

## Secondary Migration of Lower-Middle Paleozoic Hydrocarbons at the Delaware Basin, Tobosa Basin Formations

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### Summary

Knowledge of the secondary migration of “hydrocarbon families” (genetic groups) from the Lower-Middle Paleozoic formations in the Delaware Basin, is vital for exploration and development of hydrocarbon accumulations in the region. Available chemometric methods offer unique advantages in classifying petroleum (oil and gas) samples into genetic groups, serving as a powerful tool to support the definition and simulation of petroleum systems in a basin model and, consequently, the migration model. Variations of stable carbon isotopes, biomarker composition, and chemometric analyses, such as Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA), were employed to correlate four genetic families from the oil samples collected. Three organic-rich type II – II/III source rocks are considered: the Simpson Group Shale, Woodford Shale, and the Barnett Shale/ Mississippian Limestone. Maturity analysis and modeling separate the genetics groups into the most mature oil samples (Simpson) and least mature samples (Barnett, Woodford). Gas samples were subsequently analyzed using compositional ratios associated with migration and maturation.

### Introduction

The Lower-Middle Paleozoic Tobosa Basin forms a geologically complex system underlying the Permian basin. According to basin simulations exercises preceding the Late Pennsylvanian Ouachita-Marathon thrust, parts of the Simpson Group were buried into the hydrocarbon generation window, with shallower formations remaining immature. Aiming to investigate the migration process, hydrocarbons recovered from Lower-Middle Paleozoic aged reservoirs were chemically analyzed for composition, carbon isotopes, maturity, and biomarkers. Using chemometric methods (HCA and PCA), oil samples were analyzed and interpreted into four genetic groups migrated from primary source rocks: Simpson Group, Woodford Shale, and the Barnett Shale/ Mississippian Limestone. Using a combination of composition, isotopic ratios, and statistical analyses (PCA), gas samples were similarly analyzed into three groups according to maturity and migration. Targeting to contribute to understanding secondary migration, this research employs a chemometric approach to constrain petroleum system analysis and basin modeling of the Delaware Basin to comprehensively understand the region’s structural and thermogenic evolution and its effects on present petroleum systems. Focusing on secondary migration, this research

project is centered on the interpretation and statistical analysis of geochemical samples collected from hydrocarbons originated from and stored in Lower-Middle Paleozoic formations in the Delaware Basin. This project aims to understand the present-day hydrocarbon distribution originating from the mentioned source rocks and to explore the relationship between reservoirs and the source rocks in the multistage Delaware basin.

### Theory and Methodology

Hydrocarbon genetic groups of processed Lower-Middle Paleozoic reservoir oil samples from an extensive proprietary dataset were defined using chemometric statistical methods: Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA). The analysis also allowed the evaluation of aspects such as source rocks maturity and depositional context with the application of a select group of parameters: API gravity, carbon isotopes, saturates %, aromatics %, peak high ratios (ranging from C15 to C35), thermal maturity, sample locations, and reservoir unit. Aiming to support this approach, gas sample geochemistry analyses were also evaluated to corroborate the interpretation for maturation and migration based on gas composition ratios. Gas composition ratios were defined as eigenvectors then analyzed using PCA and later divided into three groups based on maturity and migration.

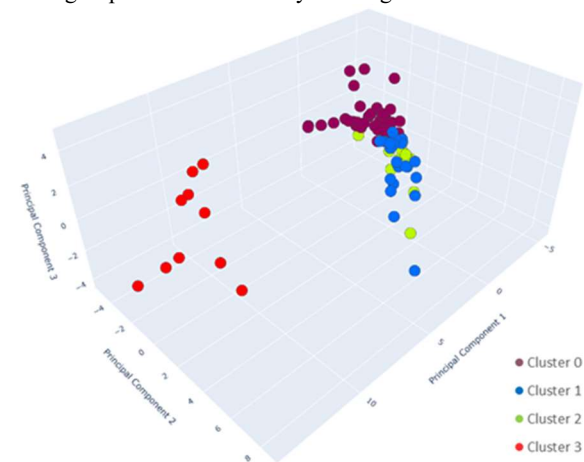


Figure 1 Scatter plot of the Principal Component clusters of Oil samples; the scatter plot shows the separation of the more mature group (cluster 3) three from the rest of the samples.

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## Results and Discussion

Chemometric methodologies were employed for the collected oil samples; HCA and PCA analysis yielded 4 clusters for the analyzed samples, with cluster 3 being the most mature samples of the clusters (Figure 1). Using the phytane to nC18 vs. pristane to nC17 relationship, we can further explore the clear separation in maturity between cluster 3, predominantly marine algal type II, and the rest of the samples (Figure 2). Using Figure 2, we can also

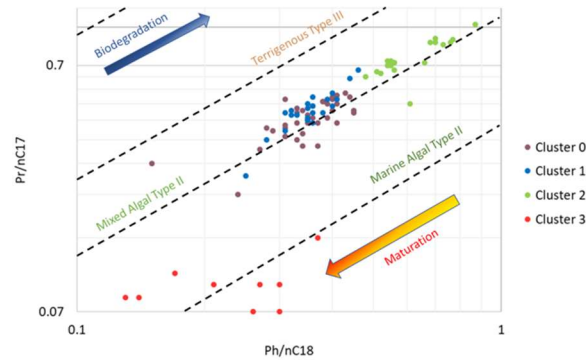


Figure 2 Cross plot of the Phytane to nC18 vs. Pristane to nC17 ratio. Comparisons between the two ratios classify organic matter in the source rock and the level of maturation.

determine that cluster 2 is the least mature cluster, with most of the samples plotted in a mixed algal type II source rock classification. The other two clusters (0 and 1) are plotted interwoven, with most samples falling within the same source rock and maturation classifications. Table 1 (Carpp et

Characteristics of Source Rock	Pr/Ph Ratio	Canonical Variable	Sulfur Wt%
Depositional Environment & Source Rock Lithology	Pr/Ph Ratio > 1 Redox of Depositional Environment: Dysoxic Lithology: Shale	Canonical Variable > 0.5 Depositional Environment: Non-Marine	Sulfur Wt% < 1 Source Lithology: Shale
	Pr/Ph < 1 Environment Anoxic Lithology: Carbonate	Canonical Variable < 0.5 Depositional Environment: Marine	Sulfur Wt% > 1 Source Lithology: Carbonate
Source Rock Age	$\delta^{13}C$ Saturate Stable Carbon Isotope (permille)		-34.00 - -30.00
	$\delta^{13}C$ Aromatic Stable Carbon Isotope (permille)		-34.00 - -29.00
Organic Matter	Ph/nC18 > Pr/nC17		Marine Algal Type II

Table 1 Interpretation criterion table used for the geochemical inversion of the interpreted source rocks of the analyzed oil groups and their characteristics. Each section quantifies the ranges for the source characteristics and the limits for the associated geochemical parameters. Edited from the thesis of Carpp, 2023.

al., 2023) was utilized to relate the analyzed oil clusters to the interpreted source rocks. This table breaks down the chemometric approach into several components: source rock lithology, source rock organic matter, redox of depositional environment, depositional environment, and source rock age. Source rock lithology is correlated using the Pr/Ph ratios, Canonical Variable, and the Sulfur wt%, as well as the relationship between Ph/nC18 vs Pr/nC17. The organic matter of collected oil samples can be classified using the relationship between Ph/nC18 and Pr/nC17. Redox of depositional environments is related to the Pr/Ph ratio. Depositional environments are interpreted using a combination of Pr/Ph ratios, Canonical Variable, Sulfur wt%, and the relationship between Ph/nC18 vs Pr/nC17. Source rock age is interpreted using Saturate Carbon Isotope and Aromatic Carbon Isotope, and the relationship between Ph/nC18 vs Pr/nC17.

Gas composition samples were analyzed as eigenvectors, principal component 1 and principal component 2. Principal component 1 was defined by maturity compositional values such as C1, C2, C3, nC4, and isoC4, whereas principal component 2 emphasized migration compositional values such as C3, isoC4, nC4, isoC5, nC5, and C6+. The two defined principal components show apparent clustering into three groups: group zero, characterized by low levels of maturity, an estimated vitrinite reflectance of less than 1.0 and a relatively low level of migration; group one, high level of maturity, estimated vitrinite reflectance greater than 2.5 with a relative higher level of migration; and group 2, intermediate levels of maturity estimated vitrinite reflectance ranging from 1.0 to 2.5 with relative low levels of migration (Figure 3, Figure 4). The relationships between principal component 1 and principal component 2 are supported by gas compositional analysis; using the natural log relationship of the C1 to C2 and the C2 to C3 ratios

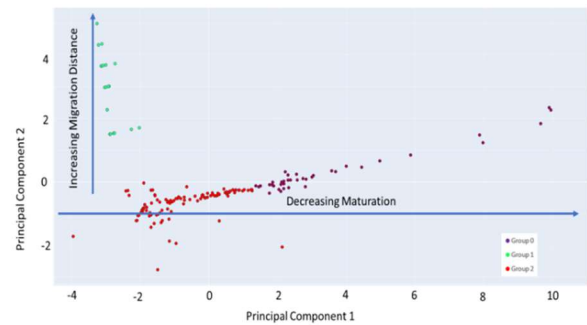


Figure 3 Principal component analysis (PCA) of Gas composition was divided into principal component 1 and principal component 2. Principal component 1 is defined by factors associated with the maturation and preservation of hydrocarbons, such as compositional values such as C1, C2, C3, nC4, and isoC4. Principal component 2 puts a lot more emphasis on C3, isoC4, nC4, isoC5, nC5, and C6+. Plot adapted from Prinzhofer et al., 2000.

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(Figure 4), we can differentiate between kerogen-cracking gas and oil-cracking gas and infer the gas maturation level. In Figure 4, separation of one of the three PCA groups is evident, with group 1 having the highest maturation and is

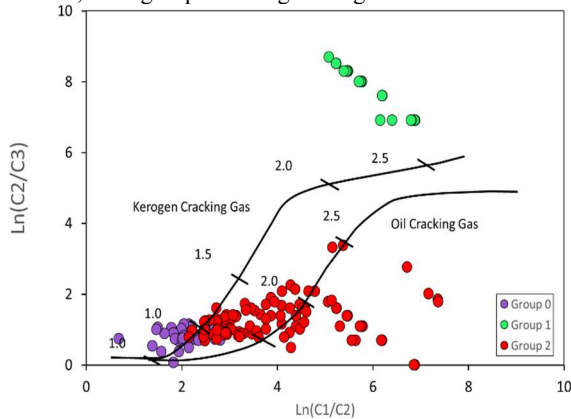


Figure 4 The cross plot of the natural logs of the C1 to C2 ratio and C2 to C3 ratios demonstrate the maturity and generation origin of the natural gases in this study, differentiating between primary cracked gas and secondary cracked gas. Geomark donated natural gas composition data. Adjusted from Behar et al., 1995 and Liu et al., 2018.

related to kerogen cracking gas. Group 2 has a broader range of maturity with an estimated vitrinite reflectance ranging from 1.0 to 2.5, produced mainly from a combination of primary and secondary cracking (Figure 4). The interpreted

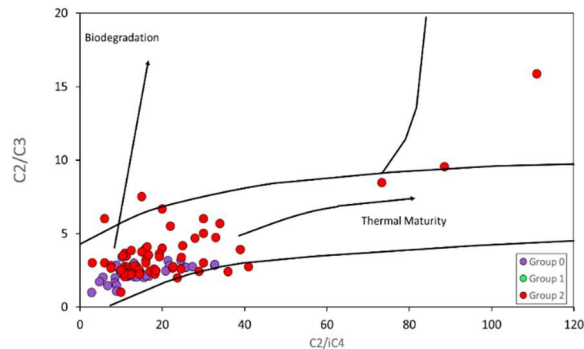


Figure 5 Cross plot of C2/isoC4 versus C2/C3 shows the relationship between increasing thermal maturity and biodegradation. N-alkenes are rapidly affected during biodegradation, leading to a high C2/C3 v C2/ isoC4 ratio. Group two shows higher thermal maturation, with four samples showing signs of biodegradation. Group 1 cannot be found in the plot since it is interpreted as a high-maturity dry gas and did not return any values for C3 and isoC4. Adjusted from Prinzhofer and Battani 2003.

group zero having low maturation of estimated vitrinite reflectance of less than 1.0 and predominantly produced from primary cracking (Figure 4). The adjusted relationship between C2 to C3 and C2 to iC4 indicates that the gas

samples collected are controlled by thermal maturity, with four samples showing signs of biodegradation (Figure 5).

### Conclusions

Three organic-rich type II – II/III source rocks were considered: the Simpson Group Shale, Woodford Shale, and the Barnett Shale/ Mississippian Limestone. Four oil genetic families were identified using chemometric methodologies, maturity analysis, and modeling. These four groups can be separated into the most mature oil samples (Simpson) and the least mature samples (Barnett/ Mississippian Limestone, Woodford). Gas chemometrics analysis identifies three distinct groups with varying maturity and migration. One of these groups, probably the most mature Group 1 or 2, can be correlated to be sourced from the Simpson Group Shale. Interpreted gas analysis showed that the gas samples came from primary cracking of type II and II-III source rocks, meaning the gas was cogenerated with the oil samples. Gas composition values show relatively low thermogenic maturity levels, indicating the samples' thermogenic preservation. Specific source rocks were tentatively linked to the genetic oil families identified in the Lower-Middle Paleozoic formations, setting the stage for advanced studies of secondary migration routes and trapping locations based on mapped permeable carrier beds facies and open structures framework according to the tectonic evolution superposed to the multistage Delaware basin.

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