

## Maturity Assessment and Characterisation of Jurassic Crude Oils

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**Abstract:** In this study, the thermal maturity of crude oil samples from the Kimmeridge Clay Formation (UK) were assessed and characterised using the following methods: calibration of the oil samples against source rock biomarker dataset of which the maturities are known, use of established empirical relationships between Vitrinite Reflectance Equivalent (VRE) and aromatic molecular ratios, use of phase diagram as a relative maturity indicator and use of GOR as a relative maturity indicator. The results show that the biomarker maturity parameters are only diagnostic of a broad maturity range (VRo ~ 0.65-1.0%), aside, there was no significant increase in the ratios of virtually all parameters (e.g., %29 $\beta\beta$  Sterane, %29 $\alpha\alpha$  Sterane, %27Ts, %29Ts) in this maturity range, and in most cases their inversion complicates their application. Vitrinite reflection equivalent (VRE) values derived from the aromatic molecular ratios mainly range from ~0.64-0.89%. These results indicate that virtually all the oils are early mature to mid mature. This assertion is only broadly true as reservoired oils are mixtures of petroleum from source rocks at different levels of maturity. Our dataset also displays poor correlation between GOR and biomarker/aromatic related maturity parameters, indicating the need to (a) carefully consider how these parameters should be used and (b) unravel the effects of petroleum mixing when looking for trends between maturity and bulk composition.

**Key words:** Aromatic, biomarker, crude oil, gas oil ratio, thermal maturity, vitrinite reflectance equivalent

### INTRODUCTION

Biomarkers are complex molecular fossils derived from once living organisms that occur in crude oils and source extracts. Conventional approaches of thermal maturity assessment of oils rely on the distribution of various classes of biomarkers. Biomarker analysis is a routine tool used for the evaluation of organic matter type, biodegradation and migration in geological samples (Van Graas, 1990; El-Nady, 2008). Because biomarker patterns in oils are inherited from their respective source rocks, assessment of the level of thermal maturity of oils using biomarker maturity parameters assist in correlation studies which provide important information on the origin, distribution and possible paths of migration of oils that can lead to additional exploration plays.

Among the saturated hydrocarbons, concentration ratios based on steranes and pentacyclic triterpanes of the hopane type have attracted much attention as maturity indicators although the dynamic range of most of the ratios appears to be restricted to rather low maturation levels (Radke, 1988; Van Graas, 1990; Sajgo, 2000; Zhang *et al.*, 2005), and in most cases their inversion at high maturity complicates their application. These caveats re-emphasize the need for multiple lines of evidence in determining oil maturities. In this study, we use biomarker maturity parameters, aromatic molecular parameters, phase diagrams and Gas-oil Ratio (GOR) to assess and characterise approximate maturity levels for 13

crude oil samples from the Kimmeridge Clay Formation (UK).

### MATERIALS AND METHODS

This study was carried out between 2001 and 2005 at the University of Newcastle. A total of 13 representative Kimmeridge Clay Formation sourced petroleum samples from 13 exploration wells and source rock extract (biomarker) data from 5 exploration wells from the North Sea (Fig. 1), made available by Norsk Hydro (Norway) was used in this study. The oils are from Repeat Formation Tests, Drill Stem Tests or Production Tests, and consist of PVT data (fluid composition, GOR, etc.), and saturated and aromatic molecular marker data. The aromatic data was only available for 11 wells.

The maturities of the oil samples were calibrated against a set of KCF source rock biomarker dataset for which the maturities (vitrinite reflectance -VRo) have been determined. This stems from the fact that the composition of the organic components in the source rock are transmitted to the expelled oil (Moldowan *et al.*, 1992; Peters and Moldowan, 1993), and thus would have the most similar combination of source rock input plus source rock catalytic effect. Parameters used for the maturity correlation are listed in Table 1 and 2. Maturity levels were assigned to the oil samples using the classification scheme shown in Table 3. The maturity levels given in Table 2 range from early mature (1) to peak maturity (2).

Table 1: Maturity parameters of source rock extracts

Well name	Depth (m)	%29 $\alpha\alpha$ S	%29 $\beta\beta$	%Tri	%27Ts	%29Ts	VRo
31/4-6	2132.2	21	32	3	21	31	0.44
31/4-6	2132.6	29	48	5	29	22	0.44
31/4-6	2134.5	20	55	5	12	14	0.45
31/4-9	2117.5	11	28	2	27	31	0.41
6407/8-1	4257.0	69	80	51	94	57	0.64
6407/8-1	4260.0	58	66	55	92	52	0.64
6407/8-1	4263.0	56	76	70	96	62	0.64
6407/8-1	4266.0	58	74	59	88	49	0.64
6507/2-3	3845.0	58	75	20	78	42	1.06
6507/2-3	3847.0	52	76	13	73	43	1.06
6507/2-3	3850.0	49	75	13	74	43	1.07
6507/2-3	3855.0	48	72	13	74	43	1.07
6507/2-3	3860.0	48	68	12	75	46	1.07
6507/2-3	3865.0	50	71	11	75	45	1.08
6507/2-3	3870.0	50	73	13	74	44	0.91
6507/2-3	3875.0	49	71	12	76	47	1.08
6507/2-3	3880.0	48	71	12	75	44	1.09
6507/2-3	3885.0	53	74	12	75	44	1.09
6507/2-3	3890.0	50	70	11	75	45	1.09
6507/2-3	3895.0	51	73	12	76	46	1.10
6507/2-3	3900.0	50	72	12	78	45	0.96
6205/3-1R	4449.5	38	75	33	59	27	1.12
6205/3-1R	4450.7	57	56	n.d	58	29	1.16

VRo values are measured

Table 2: Maturity parameters of oils

Well name	Depth	%29 $\alpha\alpha$ S	%29 $\beta\beta$	%Tri	%27Ts	%29Ts	GOR	Maturity level
2/1-4	4130	57	65	11	76	41	n.d	2
2/1-8	3926	59	65	13	77	51	n.d	2
2/2-1	3730	51	53	5	32	24	70	2
2/2-5	3670	44	62	7	37	21	59	2
2/4-1	3145	47	78	9	72	50	n.d	2
2/4-17	4388	51	79	n.d	72	100	n.d	2
7/7-2	3342	44	73	12	53	37	38	1
7/8-3	3767	56	69	n.d	49	n.d	n.d	2
7/12-6	3612	51	70	15	95	65	114	2
9/2-1	3210	43	57	5	68	37	320	2
9/2-3	3268	45	54	6	55	33	n.d	1
17/12-1	2341	39	57	5	53	29	n.d	1
18/10-1	2417	451	54	5	49	29	16	1

%29 $\alpha\alpha$ S = %C29 $\alpha\alpha$  Sterane; %29 $\beta\beta$  = %C29 $\beta\beta$  Sterane; %Tri = % Tricyclic terpane; %27Ts = % 27Trisnorhopane; % 29Ts = %29Trisnorhopane; 1 = Early mature; 2 = Peak maturity

Aside, we have used established empirical correlations of aromatic molecular parameters and vitrinite reflectance equivalent (Radke and Welte, 1983) to determine approximate maturity values of the molecular ratios of the oils expressed as VRE (Table 4). The correlations are as follows:

$$\text{VRE} = 0.6 (\text{MPI-1}) + 0.40 \quad (1)$$

$$\text{MNR} = 2.92 * \text{VRE} - 1.19 \quad (2)$$

$$\text{DMN} = 4.15 * \text{VRE} - 2.18 \quad (3)$$

$$\text{MDR} = 49.6 * \text{VRE} - 35.5 \quad (4)$$

where,

- MPI-1 = Methylphenanthrene 1
- MNR = Methylnaphthalene ratio
- DNR = Dimethylnaphthalene
- MDR = Methyl dibenzothiophene
- VRE = Vitrinite reflectance equivalent

Table 3: Biomarker maturity classification scheme

Biomarker	Parameter	Range	VRo Range	Remark
%29 $\alpha\alpha$ S		20-45	0.4-0.5	Immature
		46-55	0.51-0.69	Early mature
		56-70	0.7-0.9	Peak maturity
%29 $\beta\beta$		30-50	0.4-0.5	Immature
		51-65	0.51-0.69	Early mature
		65-75	0.7-0.9	Peak maturity
%Tri 11-69		1-10	0.4-0.5	Immature
		0.6-1.0		Peak maturity
%27Ts		10-40	0.4-0.5	Immature
		41-95	0.6-1.0	Peak maturity
%29Ts		10-40	0.4-0.5	Immature
		41-65	0.6-1.0	Peak maturity

We also input the primary compositions of the oil samples into PVT-Sim v.10 (an equation of state based pressure, volume and temperature simulation software), and flashed at the appropriate temperatures and pressures to determine the changes in the physical properties and predict phase

Table 4: Aromatic molecular parameters and maturity of petroleum

Well name	Depth (m)	Molecular parameter	Ratio	GOR (Sm <sup>3</sup> /Sm <sup>3</sup> )	VRE (%)
2/2-1	3730	MPI-1	0.63	70	0.78
		MNR	1.27		0.84
		DNR	3.6		1.39
		MDR	5.63		0.83
2/2-5	3671	MPI-1	0.59	59	0.78
		MNR	1.15		0.8
		DNR	2.65		1.16
		MDR	0.042*		0.72
2/4-11	3145	MPI-1	0.77	n.d	0.86
		MNR	1.4		0.89
		DNR	3.21		1.39
		MDR	6.26		0.84
7/7-2	3342	MPI-1	0.5	38	0.70
		MNR	0.67		0.64
		DNR	0.8		0.72
		MDR	1.88		0.75
7/12-6	3612	MPI-1	0.55	114	0.73
		MNR	1.02		0.76
		DNR	2.28		1.07
		MDR	6.39		0.84
2/9-1	3210	MPI-1	0.56	320	0.74
		MNR	0.13		0.45
		DNR	2.92		1.23
		MDR	2.46		0.77
9/2-3	3268	MPI-1	0.6	n.d	0.76
		MNR	1.27		0.84
		DNR	2.97		1.24
		MDR	2.28		0.76
		GOR			
17/12-1	2341	MPI-1	0.61	n.d	0.77
		MNR	1.11		0.79
		DNR	2.22		1.06
		MDR	1.41		0.74
18/10-1	2417	MPI-1	0.56	16	0.74
		MNR	1.23		0.79
		DNR	2.49		1.06
		MDR	1.77		0.74
2/4-17**	4388	n.d	n.d	1121	n.d
3/7--4**	3471	n.d	n.d	1285	n.d

\*\* : gas condensates

behaviour in the fluids. The critical point on the PT diagram gives an indication of the relative maturity level of the oil (di Primio *et al.*, 1998). Phase diagrams of five selected oils are shown in Fig. 1a-e.

Additionally, the GOR of petroleum generated from a source rock is known to increase systematically with increasing maturity (di Primio *et al.*, 1998). This effect has been recognised and described in a multitude of publications based on natural datasets as well as on laboratory experiments (e.g., England and Mackenzie, 1989; Duppenbecker and Horsfield, 1990; Karlsen *et al.*, 1995). We thus use the GOR as a tool to estimate the relative maturities of the oil (Table 4). We

thus related maturity (VRE) determined from the aromatic molecular parameters to the GOR of the oils so as to establish maturity-GOR trend (Table 4).

## RESULTS AND DISCUSSION

Making maturity inferences using biomarker maturity ratios in oils is more difficult than for determining rock extract maturity. This is because, with rock extracts, various biomarker ratios can be plotted against accepted rock maturity parameters such as vitrinite reflectance and Tmax (from Rock-Eval data). This kind of comparison is not possible for oils.

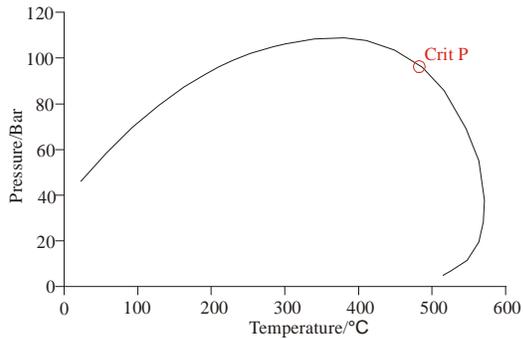


Fig. 1a: Phase envelope for oil sample 7/7-2 (VRo ~ 0.64-0.70%)

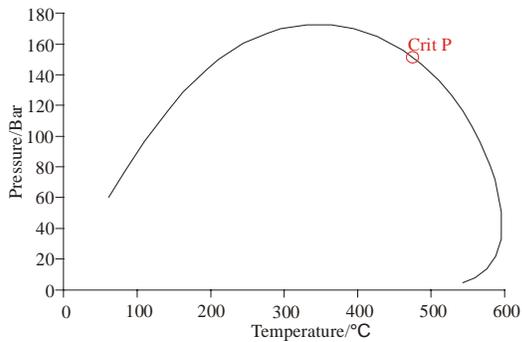


Fig. 1b: Phase envelope for oil sample 7/12-6 (VRo ~ 0.73-0.84)

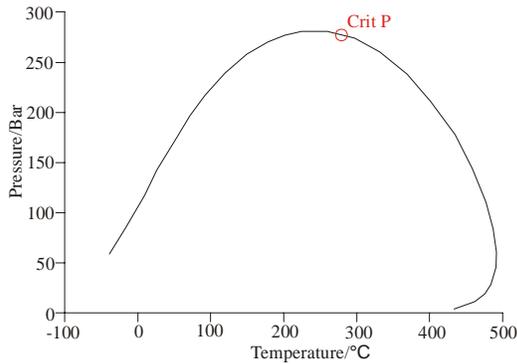


Fig. 1c: Phase envelope for oil sample 2/1-9 (VRo ~ 0.74-0.77)

However, since biomarker maturity controlled ratios allow the establishment of a direct genetic link via a maturity-based oil/source rock correlation (Cornford *et al.*, 1983; Bjoroy *et al.*, 1996), we have compared the biomarker ratios of the oils and a set of KCF source rock biomarker data for which the maturities (vitrinite reflectance) have been determined. This is based on the principle that the composition of the organic components in the source rock is transmitted to the oil (Peters and Moldowan, 1993; Moldowan *et al.*, 1992), and thus would have the most similar combination of source input.

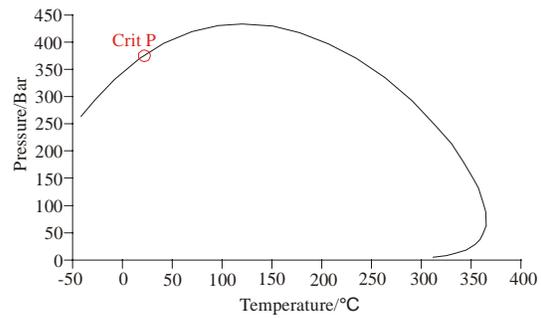


Fig. 1d: Phase envelope for oil sample 3/7-4 (condensate)

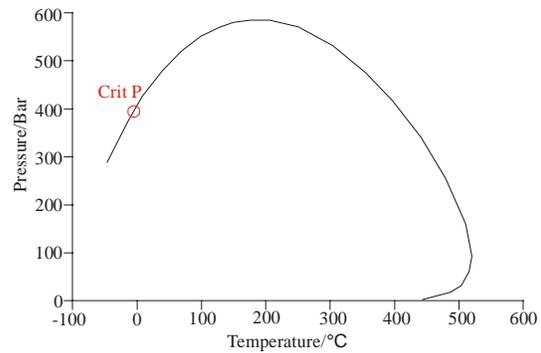


Fig. 1e: Phase envelope for oil sample 2/14-17 (condensate)

Parameters used for the maturity correlation are shown in Table 1 and 2.

To assign maturity levels to the oils, we employ a classification scheme (Table 3) in which the source rock biomarker ratios were divided into three categories based on maturity (immature, early mature, and peak maturity). Thus, depending on the magnitude of the ratio, the oil was designated as either early mature (1) or peak maturity (2). We were faced with two main problems in using biomarker ratios derived from source rock extract to constrain oil maturity: (1) There is no significant increase in the ratios of virtually all parameters from VRo ~ 0.6-1.0% (Table 2), therefore making it difficult to rank oils in order of increasing maturity. Similar observations have been reported elsewhere by Van Graas (1990) based on KCF source rock extract data where the widely applied ratios (e.g., %C29 $\alpha\alpha$  Sterane and %C29 $\beta\beta$  Sterane) show no increase from VRE ~ 0.55-1.0%. These parameters thus have a limited usability in oils and mature source rocks as their working range ends before or just inside the oil window (Van Graas, 1990). (2) There are indications of an inversion of certain molecular ratios at high maturities (Table 2). A high maturity oil could therefore be wrongly interpreted as low maturity or even immature oil. As a result, the maturities assigned to the oils based on the biomarker ratios are suspect. For instance, we have classified oils with %C29 $\alpha\alpha$  Sterane between 45-55% as

early mature. Table 1 shows %C29 $\alpha\alpha$  sterane ratios <40% at VRo >0.9%.

These caveats re-emphasize the need for multiple lines of evidence in determining oil maturities which will increase reliability of interpretation. To this end, we have used a set of aromatic molecular parameters employed in established empirical correlations (Radke and Welte, 1983) to estimate approximate maturity levels for each of the oil samples. The maturities of the oils in equivalent vitrinite reflectance units are listed in Table 4. Table 4 shows that VRE values derived from MPI-1 vary from 0.7-0.86%, VRE values derived from MNR vary from 0.64-0.84, while those for MDR vary between 0.75-0.84. The results indicate that virtually all the oils are early mature to mid maturity, though it must be remembered that reservoir oils are mixtures of petroleum from source rocks at different maturities. Also note that VRE values determined using dimethylnaphthalene (DNR) do not correlate with VRE values determined from the rest of the molecular parameters, and therefore are not used in the assessment of the oil maturities.

di Primio *et al.* (1998) reported that low maturity oils with high molecular weight compounds (and high densities) are characterised by dew point curves with critical points extending to high temperatures, while high maturity oils with low molecular weight compounds (and low densities) are characterised by bubble point curves with critical points extending to high pressures on pressure-temperature (PT) diagram. We thus use this concept as a tool to estimate the relative maturity of the oil samples. PT diagrams of oil samples with critical points extending to high temperatures are classified as low maturity oils, samples with critical points extending to high pressures are classified as high maturity oils, while samples with critical points in between these two extremes indicate mid maturity oils. We have assumed that the position of the critical point in a phase diagram is a function of maturity. Figures 1a-e show phase diagrams of five selected oils in order of increasing maturity.

Additionally, gas oil ratio (GOR) is another important property often used for the evaluation of the oil maturities (di Primio *et al.*, 1998). GOR data could not be obtained in all the oil samples, but the sparse data range from 16-1285 Sm<sup>3</sup>/Sm<sup>3</sup>. Since GOR exerts the greatest effect on generation volumetrics within a source rock, therefore relating GOR values to specific maturity levels is crucial. We estimated the Vitrinite Reflectance Equivalent (VRE) of the oils using aromatic molecular ratios, and related the VRE values of the oils to the respective GOR values (Table 4). We determined the strength of the correlation between GOR and the aromatic maturity parameters by using regression analysis. We observed that GOR vs MPI-1, r = 0.07, GOR vs MDR, r = 0.074, GOR vs MDR, r = 0.303, and GOR vs MNR, r = 0.827. From the

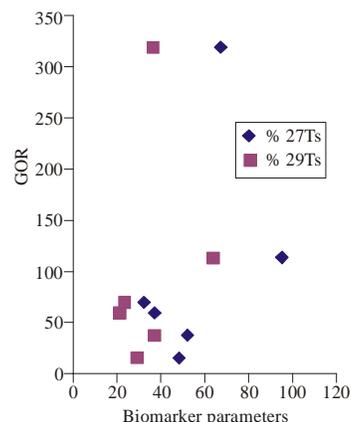


Fig. 2a: GOR versus %27Trisnorhopane (%27Ts) and %29Trisnorhopane (%29Ts) for oil

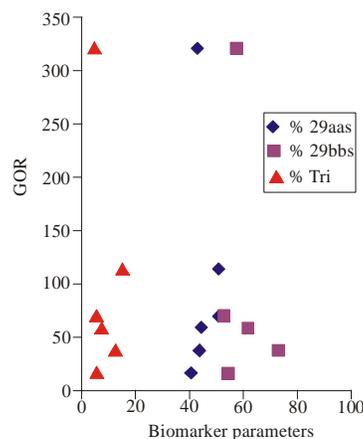


Fig. 2b: GOR versus %29 $\alpha\alpha$ Sterane (%29 $\alpha\alpha$ s), %29 $\beta\beta$ Sterane (%29 $\beta\beta$ s) and % Tricyclic Terpane (% Tri) ratios for oil

correlation coefficients, VRE determined from methyl naphthalene ratios show a better correlation with GOR.

We also plotted GOR as a function of biomarker and aromatic maturity parameters (Fig. 2 and 3). Generally our dataset displays a poor correlation between GOR and biomarker based-maturity parameters. For instance, in well 18/10-1, VRE ranges between 0.74-0.79% (VRE values from DNR are excluded, see above), the GOR of the oil is 16 Sm<sup>3</sup>/Sm<sup>3</sup>, whereas, well 2/1-9 with seemingly lower maturity range (VRE ~ 0.74-0.77) has a GOR of 320 Sm<sup>3</sup>/Sm<sup>3</sup>. We thus observe that it is very difficult to establish a robust relationship between GOR and maturity. We were only able to differentiate low GOR oil from high GOR oil based on the GOR values. Using the premise that increasingly gassy petroleum is generated with an increase in maturity (di Primio, *et al.*, 1998), low GOR oils thus indicate low maturity and high GOR oils

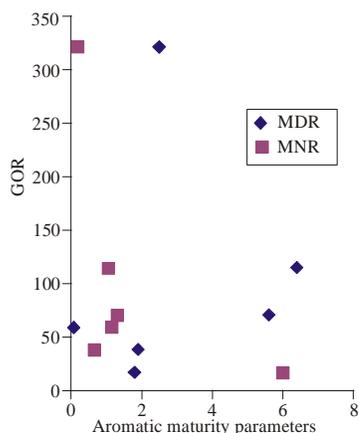


Fig. 3a: GOR versus Methyl dibenzothiophene (MDR) and methylnaphthalene (MNR) ratios for oil

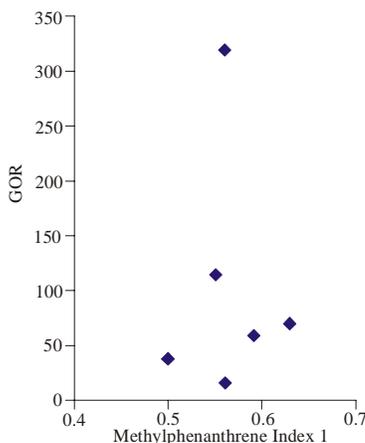


Fig. 3b: GOR versus methylphenanthrene index 1 ratio for oil  
GOR = Gas Oil Ratio

indicate higher maturity. This qualitative approach is, however, broadly consistent with the positions of the critical points on the PT diagrams (Fig. 1a-e).

Using the above GOR interpretation that high GOR oils indicate higher maturity to determine the maturity of oil samples 2/4-17 and 3/7-4 yielded mixed results. This is because from the general interpretation mentioned above, it implies that sample 3/7-4 with GOR ~1285 Sm<sup>3</sup>/Sm<sup>3</sup> is of a higher maturity than sample 2/4-17 with GOR ~1121 Sm<sup>3</sup>/Sm<sup>3</sup>. Flash results at their respective temperatures and pressures show that sample 3/7-4 with GOR ~1285 Sm<sup>3</sup>/Sm<sup>3</sup> has a density of 0.3846 g/cm<sup>3</sup>, while sample 2/4-17 with a GOR ~1121 Sm<sup>3</sup>/Sm<sup>3</sup> has a density of 0.3608 g/cm<sup>3</sup>, respectively. Though similar densities, it implies that sample 3/7-4 is a relatively higher molecular weight compound and hence lower maturity compared to sample 2/4-17. It means therefore that

sample 3/7-4 is expelled from a source rock relatively less mature than sample 2/4-17. The high gas content of sample 3/7-4 could mean that this oil is a mixture of perhaps moderately mature oil and a gas condensate. Similar observations have also been reported elsewhere by Swarbrick *et al.* (2000) on a set of North Sea oils used for an integrated study of the Judy Field. Swarbrick *et al.* (2000) reported that variations in GOR are not the result of the trapping of increasingly mature petroleum generated from a single source rock, but rather, the variations reflect late and spatially variable injection of lighter petroleum. This re-emphasizes the need to carefully consider how GOR should be used when looking for trends between maturity and bulk composition. The maturity of the condensates (3/7-4 and 2/4-17) could not be determined due to lack of data but Radke (1988) suggested that most condensates analysed for aromatics in the North Sea show a Vitrinite Reflectance Equivalent (VRE) values in the range 0.9-1.0%. We believe that in instances where strong correlation exists, indicates a reflection of the true maturity range of the oil.

### CONCLUSION

The thermal maturities of crude oil samples from the Kimmeridge Clay Formation (UK) were determined using four different methods. The results show that the biomarker maturity parameters are only diagnostic of a broad maturity range (VR<sub>o</sub> ~ 0.65-1.0%); there was no significant increase in the ratios of virtually all parameters (e.g., % 29ββ Sterane, % 29αα Sterane, % 27Ts, % 29Ts) in this maturity range. Vitrinite Reflection Equivalent (VRE) values derived from MPI-1 varied from 0.7-0.86%, VRE values derived from MNR varied from 0.64-0.89%, while VRE values derived from MDR varied between 0.74-0.84%. These results indicate that virtually all the oils are early mature to mid mature. This assertion is only broadly true as reservoir oils are mixtures of petroleum from source rocks at different levels of maturity. Our dataset also displays poor correlation between GOR and biomarker/aromatic related maturity parameters, indicating the need to (a) carefully consider how these parameters should be used and (b) unravel the effects of petroleum mixing when looking for trends between maturity and bulk composition.

### ACKNOWLEDGEMENT

I would like to thank Ian Harrison, Trevor Whitfield, Rob Hunter, Yvonne Hall, Michelle Morrison and Dr Angela Brown for their invaluable help during the course of this project in the University of Newcastle Upon Tyne, United Kingdom. I wish to also to thank His Excellency, Chief D.S.P. Alamiyesegeha for initiating the Hipact UK training programme.

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