

The Utilization of Carbazole and Benzocarbazole as Possible Indicators of Relative Migration Distances for Woodford Oils in the Anadarko Basin*

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Abstract

The organic nitrogen content of most oils ranges from 0.1 to 2.0%. Migration distance, thermal maturity and depositional environments can potentially affect the distribution of carbazole and benzocarbazole isomers in the oils. However, the extent of variation within these compounds during migration is still poorly understood. In this study, the relationship between the distribution of organic nitrogen compounds in Woodford oils and source rocks in the Anadarko Basin has been investigated. 22 Oil samples and 4 rock samples from the Woodford have been investigated. 12 Woodford oils and 1 rock sample are from the Pauls Valley-Hunton Uplift area and 10 Woodford oils and 3 rock samples are from the Cherokee Platform region. The maturity of oil samples from Pauls Valley-Hunton Uplift is in the range of 0.58 to 0.69 (R_c) estimated from the methylphenanthrene index (MPI). Such small range maturity variations minimize the maturity impact on the distribution of nitrogen compounds.

The content of nitrogen shielded carbazoles is low near the Anadarko Basin but high in the Pauls Valley-Hunton Uplift. The benzo-[a]/[(a)+(c)] - carbazole ratio (BC) is increasing from the Pauls Valley-Hunton Uplift to the Anadarko Basin. This trend suggests the migration pathway is from the center of the Anadarko Basin to the Pauls Valley-Hunton Uplift. Oil samples from the Cherokee Platform are produced from horizontal wells in the Woodford Shale. The maturity of the source rock and oils is higher than that of Pauls Valley-Hunton Uplift samples. The oils have a low abundance of both the carbazole and benzocarbazole isomers. Biomarker distributions indicate the organic matter input in Cherokee Platform is different from that in the Pauls Valley-Hunton Uplift. The organic facies might potentially affect the distribution of nitrogen compounds. Another possibility is that the Cherokee Platform oils have already migrated long distances, leading to a depletion of the carbazole and benzocarbazole isomers. Future work will focus on elucidating organic facies, depositional environments and maturity of these samples by studying aliphatic and aromatic compounds. Such research will potentially aid in the interpretation of migration pathways by using the distributions of carbazole and benzocarbazole isomers in the Anadarko Basin petroleum system.

Selected References

Larter, S., B. Bowler, M.Chen, D. Brincat, B. Bennett, K. Noke, P. Donohoe, M. Li, D.J. Simmons, M. Kohen, J. Allan, N. Telnaes, and I. Horstad, 1997, Chemical tracking of secondary oil migration: Petroleum Review London, v. 51; 601, Pages: 68-70.

Rascoe, B., and N.J. Hyne, 1988, Petroleum geology of the Mid-Continent: Tulsa Geological Soc., Special Pub. No 3.

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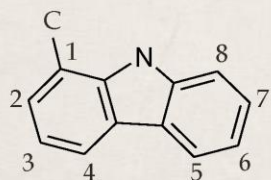
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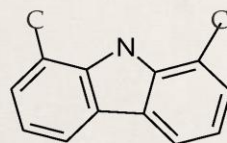
Outline

- * Research backgrounds
- * Geological setting in research areas
- * Pyrrolic compounds SMFI (Secondary Migration Fractionation Index) and migration distance
- * Pyrrolic compounds in suspected oil mixtures
- * Summary and Conclusion

Chemical Structures of Pyrrolic Compounds

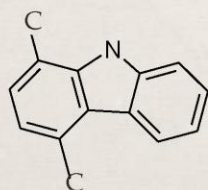


1- Methylcarbazole

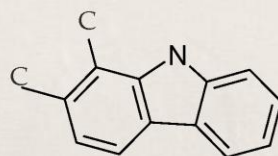


1, 8- Dimethylcarbazole

N-Shielded
Compounds



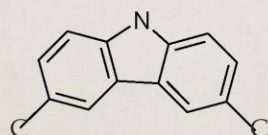
1, 4- Dimethylcarbazole



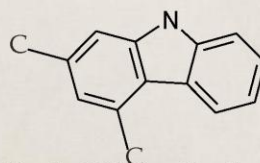
1, 2- Dimethylcarbazole



N Semi-Shielded
Compounds



3, 6- DimethylCarbazole



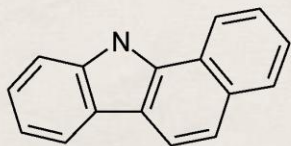
2, 4- Dimethylcarbazole



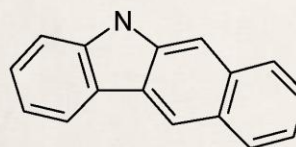
N-Exposed
Compounds

Presenter's notes: This is just a brief introduction of pyrrolic compounds chemical structures. When the hydrocarbon groups attached to the position right next to the nitrogen atom in the pyrrole ring, they are called n-shielded compounds. If there is only one methyl group attached to the position next to the nitrogen atom, then we call them semi-shielded compounds. If there is no hydrocarbon next to the nitrogen atom, then the nitrogen atom in the pyrrole ring is exposed so we call it n-exposed compound. Alkylcarbazoles present in oils undergo systematic fractionations. Comparing to others, N-Shielded alkylcarbazoles are more resistant to adsorption onto the surface of clay minerals. So we can use this in the relative migration distances determination.

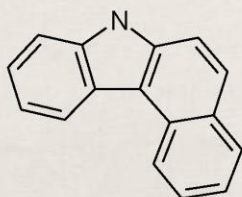
Chemical Structures of Pyrrolic Compounds



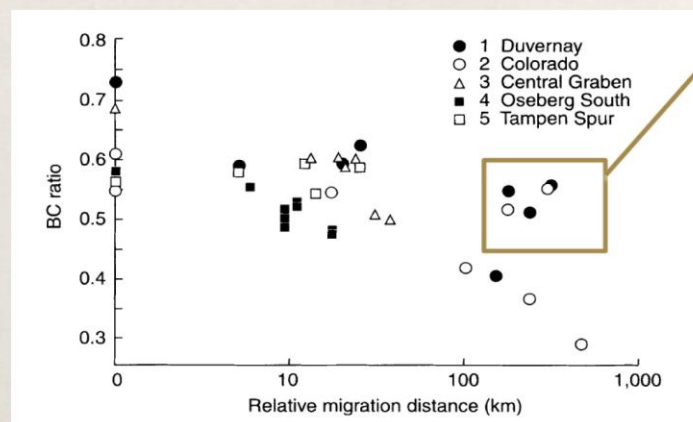
Benzo[a]carbazole



Benzo[b]carbazole



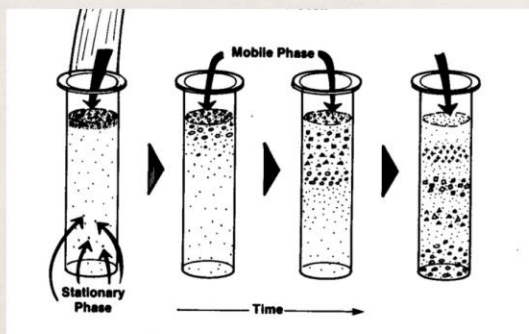
Benzo[c]carbazole



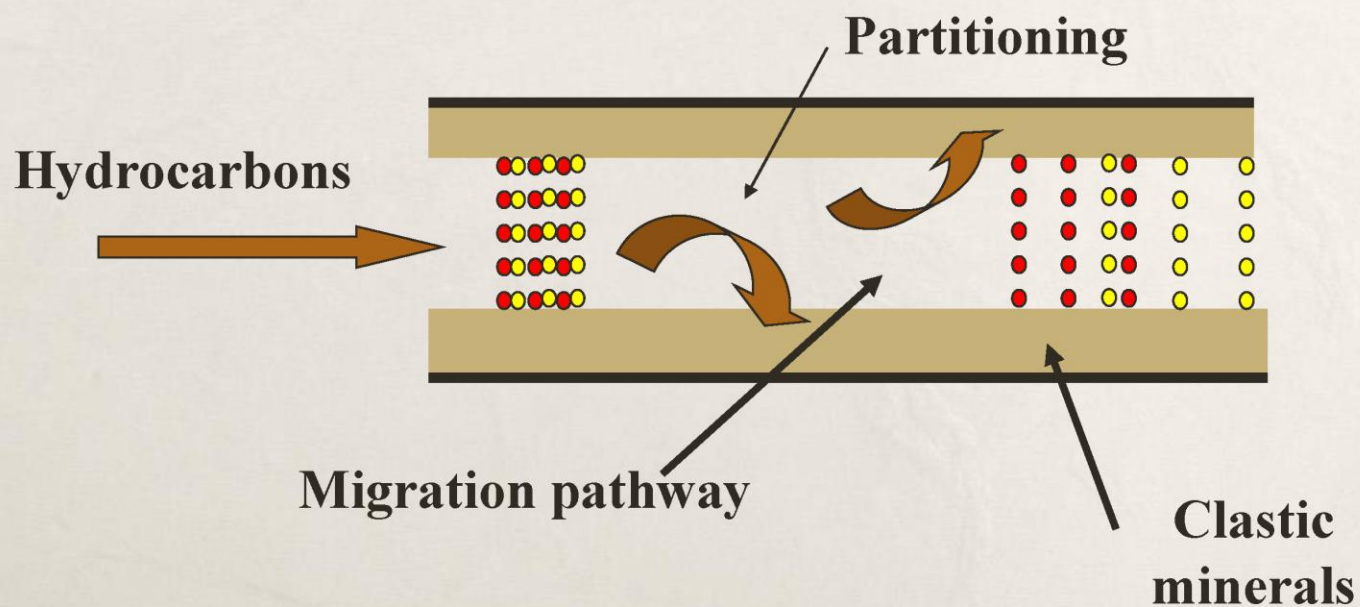
When migration distance is longer than 100 km, the absolute concentration of benzo[a+c]carbazole is very low ($< 0.16 \mu\text{g/g}$).

The BC ratio is benzo[a]carbazole / (benzo[a]carbazole + benzo[c]carbazole) (Larter et al., 1997).

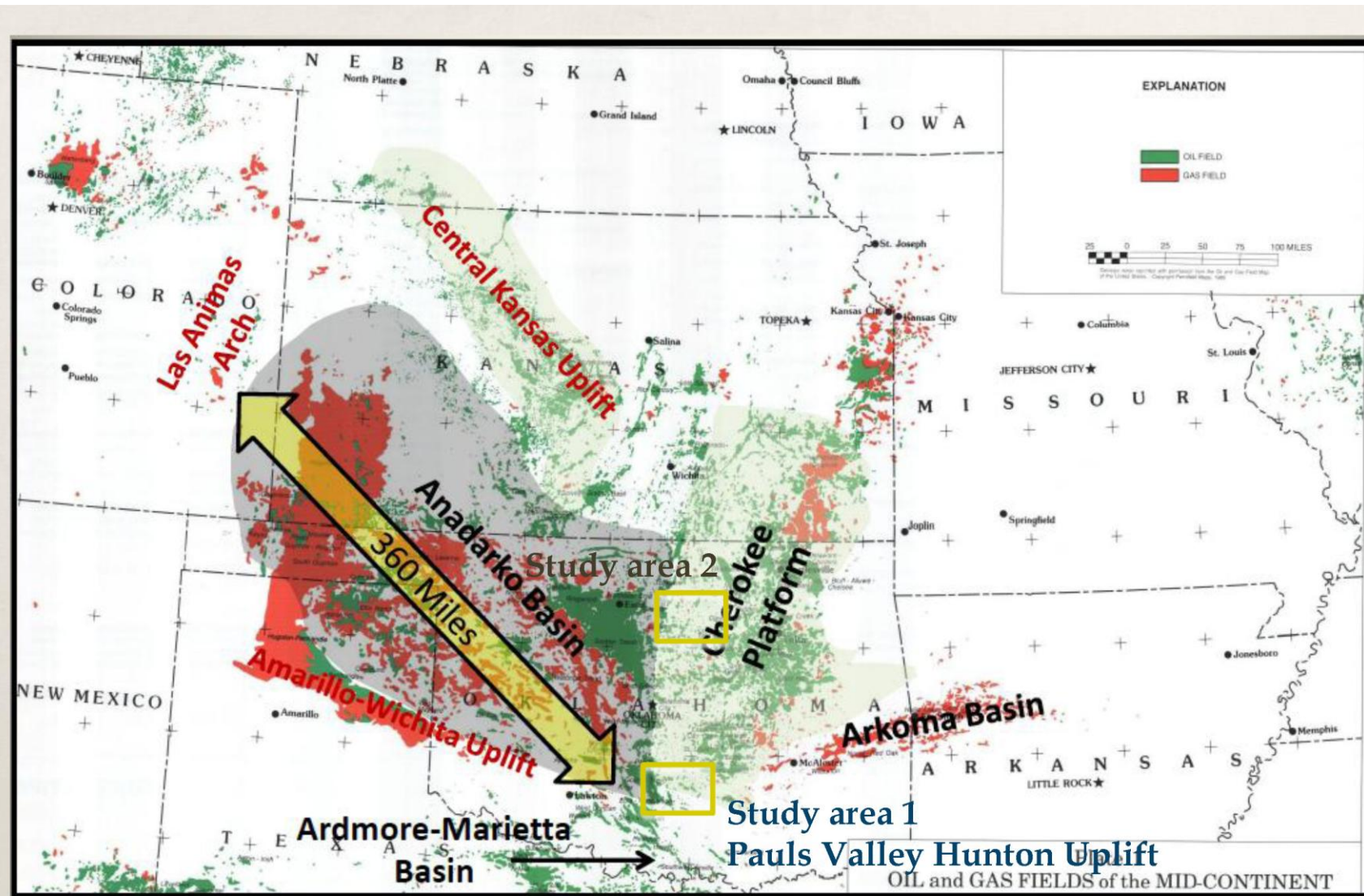
Presenter's notes: Benzocarbazole has three isomers distinguished by different positions benzene rings attached to the original carbazole. These compounds are believed also affected by clay mineral chromatographic absorption during migration. Specifically benzo[a] and benzo[c] carbazole, they are preferentially removed. Along the migration, the benzo[a] adsorption process is faster than the benzo[c]. Therefore, the BC ratio decreased when the migration distance is longer.



Extended Length Chromatography

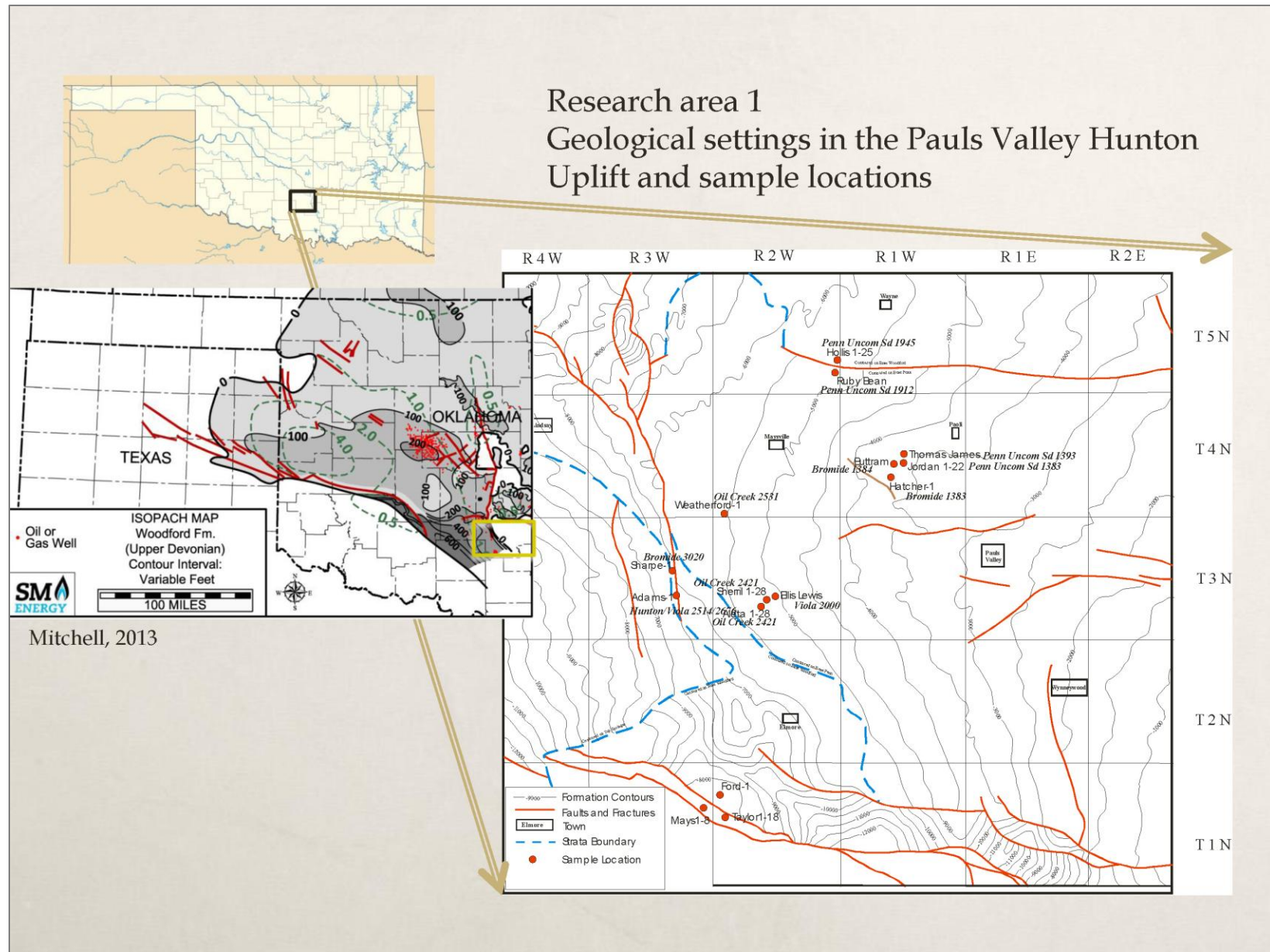


Presenter's notes: The process of hydrocarbons migration, which was talked by many other geochemists before, is just like an extended chromatography process. Different molecules were absorbed or retented selectively onto the clay minerals surrounded due to their different chemical and physical properties. So these molecules distribution can be an indication of the relatively migration distance, as long as we know they are from the same source.

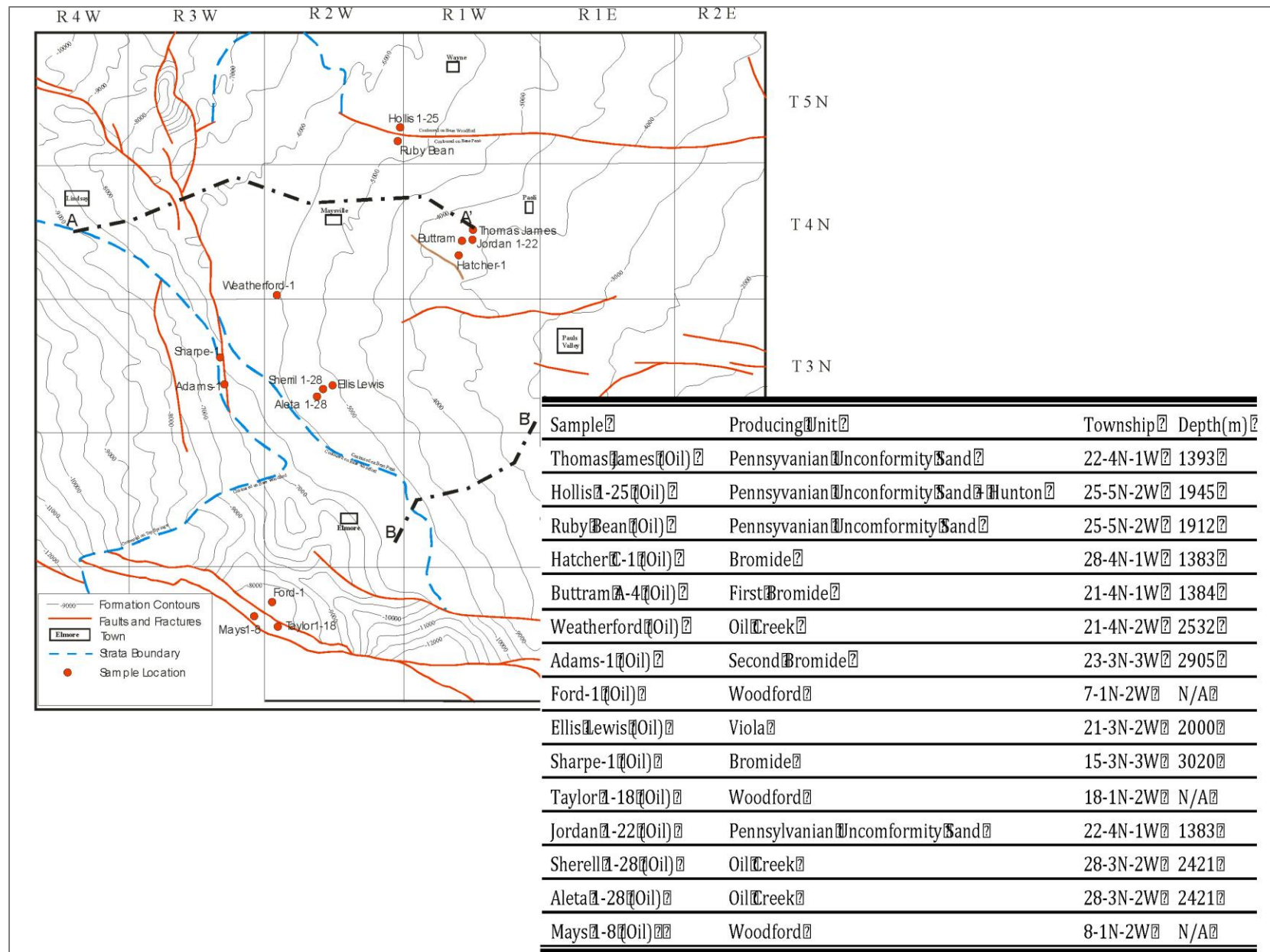


Regional geological settings map (Rascoe & Hyne, 1988).

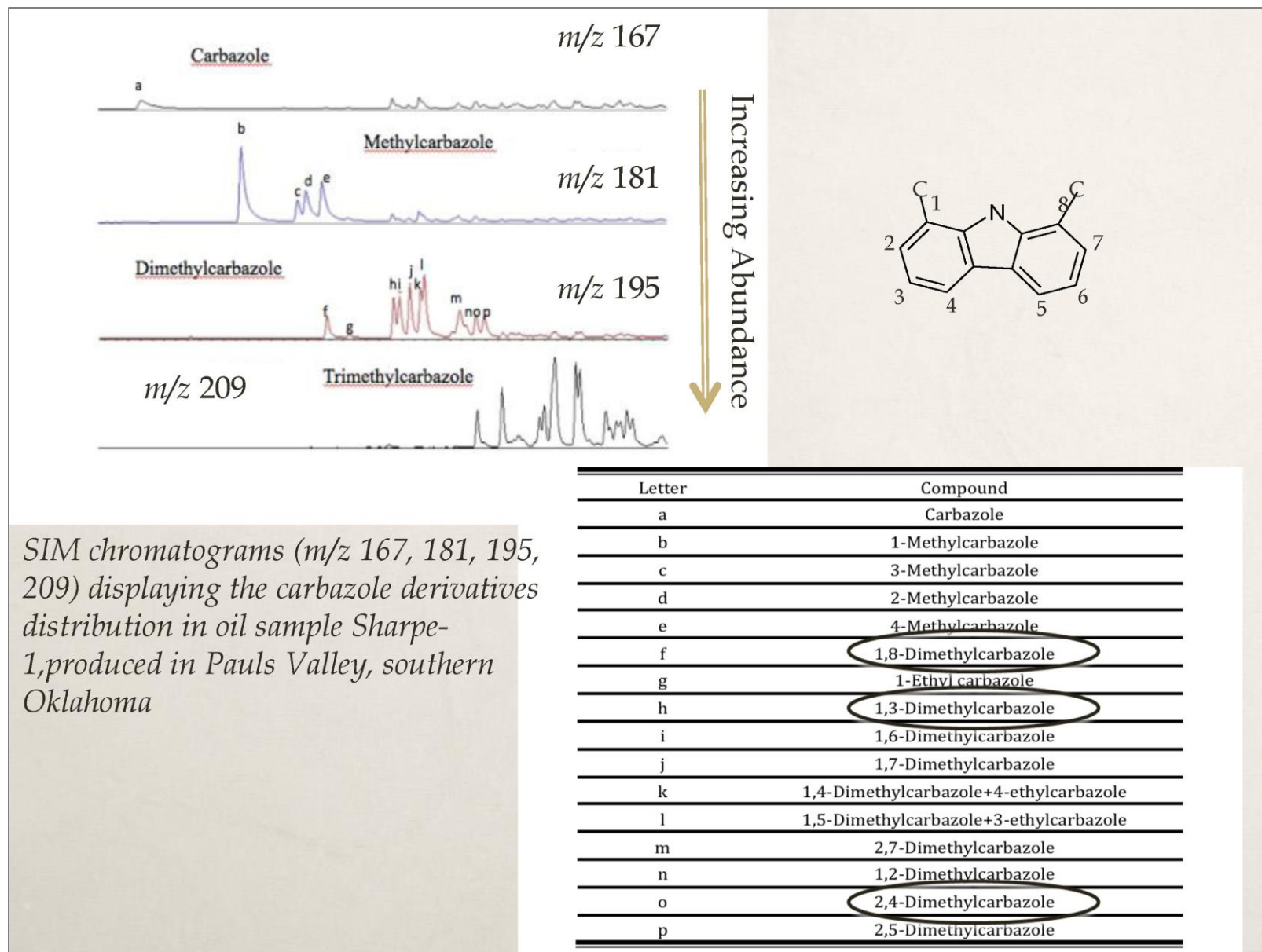
Presenter's notes: This is where Anadarko Basin and Cherokee platform are located in central US. The research area 1 is located in the Pauls Valley-Hunton Uplift, part of the Arbuckle Uplift. The boundary between the Anadarko Basin and Cherokee Platform is the Nemaha Fault. This fault is believed to be a major seal preventing the hydrocarbons from the Anadarko Basin migrating eastwards.



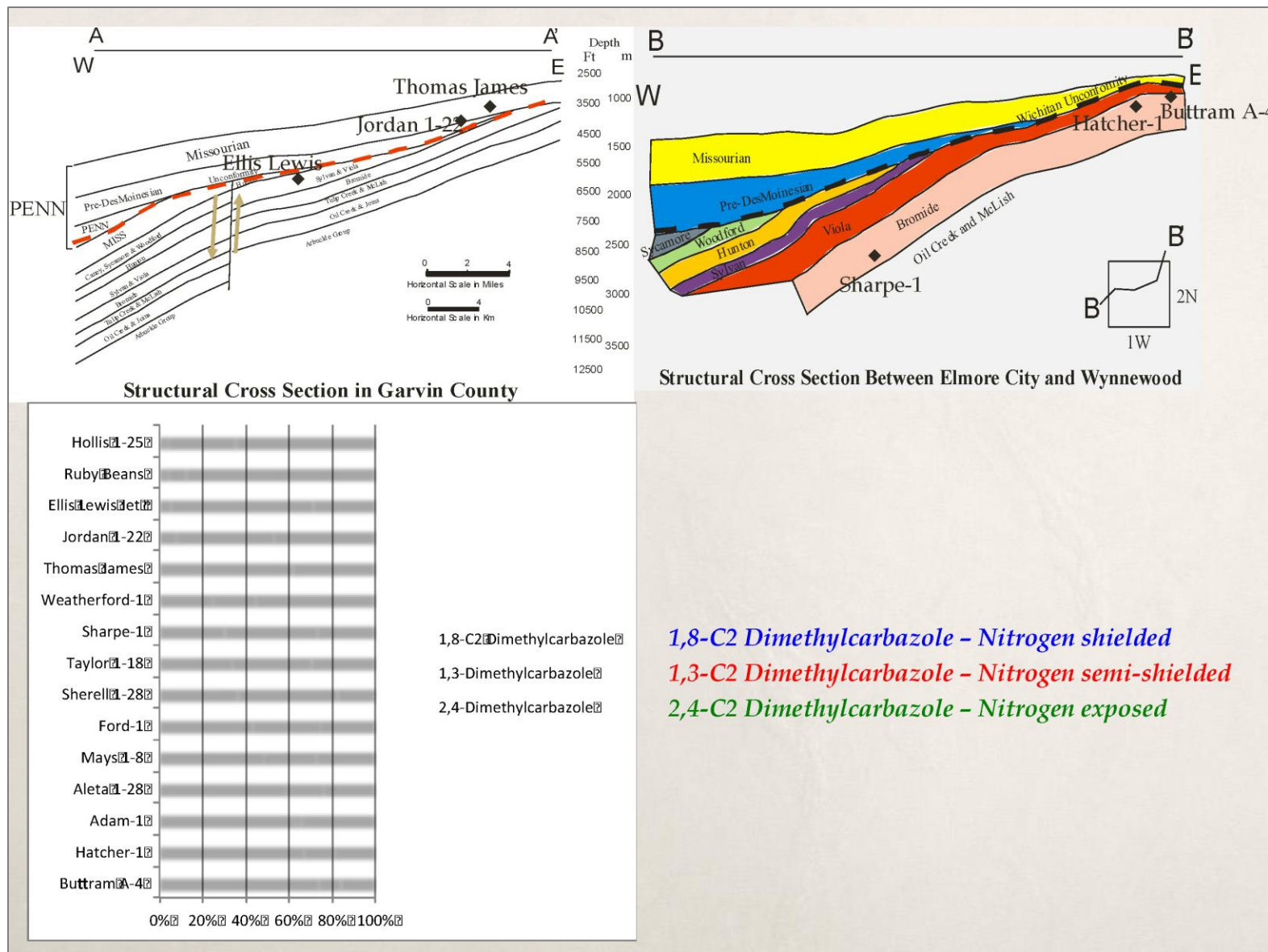
Presenter's notes: The map on the left is isopach map and maturity map of the Woodford Shale. The Woodford thickens rapidly to the southeast and exceeds 600 feet in thickness in southern Oklahoma. The over-mature shale is located in the deep center of Anadarko Basin. Pauls Valley-Hunton Uplift is located in the northeastern part of the 600-foot thick Woodford formation area. However, the Woodford Formation is absent in the Pauls Valley-Hunton Uplift region. The red lines are the faults and the blue dash line is the strata boundaries.



Presenter's notes: There are two cross sections we made in this area, which are the black lines. Red line delineated the faults and blue lines is the boundary of different stratigraphy formations. Woodford Shale is absent where the Pennsylvanian sandstone dominated. Previous biomarker research of these oils were conducted by Jones, twenty years ago, verified that these oils were sourced from the Woodford Shale. This is the producing unit of each oil sample. Oils here are from conventional sandstone reservoirs.



Presenter's notes: This is the selected ion chromatogram of the pyrrolic compounds in the oils from Pauls Valley. N-shielded, semi shielded and exposed compounds are all labeled on their peaks. This oil, whose name is Sharpe-1, has clearly relatively higher contents of nitrogen shielded compounds. The abundance of homologue compounds group increases as the methyl groups increase, such a phenomenon is characterized as a typical marine sourced oil pattern. We chose 1,8 Dimethylcarbazole, 1,3 Dimethylcarbazole, and 2,4 Dimethylcarbazole to represent shield/semi shield and exposed compounds to compare migration distances.



Presenter's notes: The Woodford Shale oils were generated in the deeper basin and migrated into different formations. Because that different sandstones layers were divided by multiple seals, normally there is no contact or mixture between them. So the individual migration system is independent and consistent. Although they are all sourced from the Woodford Shale, the distribution of pyrrolic compounds will be varied in different formations independently because of different migration patterns. Therefore we compare the oils from same the formations or from connected formations. So we chose two migration systems, one is Viola-Pennsylvanian migration system, the other is the Bromide Sandstone system.

SMFI: Secondary Migration Fractionation Index

$$C = a_1 (1 + a_2 R_0) e^{a_3 x}$$

C: Concentration of Selective Compounds (µg/g)

R_0 : Vitrinite Reflectance or Equivalent

x: Migration Distance (km)

a_1 a_2 & a_3 : Constants

Alkylcarba- zoles	$\ln C = \ln[a_1 (1 + a_2 R_0)] + a_3 x$		
	a_1	a_2	a_3
1-MCA	0.70	49.93	-0.032
1,2-DMCA	91.66	-1.00	-0.047
1,3-DMCA	7.15	6.00	-0.029
1,6-DMCA	86.60	-0.62	-0.036
1,7-DMCA	143.41	-0.72	-0.040
2,4-DMCA	0.47	52.85	-0.034
2,5-DMCA	50.60	-0.57	-0.039
2,7-DMCA	196.16	-1.02	-0.046

MCA: Methylcarbazole

DMCA: Dimethylcarbazole

Constants of SMFI calculated from Xifeng Oilfield of the Ordos Basin ($R_0 = 0.6(MPI) + 0.37$)

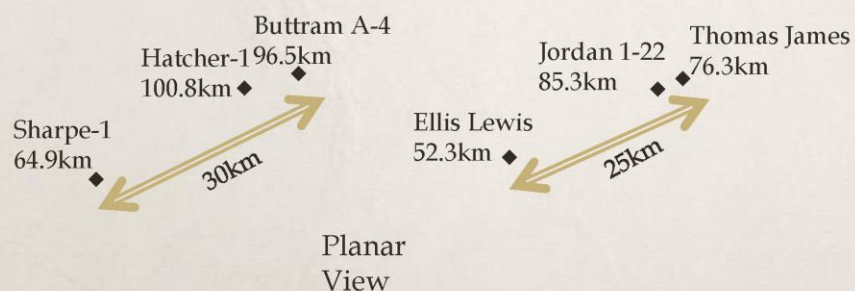
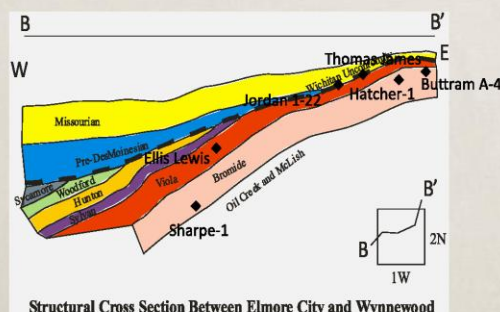
Zhang et al., 2013

Presenter's notes: This formula can be applied to the single-dimensional migration system and these three constants were calculated from the basin called Ordos in China. Different compounds has different constants depending on their chemical properties. We cited his constants and applied them in the Woodford oils in Pauls Valley Hunton Uplift.

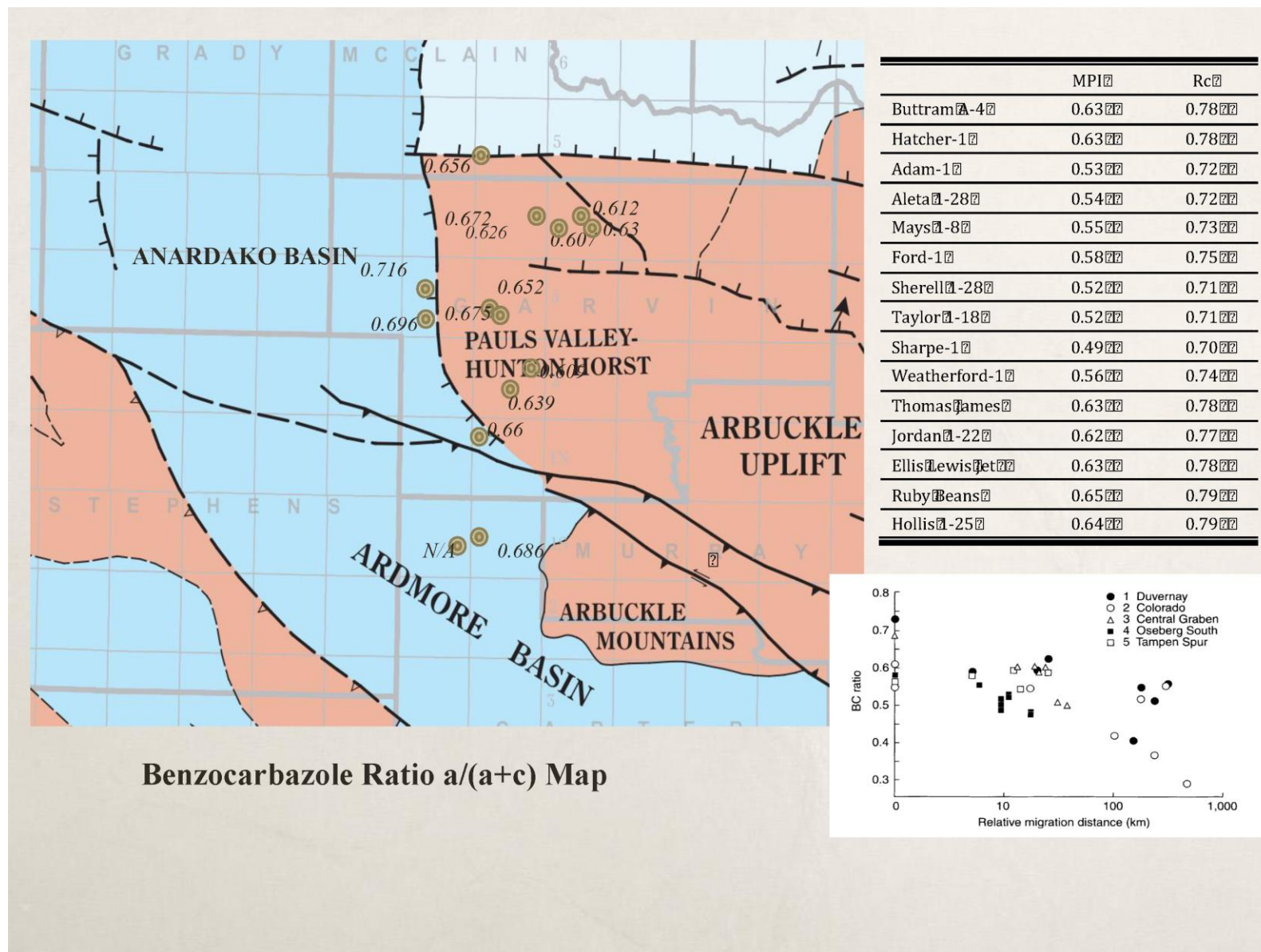
Migration System 1		X (km)									
Sample Name	Producing Units	MPI	R ₀	X	X	X	X	X	X	X	X
				(1-MC)	(1,3-DMC)	(1,6-DMC)	(1,7-DMC)	(2,7-DMC)	(1,2-DMC)	(2,4-DMC)	(2,5-DMC)
Sharpe - 1	Bromide	0.53	0.69	49.66	80.12	68.41	63.71	69.21	63.18	60.49	64.62
Hatcher - 1	Bromide	0.63	0.75	112.15	117.00	117.01	155.64	83.41	87.73	68.40	65.33
Buttram A-4	Bromide	0.63	0.75	114.94	123.89	115.17	125.33	76.50	71.96	72.69	71.87

Migration System 2		X (km)									
Sample Name	Producing Units	MPI	R ₀	X	X	X	X	X	X	X	X
				(1-MC)	(1,3-DMC)	(1,6-DMC)	(1,7-DMC)	(2,7-DMC)	(1,2-DMC)	(2,4-DMC)	(2,5-DMC)
Ellis Lewis Jet	Viola	0.63	0.75	41.50	61.18	51.63	50.52	49.24	52.96	55.31	56.40
Jordan 1-22	Pennsylvanian Sand	0.62	0.74	81.64	114.94	101.31	95.24	69.49	72.13	75.68	72.32
Thomas James	Pennsylvanian Sand	0.63	0.75	73.63	104.94	83.27	74.73	70.36	65.08	70.43	67.73

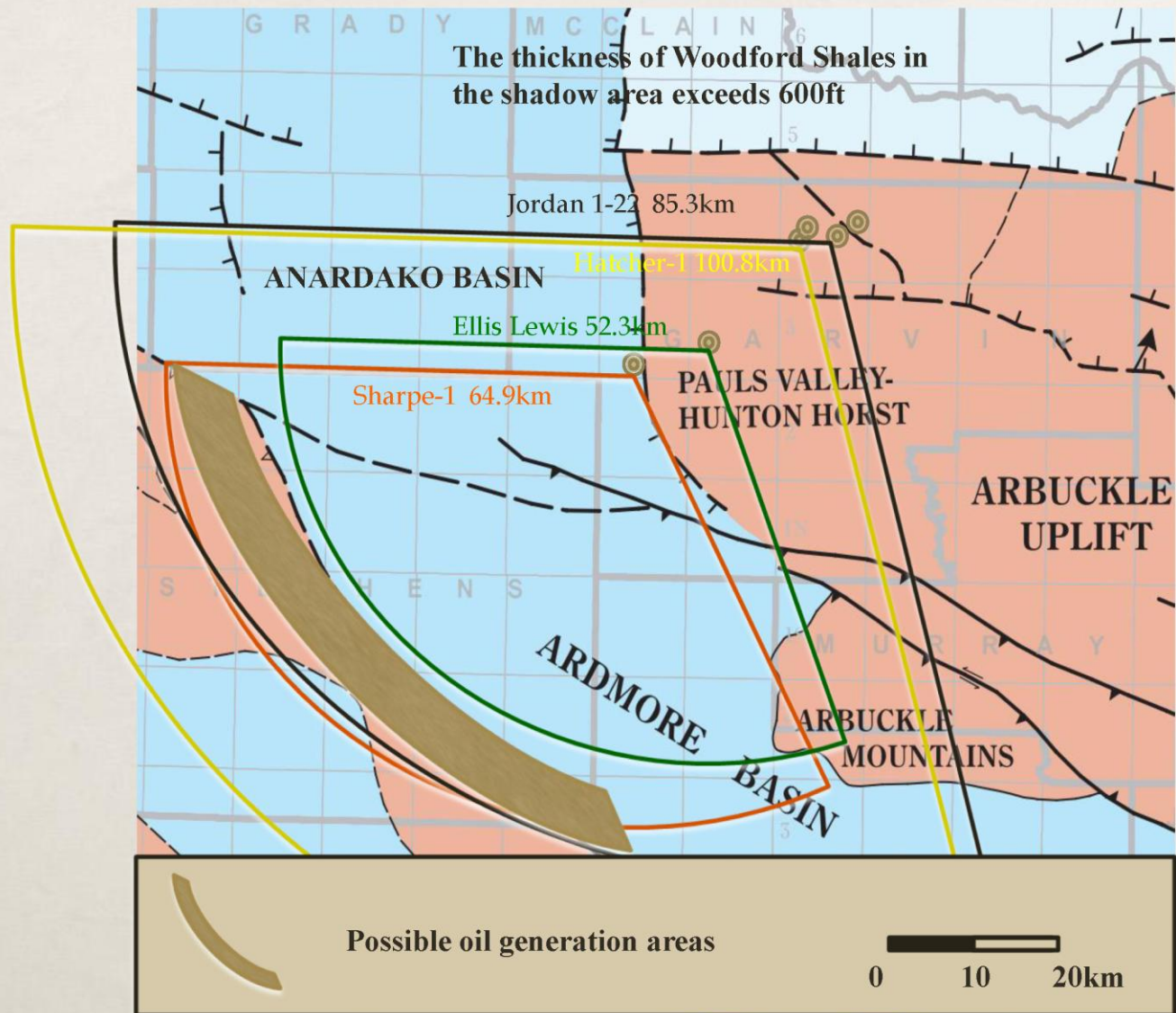
X (km)	X (Sharpe - 1)	X (Hatcher - 1)	X (Buttram A-4)	X (Ellis Lewis)	X (Jordan 1-22)	X (Thomas James)
Mean	64.9250	100.8338	96.5438	52.3425	85.3438	76.2713
N	8	8	8	8	8	8
Standard Deviation	8.60812	30.33753	25.20128	5.79121	16.61094	12.80341



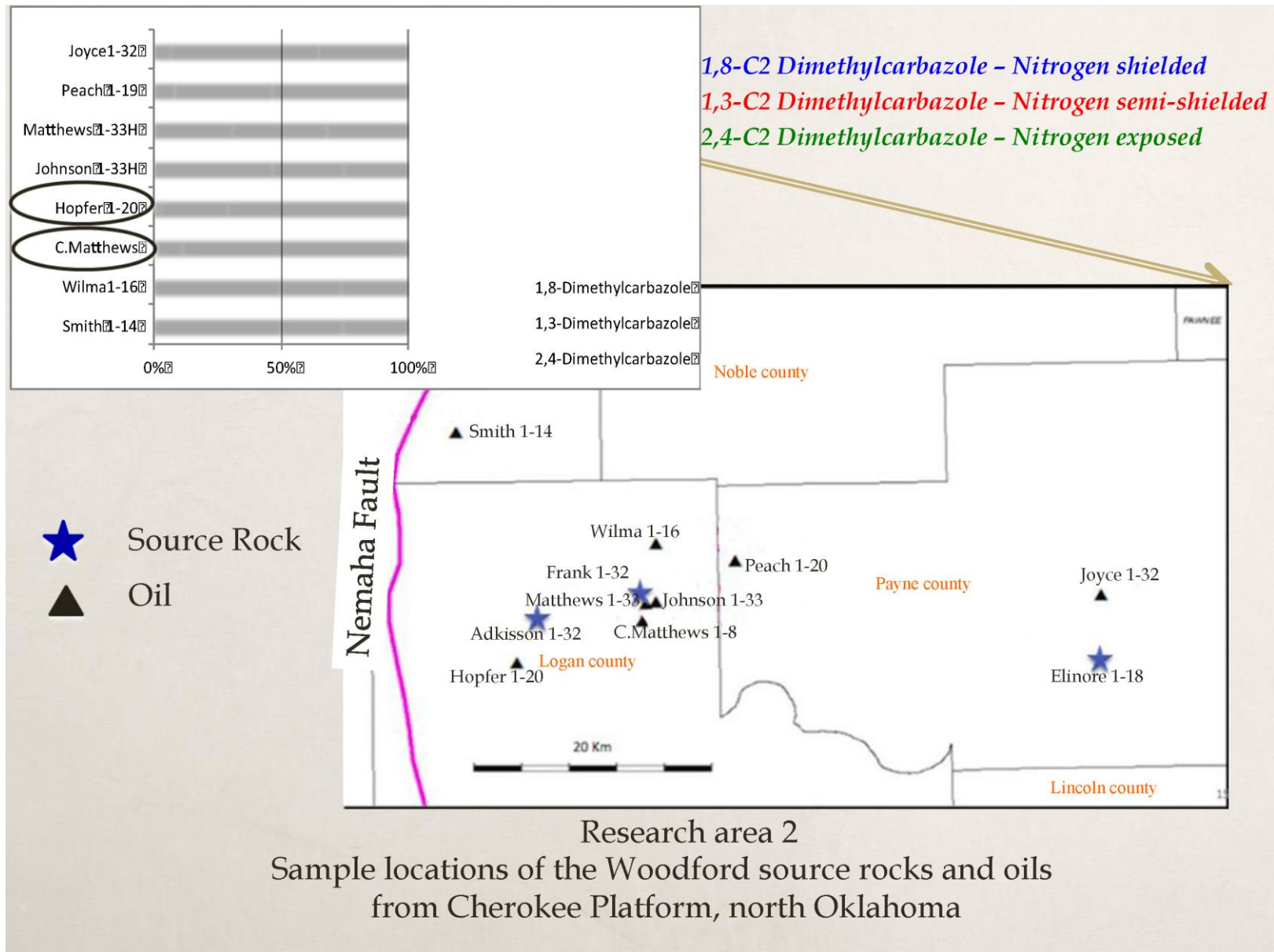
Presenter's notes: We used 8 different compounds to calculate the migration distance of one oil sample. And all these compounds are insoluble in water and will be significantly affected by migration process. Clearly we can see that the result is corresponding with the formal conclusion that these oils migrated from southwest to northeast. Although on the planar view, the linear distance between each oil sample is shorter than the calculated results, it is reasonable to imagine that most oils migrated through a curved pathway. Additionally, if we move another 50 km westwards indicated by the SMFI calculated results, the initiated migration point were located in the thickest Woodford Shale area, in the deeper basin region of the Anadarko Basin or Admore Basin.



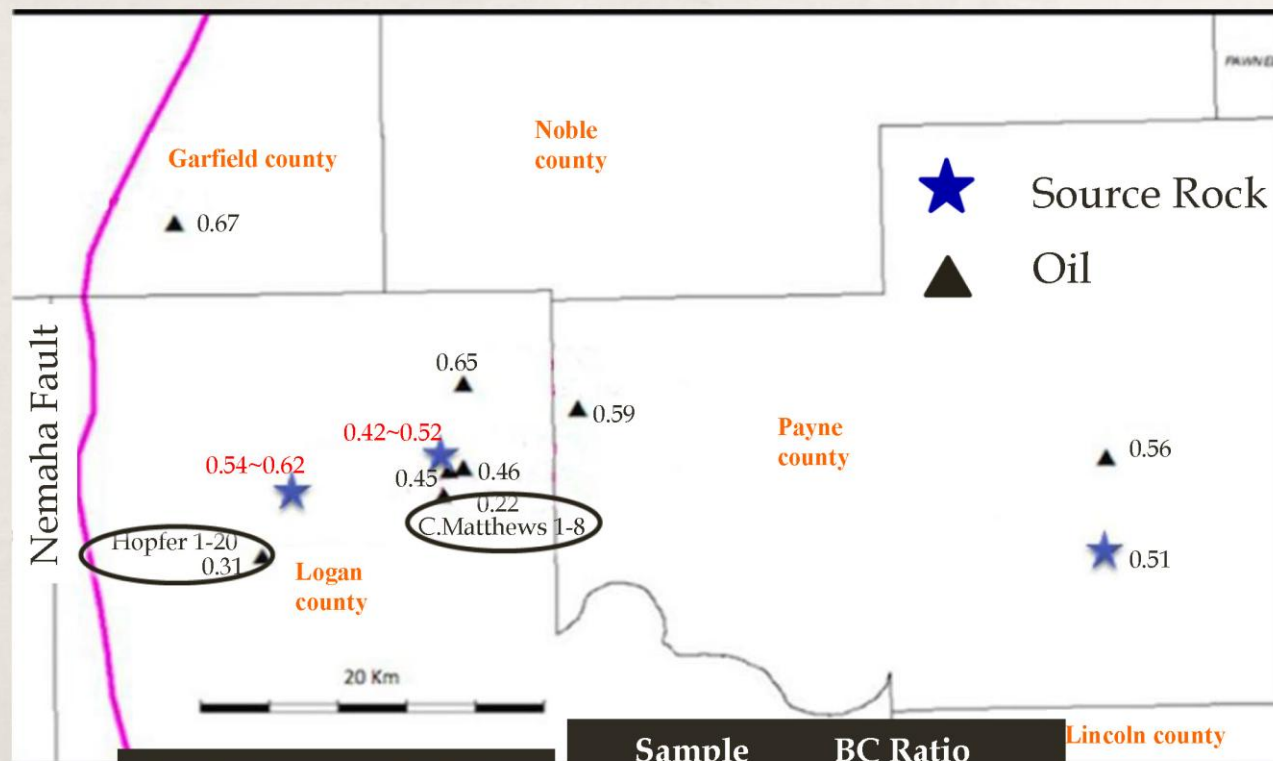
Presenter's notes: Moreover, this conclusion is also substantiated by the BC ratio of benzocarbazoles. We can observe that the BC ratio is decreasing towards the Pauls Valley-Hunton Uplift, which is part of Arbuckle Uplift. The BC ratio cannot be used to calculate a specified number of migration distance. However, we can estimate the migration distance is no longer than 100 km based on previous research in other basins. The equivalent vitrinite reflectance was calculated by methyl phenanthrene index. The maturity variation is limited, so it is unlikely these pyrrolic compounds ratios are affected by maturity.



Presenter's notes: If we traced these samples back by the distance we calculated before, it is clearly that the overlapping areas are highly possible for the original source of these oils. Additionally, these areas are the thickest area of Woodford Shale, which means they exceed 600 ft.



Presenter's notes: This is research area 2, located in the Cherokee Platform, east of the Nemaha Fault which is sealing the hydrocarbon. These oils are tight oils produced directly from the Woodford Shale Formation. Differing from the oils from southern Oklahoma, these oils are produced from unconventional reservoirs. We examined their biomarkers as well as the pyrrolic compounds distribution and we observe that kind of more random distribution instead of a nice migration direction indicators. However, what we found is two oil samples nitrogen compounds data deviated from the majority which are not far from them.



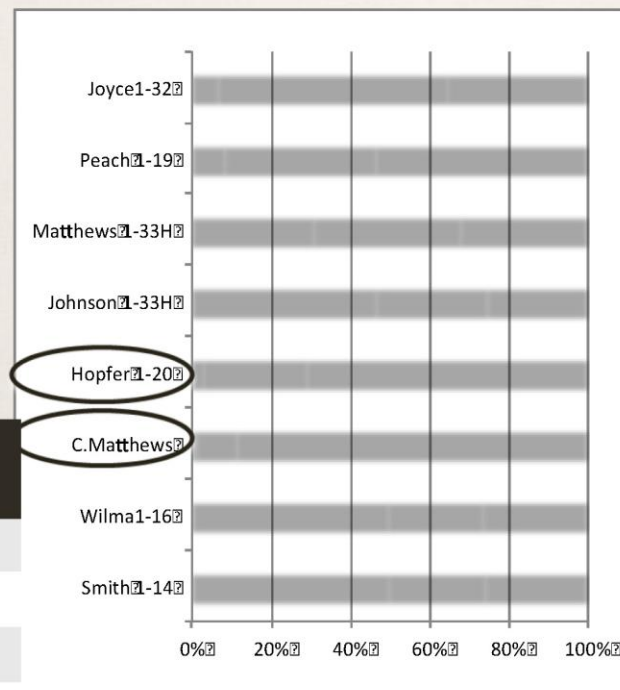
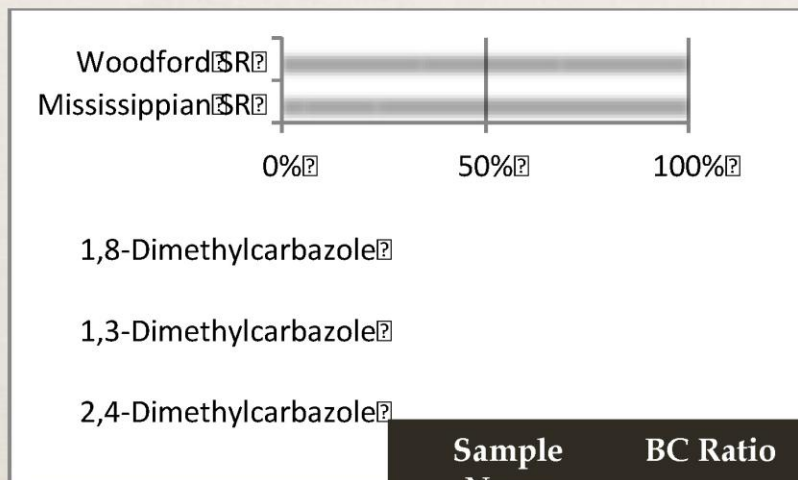
Woodford Source Rock Name	BC Ratio
Adkisson 1-32	0.54 ~ 0.62
Frank 1-32	0.42 ~ 0.52
Elinore 1-18	0.56

Sample Name	BC Ratio
Joyce1-32	0.56
Peach1-19	0.59
Matthews1-33H	0.45
Johnson1-33	0.46
Hopfer1-20	0.31
C. Matthews1-8	0.22
Wilma1-16	0.65
Smith1-14	0.67

Presenter's notes: These two oil samples, Hopfer 1-20 and C. Matthews 1-8 are located in the south, lower BC ratio and extreme low contents of nitrogen shielded compounds. Quite different from those samples produced close to them.

Unconventional reservoirs — — Research area 2 (Cherokee Platform)

High Porosity, Low Permeability



Woodford Source Rock Name	BC Ratio
Adkisson 1-32	0.54 ~ 0.62
Frank 1-32	0.42 ~ 0.52
Elinore 1-18	0.56
Mississippian Rock Name	BC Ratio
Alk-11	0.29

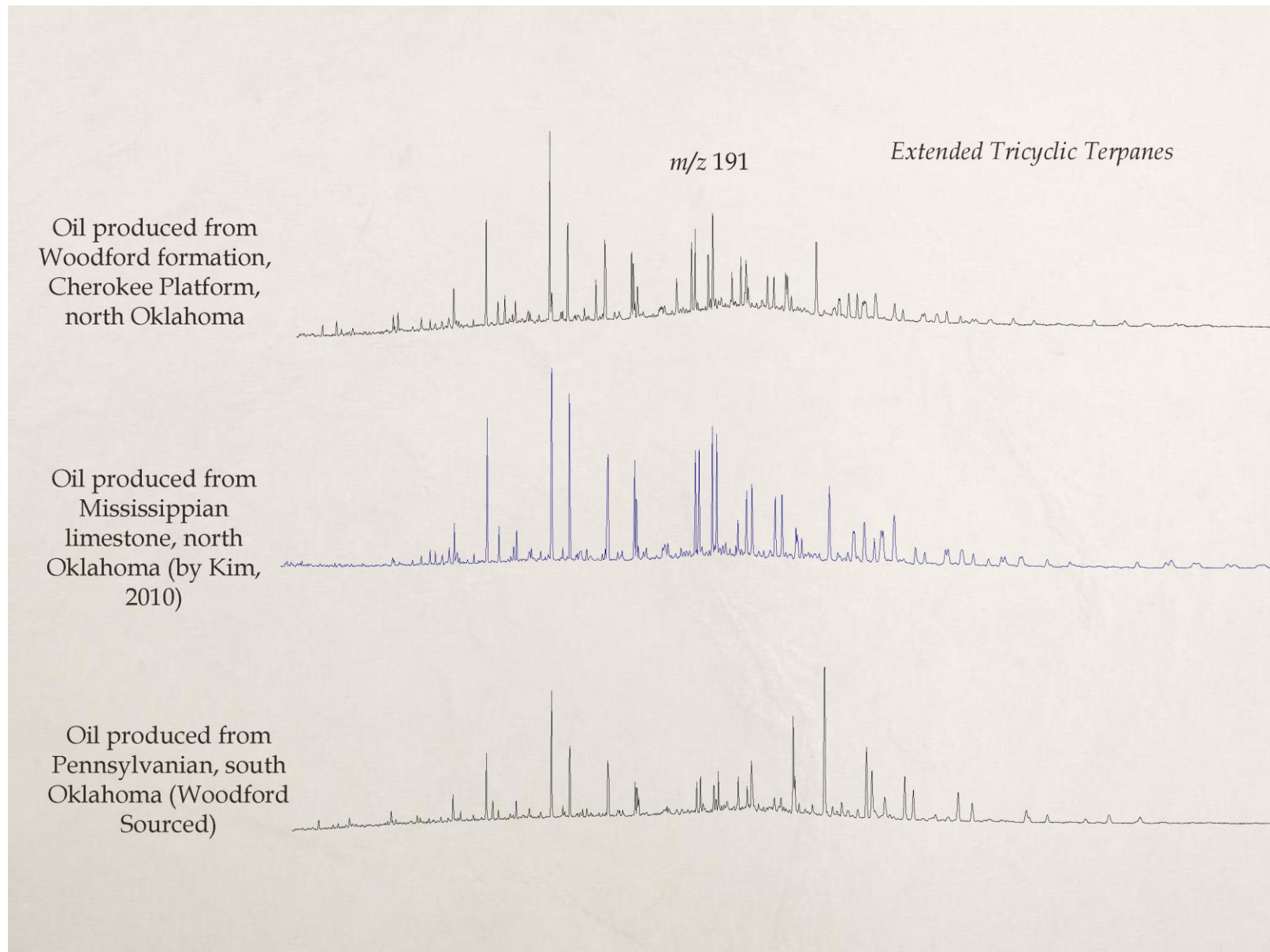
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Johnson1-33	0.46
Hopfer1-20	0.31
C. Matthews1-18	0.22
Wilma1-16	0.65
Smith1-14	0.67

1,8-C2 Dimethylcarbazole - Nitrogen shielded

1,3-C2 Dimethylcarbazole - Nitrogen semi-shielded

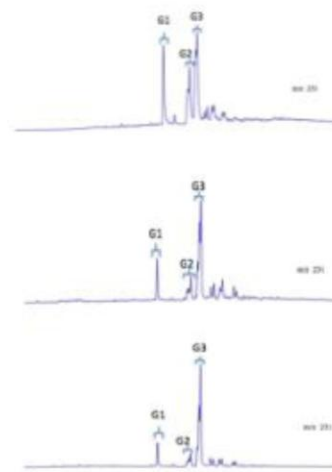
2,4-C2 Dimethylcarbazole - Nitrogen exposed

Presenter's notes: Previous pyrolysis research showed that the methylcarbazoles precursors are believed to be multiple sources, different bacteria and algae. They are not representing a specific source input. However, in unconventional reservoirs the permeability is quite low and chromatographic fractionation is not likely to happen. Therefore, these pyrrolic compounds distribution is highly possible original distributions. So the differences between Woodford and Mississippian oils pyrrolic compounds might be a tool to correlate oils.



Presenter's notes: We took a look at the SIM 191 of oils produced from Cherokee Platform, Pauls Valley and Mississippian Limestone. It is clear that the bottom one has a much lower abundance of tricyclic terpanes than the others. It is a typical Woodford oil hopane chromatogram. Mississippian Limestone oils are characteristic in their high abundance of tricyclic terpanes. Then, oils produced from Cherokee Platform exhibited somehow higher abundance of tricyclic terpanes than typical Woodford oils. So we suspected that the tight oils produced from Cherokee Platform might be a mixture of Woodford oils and Mississippian limestone oils.

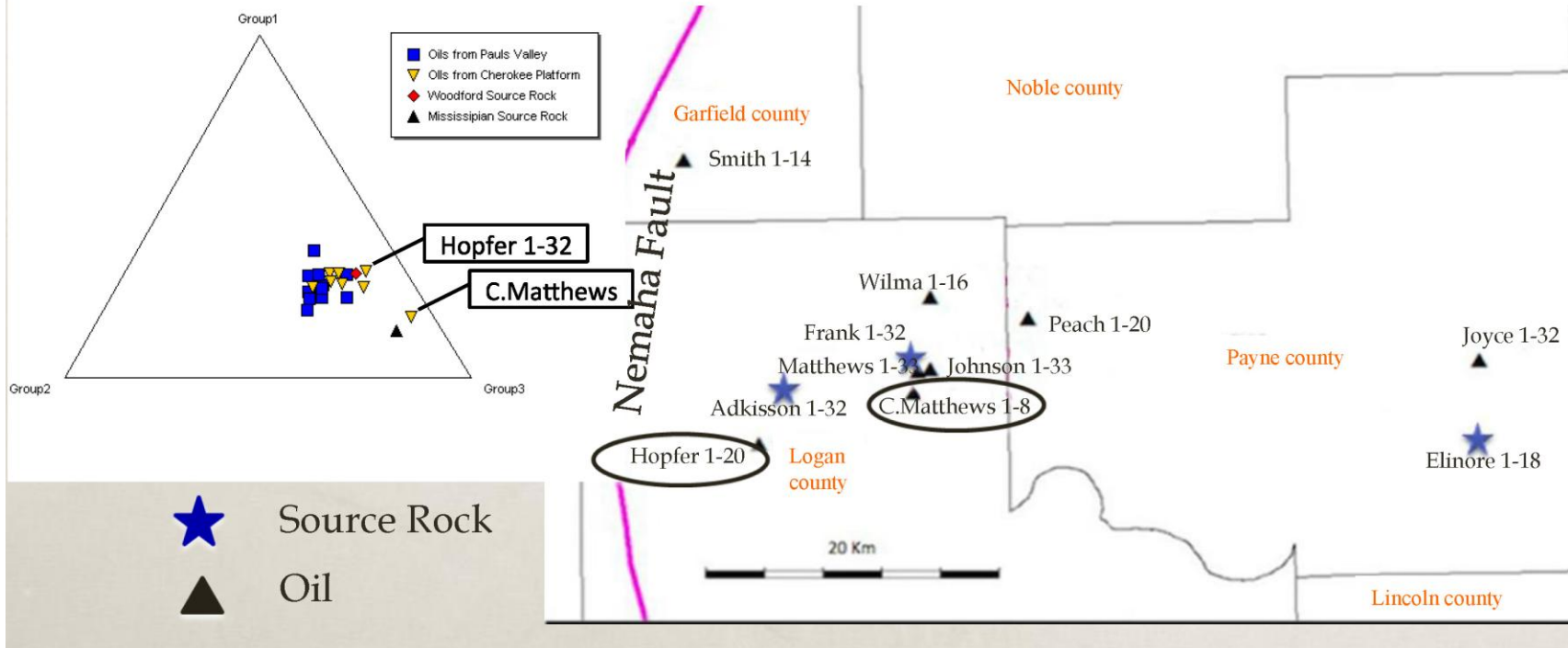
Methylbenzocarbazole (m/z 231) as a potential indicator of different sources



Woodford Oils from Pauls Valley

Woodford Source Rock from Cherokee Platform

Mississippian Limestone Sourced



Presenter's notes: We also observed that the methylbenzocarbazoles can be seen as three different groups based on different polarity and retention time in GCMS. We divided them as three groups and we observed that different source rocks exhibited different methylbenzocarbazole distributions. Clearly, the C. Matthews sample is more close to the Mississippian source-rock.

Conclusions

- ★ Woodford oils in Pauls Valley Hunton Uplift, southern Oklahoma were produced from the Anadarko Basin and Admore Basin, migrated eastward.
- ★ Oils in the Cherokee Platform, northern Oklahoma might be mixture from Mississippian and Woodford source rocks.
- ★ Pyrrolic compounds can be a good tool to determine migration distance in conventional reservoirs.
- ★ SMFI is capable of specifying and calculating migration distance in conventional reservoirs.
- ★ Organic nitrogen compounds in oils from unconventional reservoirs might help correlating oils and source rocks.

Acknowledgement

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