

PETROLEUM GENERATION KINETICS OF THE SIRTE BASIN

**Regional Evaluation of the Kinetic Properties of
the Petroleum Systems of the Sirte Basin**

GEOMARK** ■ **HUMBLE****



PETROLEUM GENERATION KINETICS OF THE SIRTE BASIN

GeoMark Research and Humble Geochemical have initiated a regional kinetics study of the Sirte Basin. This study will assess the thermal history of the basin by determining the kinetic properties of a large group of oil samples distributed throughout the basin (Appendix A). The study is being offered on a non-exclusive basis to participating companies.

The purpose of this study is to assess the kinetic parameters characteristic of each of the source rock units identified in previous studies of the Sirte Basin. Knowledge of the timing and character of petroleum formation is crucial to understanding petroleum system development of each of these four units and assess the commercial importance of each oil family. The kinetics of the petroleum asphaltene fraction is used to determine the temperature conditions of the source units at the time of generation/expulsion in this study. By combining the kinetic based generation/migration history to the distribution of oil the families, we will construct a better model of the timing, phase composition, and regional distribution of the various petroleum systems. Appendix B offers a detailed explanation and validation of the asphaltene kinetic technique to be used in this study.

In previous studies we have accomplished the following:

- Determined the number of genetically distinct oil families in the basin.
- Mapped the stratigraphic and geographic distribution of each oil family.
- Utilized geochemical characteristics of the oil families to deduce their source facies, thermal maturity level, and degree of preservation.
- Correlated each oil family to a specific stratigraphic unit.

Kinetic results will be combined with the interpretation outlined above to accomplish the following:

- Calibrated generation models using measured expulsion temperatures, biomarker ratios, light hydrocarbon ratios, kinetic models (both discrete and Gaussian) including non-first order reaction parameters.
- Determine the timing of hydrocarbon generation within each of the graben centered source kitchens.
- Determine the timing of hydrocarbon generation for the bulk conversion of organic matter to hydrocarbons and into specific hydrocarbon types (gas versus oil).
- Determine the relationship between oil quality and thermal maturity.
- Predict oil properties at different maturity levels (for example, GOR, API gravity, wax content, and light hydrocarbon characteristics)

The study will be completed by the first quarter of 2005. The cost of the study is US \$42,500.

INTRODUCTION

Asphaltene kinetics are an improvement on the conventional practice of determining kinetic parameters of organic matter (OM) taken from immature source rock samples (di Primio et al., 1999; Jarvie et al., 2004). Asphaltene fractions may more closely reveal the specific thermal history and chemical properties of an oil. The analysis of a suite of oils reflects regional organofacies and thermal variations within single sources across the basin.

Bulk kinetic parameters describe OM decomposition to hydrocarbons without any description of the oil and gas content. These data will be used to determine the timing of hydrocarbon generation and expulsion related to the availability of migration pathways, traps, and seals. Humble utilizes a single run kinetic analysis with fixed Arrhenius constant to screen samples and multiple heating rate analysis for rigorous determination of the best Arrhenius constant and activation energy distribution.

Compositional kinetics describe OM decomposition into dry gas, wet gas, condensate, and black oil as well as coke formation. These data will provide specific information on the type and yield of hydrocarbons generated from each source unit across the basin. Results predicted from the bulk kinetic analyses can be compared to observed distribution of oils. Differences between predicted and observed can potentially be useful to future exploration in the basin.

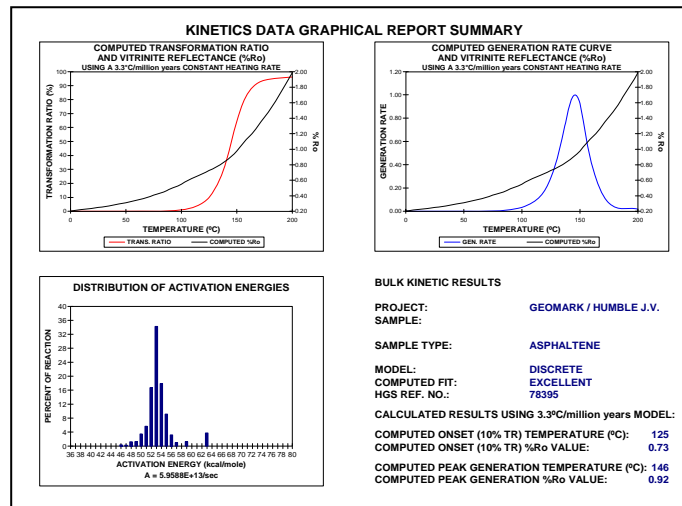


Figure 1. Kinetic results from an asphaltene cut of a Sirte Shale source oil.

Closed-system pyrolysis will be used to measure the specific composition at various levels of thermal maturity on a select suite of samples. These data will be comparable to hydrous pyrolysis composition and yields, but will be completed on very small amounts of asphaltenes using micro-sized quartz tubes with micro-sized mass of oil asphaltenes. A fully generated oil fingerprint will be obtained including gas, light hydrocarbons, intermediate range hydrocarbons, and biomarker geochemistry. These data will allow assessment of pristine oil compositions at different maturity levels. Analysis of the predicted compositions to observed compositions can add substantially to an interpretation of oil genesis in the basin. Any improvement in this kind of knowledge can contribute to the identification of new exploration opportunities.

OBJECTIVES

GeoMark's 1993 study of the Sirte Basin demonstrated that at least four distinct source rock units have generated the oil produced across in the Sirte Basin. Subsequent works have independently supported this interpretation (Burwood et al., 2003 and Humble, 2001). The geographic distribution of these families with respect to regional structural highs and lows is shown in Figure 2.

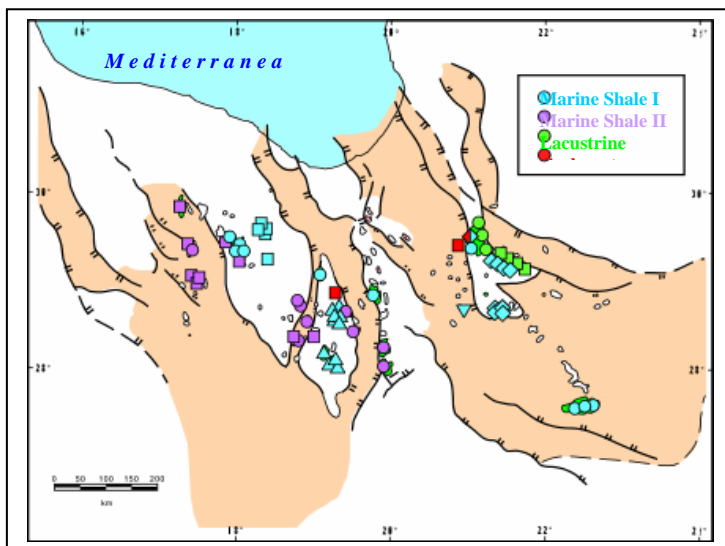


Figure 2. Distribution of oil families shown with structural graben patterns (GeoMark Sirte Basin Study, 1993).

We propose to extend the understanding of the origin of petroleum systems in the Sirte Basin by performing a regional kinetics study. This will enable us to make regional predictions of the relative timing and composition of generated hydrocarbons. The main objectives of this study are outlined in the following.

- Use new oil samples to refine and expand identification of petroleum systems present in the Sirte Basin (source numbers and maturity ranges)
- Critically describe the nature of source rock compositions based on range of organofacies implied by bulk kinetics differences for each oil family
- Characterize the expected compositional yield(s) for the source rocks for each oil family (wet gas, dry gas, condensate, black oil, and coke)

ANALYTICAL PROGRAM

In this study, we will analyze 100 samples for screening kinetics, 30 samples for full bulk kinetics, and 6 samples for compositional kinetics. This will allow us to offer a regional assessment of the timing of hydrocarbon generation and provide detailed predictions of both the geographic and stratigraphic distribution of hydrocarbon type

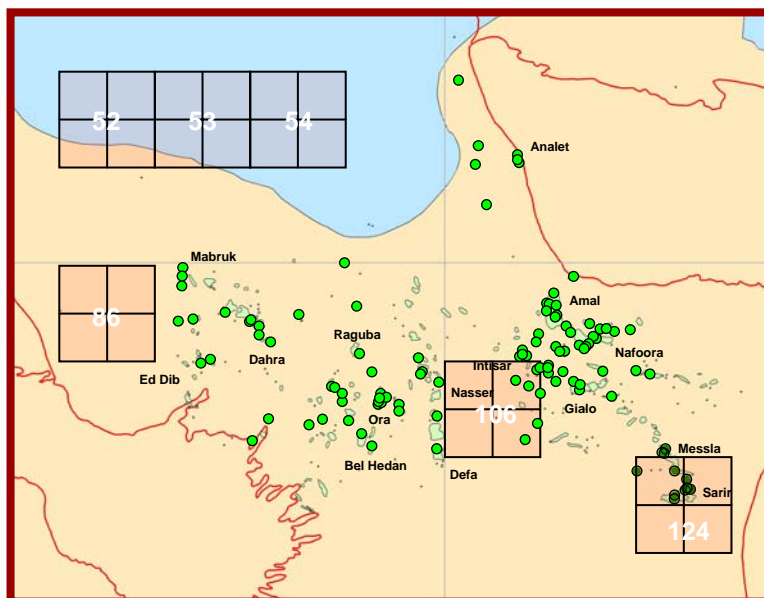


Figure 3. Distribution of GeoMark's 160 oil samples in the Sirte Basin.

The results of GeoMark's 1993 study will be used to select samples for each of the kinetic programs.

Screening Kinetics

Asphaltene samples will be screened for kinetic analysis by performing a single heating rate analysis utilizing a fixed Arrhenius constant for the calculation. This insures that the asphaltene fraction is clean (i.e., does not contain entrained paraffins) and that the pyrolysis response has suitable response. As this analysis is completed at a fast heating rate (30°C/min), many samples can be analyzed to assess any differences in organofacies from the original source rock.

Bulk Kinetic Analyses





Once asphaltene fractions have been screened using the single heating rate experiment, a rigorous analysis and computation is performed. Bulk kinetics describe the rate at which organic matter decomposes into hydrocarbons without any description regarding the yield or distribution of hydrocarbons. A minimum of two heating rates are utilized, but five are preferred with the slowest and fastest heating rates completed in duplicate, whenever possible. The analytical data are processed in both discrete and Gaussian models. The discrete model has two calculations: one with the best Arrhenius factor calculated and the other with the Arrhenius factor fixed (1.0E+14/sec). The Gaussian model also has two calculations: one with the reaction order set to 1.0, and a second where the best reaction order is calculated.

Results are presented in tabular and graphical form showing the onset and peak generation temperatures and vitrinite reflectance values based on a 3.3°C/my heating rate. This is strictly for comparative purposes and to assess the reasonableness of the data.

Compositional Kinetic Analyses

Compositional kinetics describe the rate at which specific hydrocarbon fractions are formed and their yields. This will be completed on 2 asphaltene cuts from each of the four source rock units. This technique uses a modified MCTP approach developed by scientists at Chevron's research laboratory in La Habra (Tang and Stauffer, 1994). We have taken their approach and added the capability to completely trap and resolve all light hydrocarbon gases including methane using Humble Instruments MACT10 instrument. The new trap design is sequential permitting the trapping of these very volatile gases while allowing the heavier hydrocarbons to release completely and reproducibly from the traps.

Compositional kinetic data will be reported for:

-  Dry gas (methane) generation
-  Wet gas (ethane, propane, and butane) generation
-  Light oil (C₅-C₁₄) generation
-  Heavy oil (C₁₅+) generation

The objective of this analysis is to report dry and wet gas generation kinetics as well as light and heavy oil generation kinetics from various source rocks. This will permit modelers to accurately model both oil and gas generation.

Results are presented in tabular and graphical form using a constant heating rate model (3.3°C/my) for each of the fractions.

PRESENTATION OF RESULTS

Results of the study will be presented in both analytical and interpretive formats to insure that all findings are readily accessible to explorationists and research personnel. All of the analytical data will be provided in hard copy and on personal computer disks. Raw data results of the whole and compositional kinetic analyses will be provided. In addition, the following will be addressed in this study,

- Map and define stratigraphic distributions of compositionally discrete oils families
- Identify and map distribution of mixed oils (coincident petroleum systems)
- Define chemistry of the source rocks from which major oil families were derived, and range of “kinetic organofacies” within each major oil family
- Associate individual oil families with the “most likely” source (stratigraphic) intervals in the basin based on observed distribution of oils, available rock chemistry, and lithologic descriptions
- Define source lithology shifts associated with kinetic organofacies within major oil families
- Map distributions of kinetic organofacies of each major oil family and infer migration histories from map distributions
- With limited burial history data, define gross time interval represented by peak generation periods in subbasins containing more than one major oil family
- Identify “exotic” oils and determine if their existence implies existence of oils not found in the extant data set
- Correlate major oil families with expected compositional yields from asphaltene compositional kinetics and ascertain if individual compositional fractions are represented in the extant data set
- Evaluate oil asphaltene kinetics as a surrogate for source rock kinetics

PARTICIPATION

The cost of the study is US \$42,500. Analytical results will be completed by the end of 2004. An interpretive report will be delivered in the first quarter of 2005.

FOR ADDITIONAL INFORMATION CONTACT:

Mr. Stephen W. Brown
GeoMark Research, Ltd.
9748 Whithorn Drive
Houston, TX 77095

Telephone: (281) 856-9333

Fax: (281) 856-2987

E-mail: sbrown@geomarkresearch.com

Mr. Dan Jarvie
Humble Instruments & Services, Inc.
218 Higgins Street
Humble, Texas USA 77338

Telephone: (281) 540-6050

Fax: (281) 540-2864

E-mail: danjarvie@humble-inc.com

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Oil Samples Selected for Analysis in this Study

ID	Field	Well	Depth ft	Reservoir Age	Formation	Lat	Long
LI0014	Beda	47B	3900	Pre Upper Cretaceous	Hofra	28.358	18.996
LI0020	Waha	A1	6500	Lower Cretaceous	Waha	28.405	19.920
LI0022	Zaggut	M1	6400	Paleocene	Beda	28.471	19.529
LI0027	Ora	1	7326	Cretaceous	B	28.524	19.310
LI0032	Conc. 59	3		Eocene	Gialo	28.154	18.003
LI0037	Ed Dib	1	3698	Eocene	Gir, LI-A	28.993	17.569
LI0038	Ed Dib	1	2666	Eocene	Gir, LI-P	28.993	17.569
LI0041	Facha	11	3076	Eocene	Gir, LI-G	29.416	17.389
LI0067	Rakb	A1-12	9877	Cretaceous		29.136	21.153
LI0085	Hofra	A2-11	3042	Paleocene		29.400	17.984
LI0086	Haram	3	4885	Cretaceous	Tagrifet	28.719	18.829
LI0094	Haram	47-S	4100	Upper Cretaceous	Kalash	28.710	18.848
LI0096	Defa	59-B	4700	Paleocene-Danian	Defa	28.078	19.915
LI0102	NC 171	D1-NC 171	9200	Upper Paleocene	Upper Sabil	28.919	21.075
LI0109	Wildcat	Amoses A7a-47	160	Tertiary	Gedari	28.558	18.932
LI0110	Beda	B-1-47	3874	Paleocene	Beda	28.364	18.997
LI0111	Rakb	D-1-12	9533	Cretaceous		29.089	21.190
LI0120	Facha	L-1-11	3069	Eocene	Gir	29.416	17.389
LI0121	Facha	L-1-11	4779	Paleocene		29.416	17.389
LI0122	Facha	L-1-11	3076	Eocene	Gir	29.416	17.389
LI0123	Hofra	A13-11	3025	Paleocene	Dahra	29.393	17.979
LI0125		N-1-11	2134	Tertiary		29.388	17.234
LI0127	Ora	I-8-13	7850	Cretaceous		28.603	19.382
LI0137		H-1-12	11846	Triassic	Amal	29.179	20.947
LI0150	Ghani-Zenad	RRR-1-11	4122	Tertiary	Facha	28.961	17.467
LI0170	Mabruk	A-15-17	2500	Upper Paleocene	Dahra B	29.859	17.277
LI0171	Mabruk	A-17-17	2600	Upper Paleocene	Dahra B	29.759	17.273
LI0074	Neggazza	C1-57	6210	Cretaceous		28.319	18.590
LI0047	Sarir	C-39-65	8000	Lower Cretaceous	Sarir	27.752	22.506
LI0049	Sarir	C-175-65	8000	Lower Cretaceous	Sarir	27.653	22.503
LI0051	Sarir	L-51-65	8400	Lower Cretaceous	Sarir	27.843	22.388
LI0053	Messla	DD-20-80	8000	Lower Cretaceous	Sarir	28.037	22.259
LI0054	Messla	DD-26-80	8200	Lower Cretaceous	Sarir	28.072	22.291
LI0001	Nafoora		2257	Eocene	Tamit-H	29.272	21.309
LI0003	Nafoora		3049	Eocene	Tamet	29.347	21.259
LI0004	Nafoora		2159	Eocene	Nafoora	29.155	21.483
LI0008	Gialo		2725	Eocene	Gialo	28.770	21.341
LI0009	Gialo		2256	Oligocene		28.770	21.341
LI0016	Gialo		2735	Eocene	Gialo	28.737	21.404
LI0081	Raguba	E7-20	5695	Lower Cretaceous	Waha	29.063	19.114
LI0083	Idris	A-103	9400	Paleocene	Upper Sabil	29.033	20.774
LI0092	Intisar L	L-2-103	9000	Paleocene	Upper Sabil	28.722	20.871
LI0097	Gialo	59-E		Eocene	Gialo	28.686	21.402
LI0103	NC 171	C1-NC 171	8600	Upper Paleocene	Harash	28.651	20.988
LI0104	NC 171	B1-NC 171	8500	Upper Paleocene	Upper Sabil	28.865	21.076
LI0107	Shatirah	A-1NC-163	9000	Upper Paleocene	Upper Sabil	28.784	20.731
LI0108	Shatirah	A-2NC-163	8000	Upper Paleocene	Upper Sabil	28.775	20.734
LI0128	Amal	B-10-12	5300	Tertiary	Mesdar	29.571	21.079
LI0130	Amal	N-1-12	3702	Tertiary		29.559	21.151
LI0132	Bu Grea	A-3-5	2471	Tertiary	Sheighega	30.000	18.957
LI0133	Raleh	DD-1 -6	7737	Lower Cretaceous	Waha	28.764	19.943
LI0140	Amal	N-1-12	6574	Paleocene	Sabil	29.559	21.151
LI0165	NC 171	A1-NC-171	9200	Upper Paleocene	Upper Sabil	28.919	21.075
LI0166	NC 171	B1-NC-171		Upper Paleocene	Sabil	28.932	21.079

APPENDIX A (Cont'd.)

ID	Field	Well	Depth ft	Reservoir Age	Formation	Lat	Long
LI0018	Samah	L1	6300	Ord./CaMiddle		28.223	19.138
LI0024	Ora		4900		M59	28.523	19.309
LI0028	Ora	1	7058	UpperCretaceous	Sirte	28.524	19.310
LI0043	Bel Hedan	V-59	7100	Lower Ordovician	Samah	28.104	19.242
LI0077	Ora	I-1-13	5447	Paleocene		28.583	19.317
LI0078	Ora	I-1-13	7610	Jurassic		28.583	19.317
LI0089	Intisar C	C-2-103	9600	Paleocene	Upper Sabil	29.044	20.852
LI0090	Intisar D	D-13-103	8500	Paleocene	Upper Sabil	28.904	20.962
LI0098	Bel Hedan	V-59	6400	Ordovician	Hofra	28.104	19.242
LI0115	Ora	I-1-13	7821	Cretaceous		28.583	19.317
LI0116	Ora	I-2-13	5345	Tertiary		28.618	19.330
LI0117	Ora	I-2-13	5577	Tertiary		28.618	19.330
LI0118	Ora	I-2-13	7587	Cretaceous		28.618	19.330
LI0119	Ora	I-2-13	7674	Cretaceous		28.618	19.330
LI0126	Kalash	K1-12	10900	Cretaceous		29.061	20.807
LI0135	Meghil	J-2-6	5890	Paleocene	Ruaga	29.016	19.733
LI0138	Kalash	K1-12	10348	Tertiary		29.061	20.807
LI0142	Amal	D-4-12	2625	Tertiary	Gebel Akhdar	29.076	21.238
LI0145	Nafoora	G-32-51	2194	Tertiary	Gebel Akhdar	29.222	21.570
LI0146	Nafoora	G-21-51	3054	Eocene	Gialo	29.219	21.562
LI0172	Antelat	B-2	6089	Eocene	Gir	31.116	20.751
LI0173	Antelat	B-3	6043	Eocene	Gir	31.047	20.764
LI0174	Antelat	B-5	6081	Eocene	Gir	31.067	20.756
LI0046	Jakhira	A-1-96	11000	Lower Cretaceous	Nubian	29.313	21.610
LI0151	NC-84	A-1	12260	Lower Cretaceous	Nubian	29.370	21.503
LI0152	NC-84	A-1	11528	Lower Cretaceous	Nubian	29.370	21.503
LI0167	Jakhira	A-3-96	12000	Lower Cretaceous	Nubian	29.305	21.612
LI0169	As Sarah	B-15-96	12000	Lower Cretaceous	Nubian	29.317	21.672
LI0005	Nafoora		8496	Cretaceous	Tagrifet	29.141	21.454
LI0011	Sarir		7746	Lower Cretaceous	Sarir	27.643	22.523
LI0048	Sarir	C-110-65	8000	Lower Cretaceous	Sarir	27.586	22.388
LI0050	Sarir	C-262-65	8000	Lower Cretaceous	Sarir	27.558	22.377
LI0068	Amal	B1-12	9832	Jurassic	Amal	29.446	21.155
LI0095	Nafoora-Augila			Jurassic	Amal	29.272	21.309
LI0131	Amal	N-1-12	10102	Cretaceous	Maragh	29.559	21.151
LI0136		F-1-31	8466	Cretaceous	Maragh	29.858	21.333
LI0141	Sarir	C-3-65		Cretaceous		27.644	22.493
LI0147	Nafoora	G-33-51	8479	Cretaceous	Rakb	29.221	21.552
LI0148	Nafoora	G-20-51	9064	Cambrian		29.235	21.547
LI0045	Tuama	C-1-97	14000	Lower Cretaceous	Calanscio	28.882	21.983
LI0055	Bu Attifel	A-1-100	13000	Lower Cretaceous		28.845	22.120
LI0168	Nakhia/G7 - 97	G-7-97	12000	Lower Cretaceous	Calanscio	28.884	21.640
LI0066	Amal	B22-12	5891	Eocene	Mesdar	29.575	21.068
LI0113	Kalash	K1-12	9171	Tertiary		29.061	20.807
LI0069	Hagfa	A1A-13	7377	Eocene		29.552	19.086

APPENDIX B

Explanation of Asphaltene Kinetic Technique

Establishing the reaction kinetics of petroleum generation by various pyrolysis techniques using different immature source rock types/kerogen has long been employed to constrain basin models and predict the timing of generation/migration. If asphaltenes in migrated crude oil represent the labile portion of kerogen (albeit smaller molecular weight and soluble), then it may be possible to measure generation kinetics using the modified reactant (kerogen) retained and transported with the product (petroleum). Initial work by di Primo et al. (2000) suggests that asphaltene pyrolysis was useful in determining the temperature of petroleum formation from both carbonate and marine shale source rocks.

In the initial phase study, 14 asphaltene samples from crude oils were obtained by hexane precipitation. Seven of the samples were from oils generated from carbonate sources of varying ages and environments and the other seven samples are from marine shale source rocks with little or no terrigenous influence. Subsequently, asphaltenes were also obtained from source rock kerogen, source rock bitumen, and corresponding oils representing four well characterized petroleum systems: 1) Middle Cretaceous Shilaif carbonate/marl source rock of The United Arab Emirates; 2) Upper Jurassic Tuwaiq Mountain carbonate source rock of Saudi Arabia; 3) Upper Jurassic Bazhenov shale source rock of West Siberia; and 4) Upper Jurassic Kimmeridge shale of the UK North Sea. Multiple oils of different thermal maturity, as determined by terpane and sterane biomarkers, were used from each petroleum system.

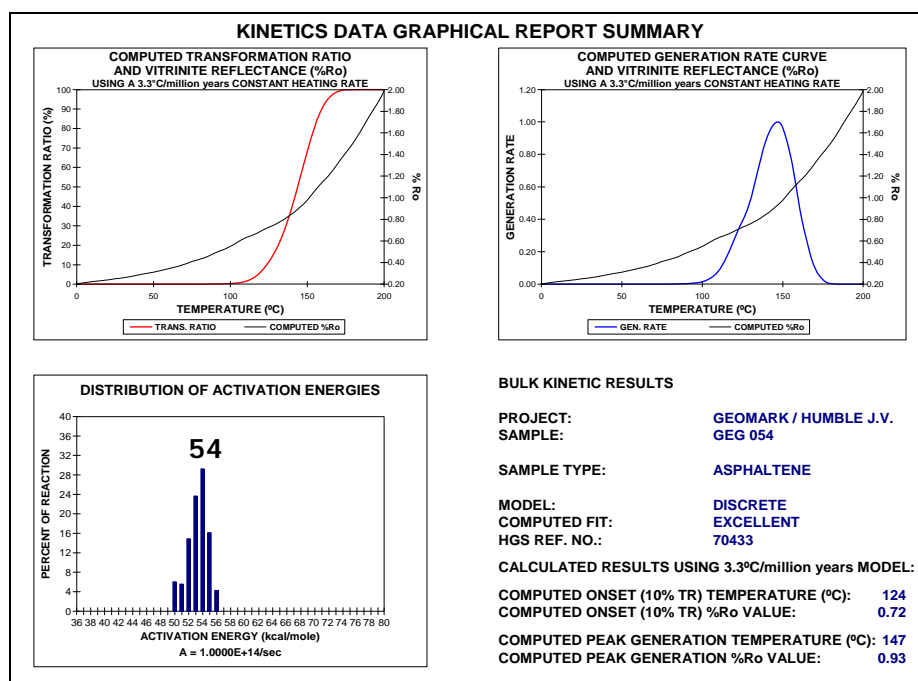


Figure 1. Gulf of Suez carbonate-sourced oil asphaltene pyrolysis.

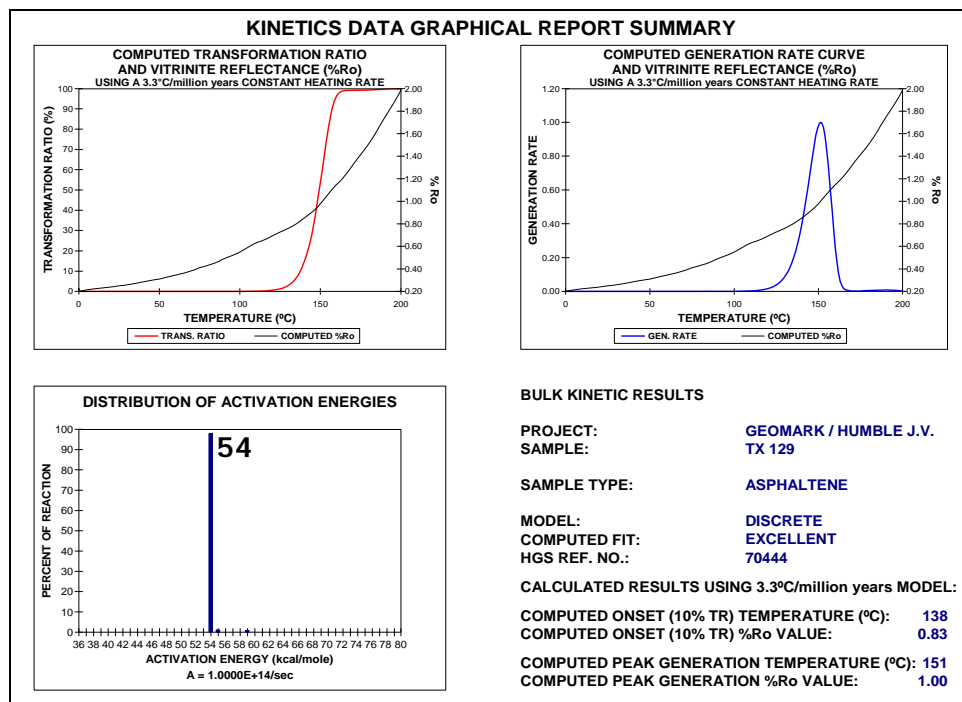


Figure 2. East Texas marine shale-sourced oil asphaltene pyrolysis.

Asphaltene samples were pyrolyzed in a Rock-Eval system at different rates (1, 5, 10, 30 °C/min), and a discrete model was used to calculate activation energy (Ea) distributions. Onset (10% reaction) and peak generation temperatures were calculated based on a 3.3 °C/my model.

Of the 14 initial oil sample asphaltenes, the results were not atypical of immature kerogen pyrolysis: some samples had broad Ea distributions about 53 to 54 kcal/mole maxima (e.g., Figure 1) while a few had essentially a single Ea at 54 kcal/mole (Figure 2). Onset temperatures varied from 124 to 139 °C and peak generation temperatures ranged from 144 to 153 °C. Weighted average Ea correlated well positively to onset temperatures as shown in Figure 3.

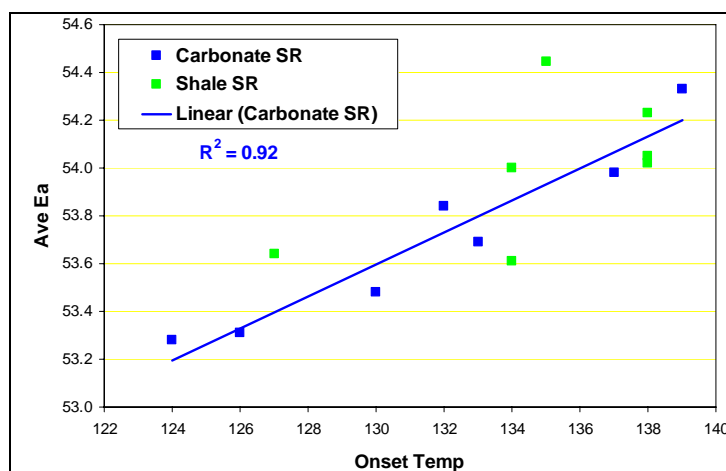


Figure 3. Carbonate oil asphaltenes show high correlation: onset temperature and average Ea.

A less well defined positive correlation was observed between peak generation temperature and apparent oil thermal maturity as defined by triaromatic steranes (TAS3 = triaromatic steranes m/z 231 [C20+C21]/[SC20-C28]) as shown in Figure 4. A measure of the broadness of the Ea distribution is plotted against the average activation energy: asphaltenes from carbonate-sourced oils generally have broader distributions than shale-sourced asphaltenes (Figure 5).

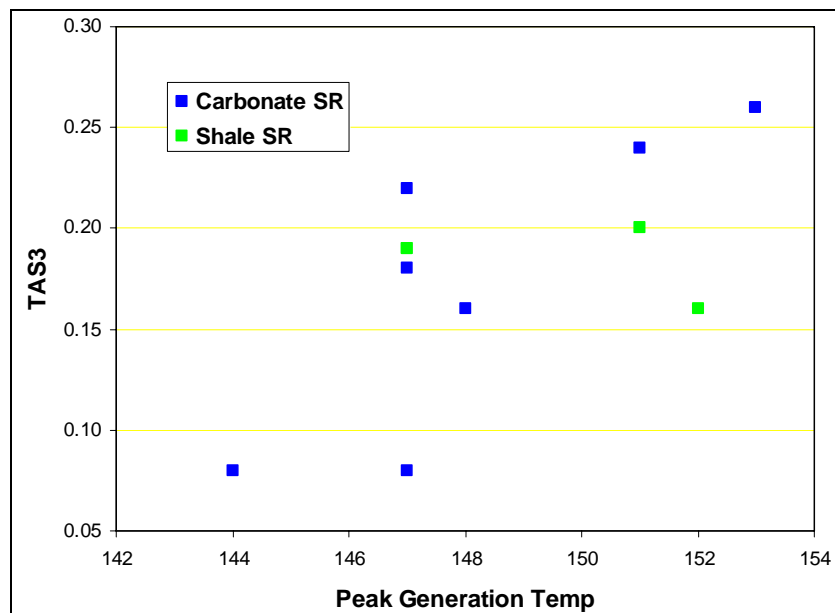


Figure 4. Peak generation versus aromatic biomarkers thermal maturity measure (TAS3).

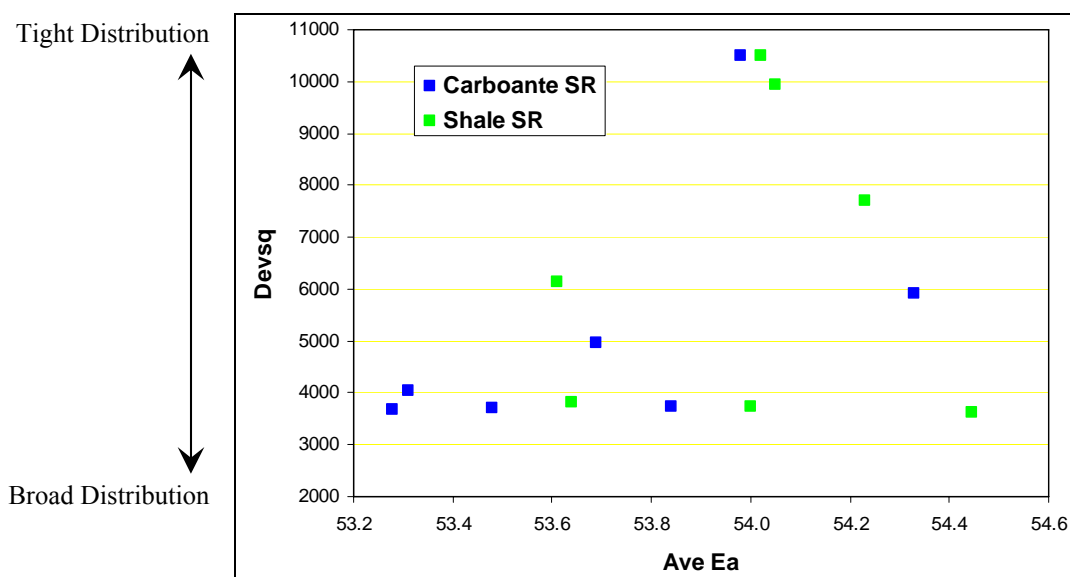


Figure 5. Average activation energy versus broadness of distribution.

A list of the petroleum systems is given in Table 1 where samples were available to conduct pyrolysis experiments on corresponding source rock kerogen, asphaltenes from the source rock bitumen, and asphaltenes from oils of different biomarker maturities. In addition, oil asphaltenes from different facies of the UK marine shale source rock in the Sirte Basin were pyrolyzed.

Petroleum Systems

SR Kerogen > SR Asphaltenes > Oil Asphaltenes

■ UAE:	Shilaif-Mishrif	MK Carbonate SR
■ Saudi Arabia:	Tuwaiq Mtn-Arab D	UJ Carbonate SR
■ West Siberia:	Bazhenov-Megion	UJ Shale SR
■ North Sea:	Kimmeridge-J	UJ Shale SR
■ Sirte Basin:	Sirte facies I	UK Shale SR
	Sirte facies II	UK Shale SR
	Lacustrine facies	Tr\Jr Lacustrine
	Carbonate facies	Paleogene Carbonate

Table 1. List of petroleum systems in which kerogen-bitumen-oil asphaltenes were pyrolyzed.

Preliminary results suggest that oil asphaltenes can act as proxies for the corresponding source rock kerogens. Bitumen asphaltenes generally have lower activation energies than the kerogen or oil asphaltenes. In Figures 6a and 6b, onset and peak generation temperatures are compared between source rock kerogen and corresponding oil asphaltenes for carbonate and marine shale systems, respectively. Oil asphaltene symbol size relates to biomarker thermal maturity. Sirte oils from different UK marine shale source facies have consistently different generation kinetics. Deeper burial and/or higher thermal gradients may be needed to generate oil from marine shale facies I than facies II in the Sirte Basin.

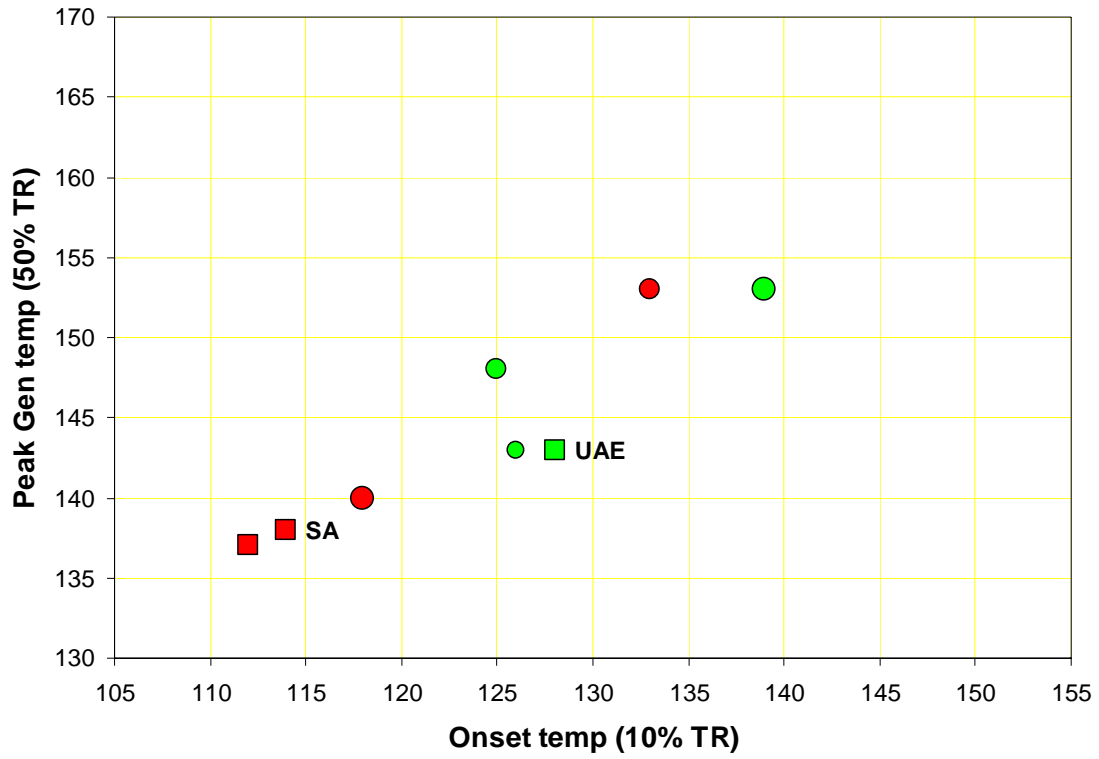


Figure 6a. Kerogen (□) and oil asphaltene (○) comparisons for carbonate source rocks.

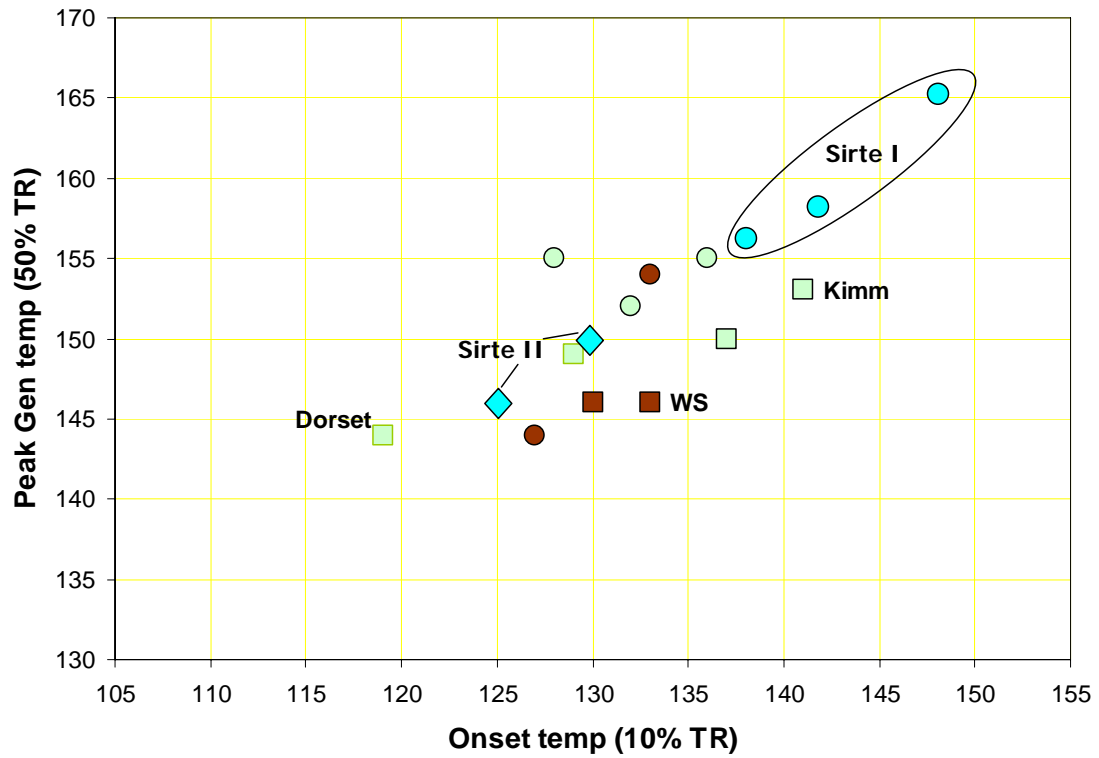


Figure 6b. Kerogen (□) and oil asphaltene (○) comparisons for marine shale source rocks.