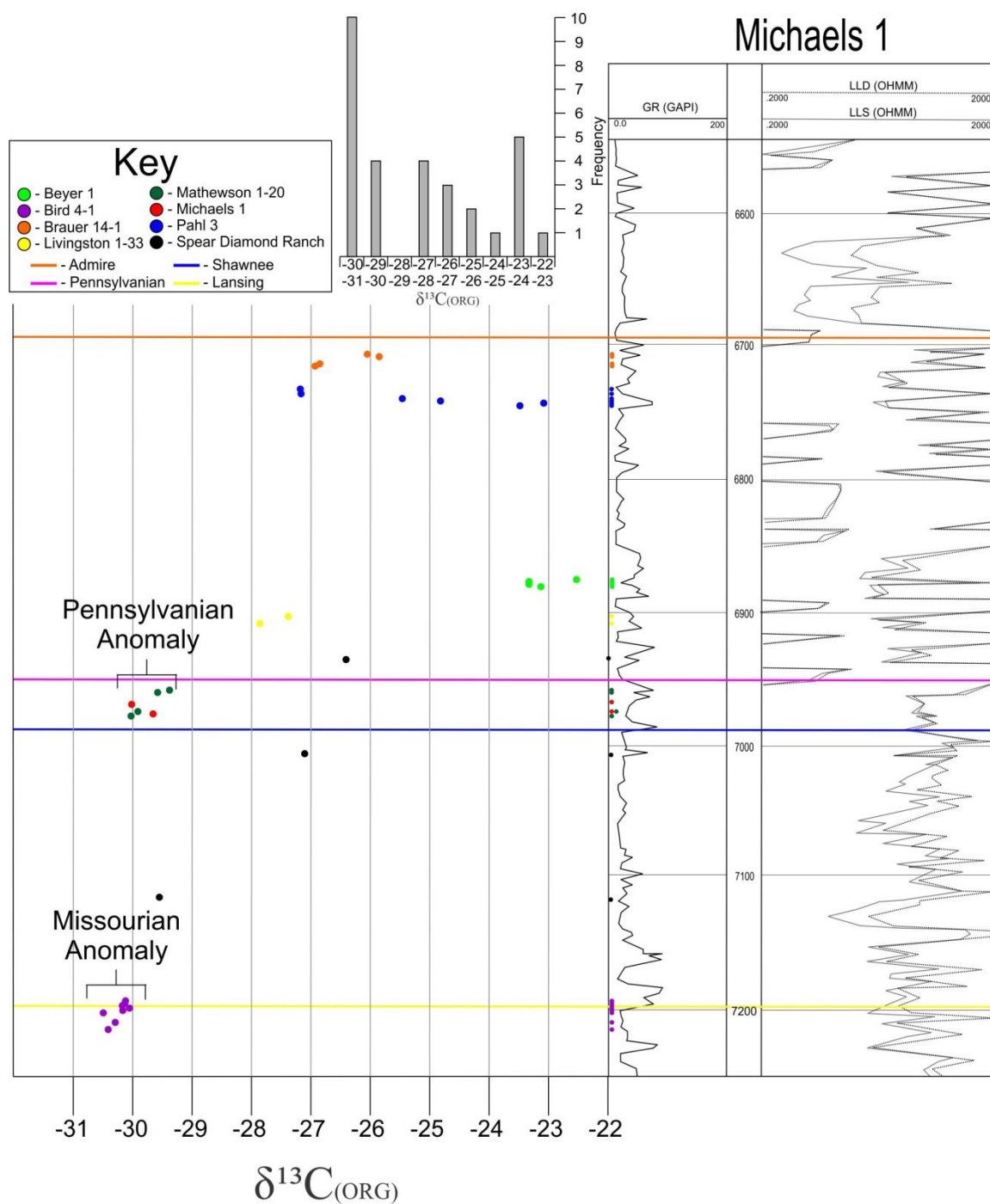


Figure 12. Carbon isotope data – Kerogen samples. The $\delta^{13}\text{C}$ values of kerogen from this study and those in the interval of interest from the 32-9 Spear Diamond Ranch, are plotted together based on their correlations to a single well log. Two anomalies are observed; one in the Virgilian (Pennsylvanian Anomaly) and again in the Missourian (Missourian Anomaly). Values as low as -30.5‰ are observed.

Michaels 1

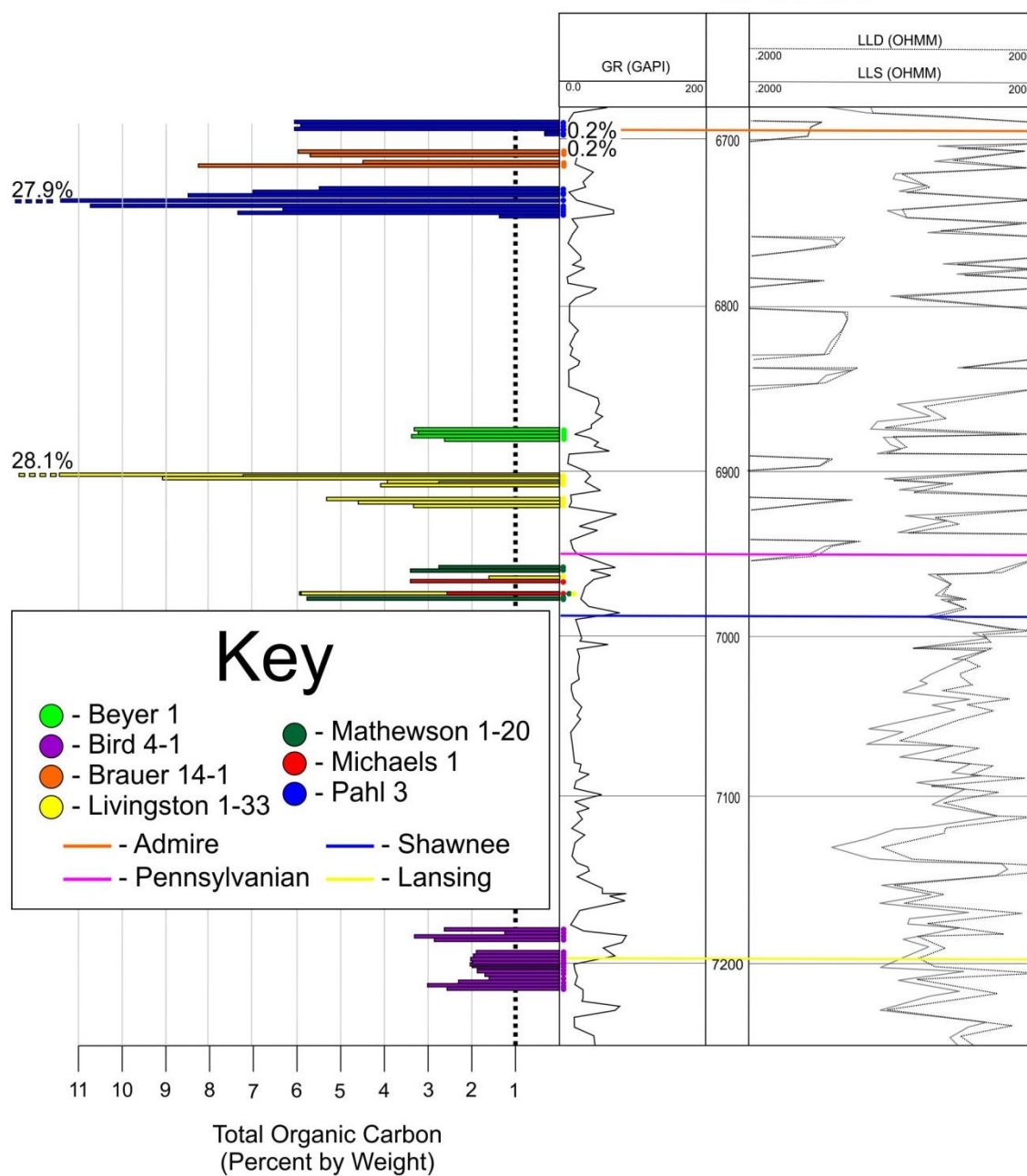


Figure 13. Total organic carbon results. The type well is the Michaels 1. Notice that all but 2 wells are above the 1% by weight cutoff used in this study. 2 wells show values that are exceedingly high.

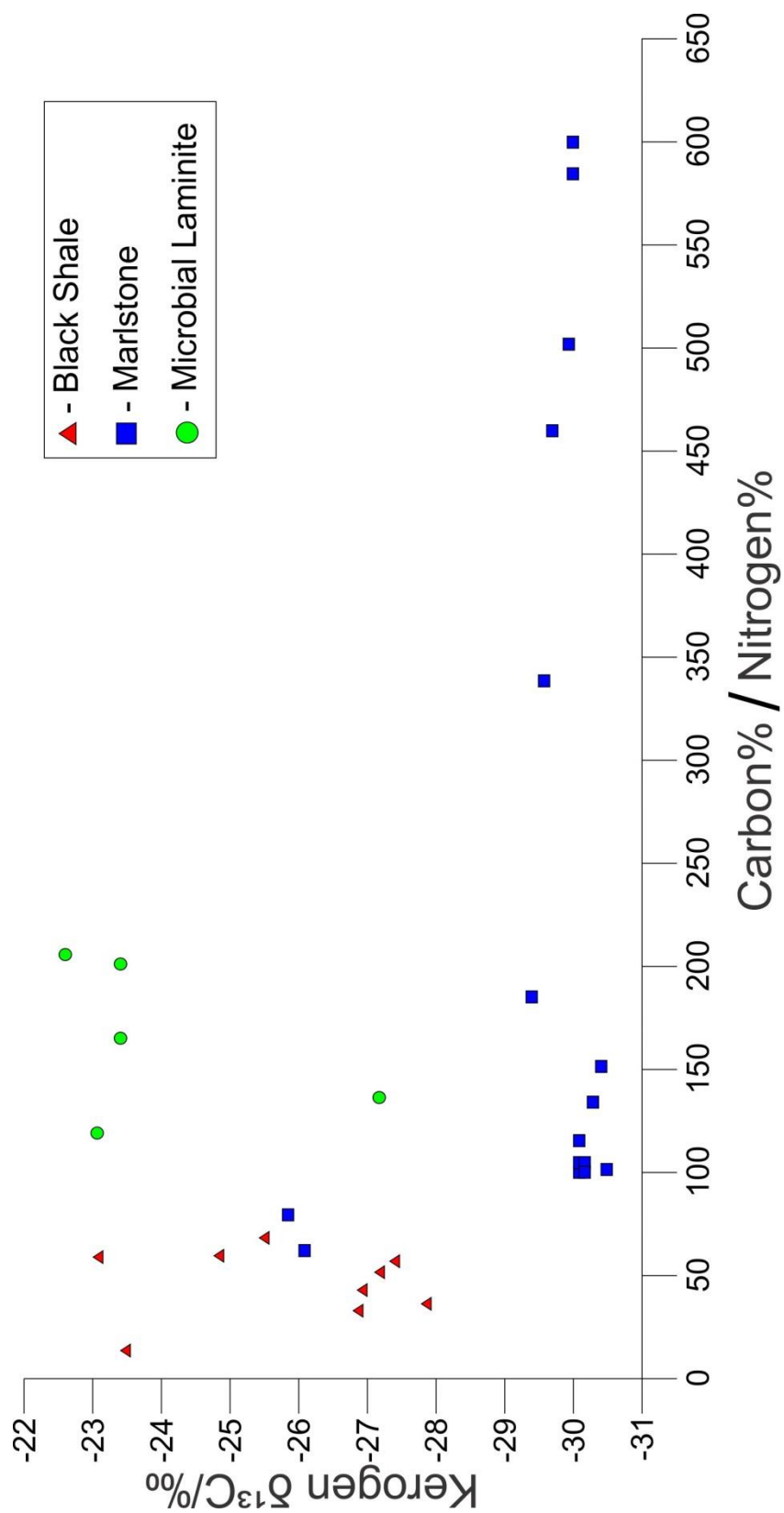


Figure 14. Crossplot of C/N ratio against kerogen $\delta^{13}\text{C}$ values. Deeper-water deposits have the lowest C/N ratios. $\delta^{13}\text{C}$ values are the lowest in the marlstones but are variable in other rock types.

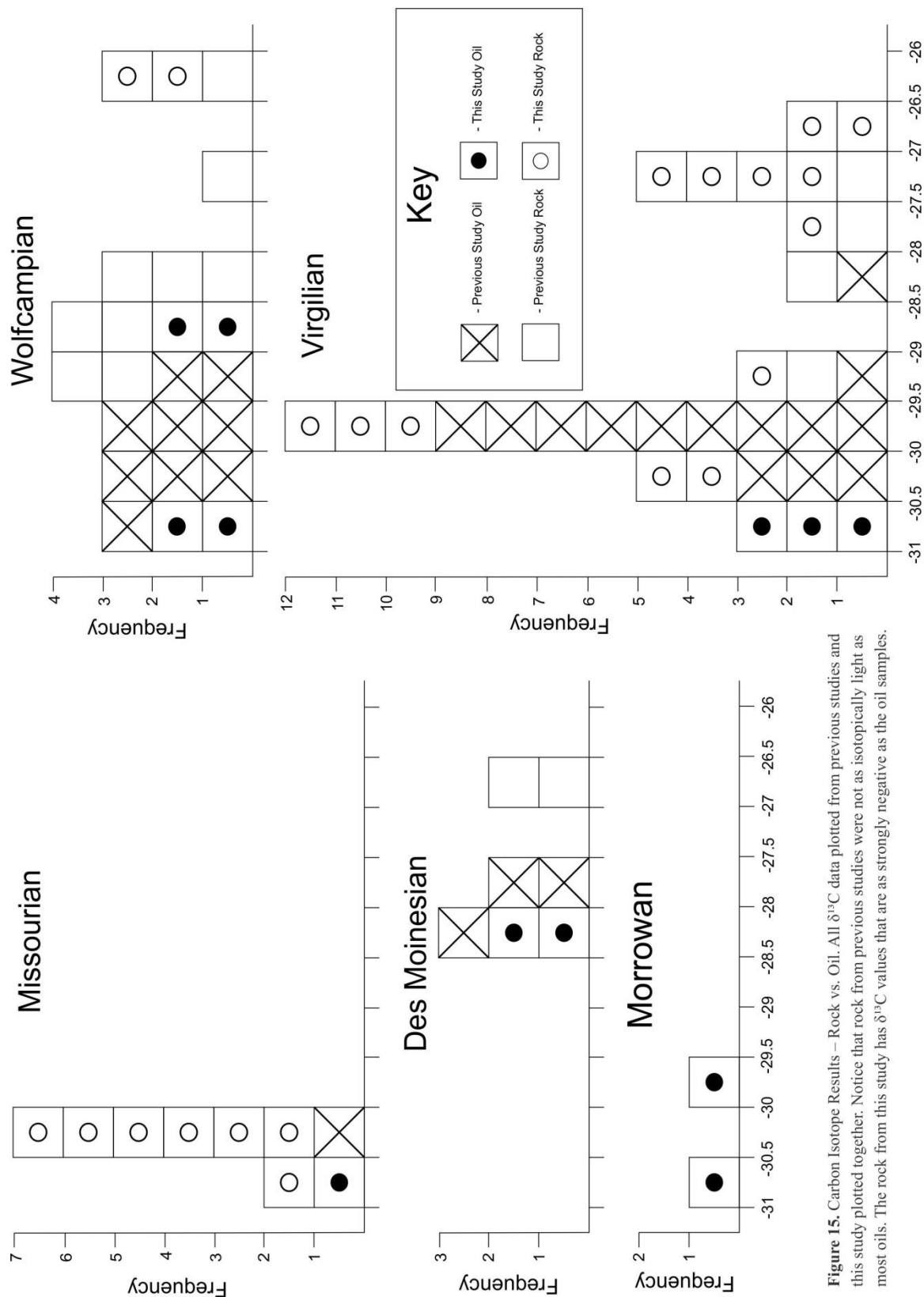


Figure 15. Carbon Isotope Results – Rock vs. Oil. All $\delta^{13}\text{C}$ data plotted from previous studies and this study plotted together. Notice that rock from previous studies were not as isotopically light as most oils. The rock from this study has $\delta^{13}\text{C}$ values that are as strongly negative as the oil samples.

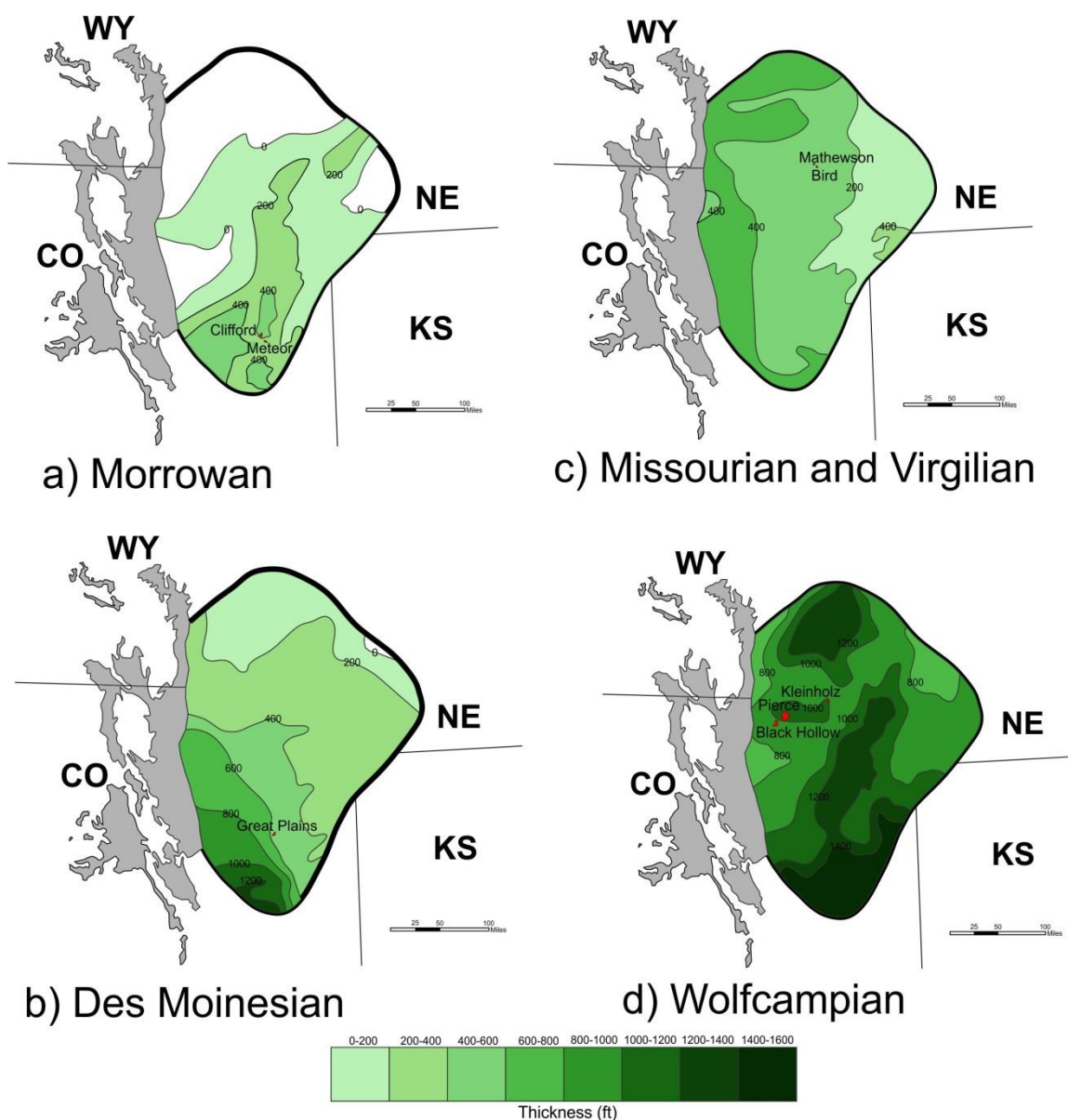


Figure 16. Pennsylvanian and Early Permian Isopachs modified from Martin (1965). Isopach maps show total thickness of the Morrowan, Des Moinesian, Missourian and Virgilian, and Permian (a,b,c,d respectively). Notice the basinward thickening of the Missourian and Virgilian isopach. This affirms the notion that there would be more accommodation space nearer to the basin axis and therefore more volume for potential source rocks to fill.