

SOURCE ROCK MATURITY IN THE CENTRAL AND VIKING GRABEN STRUCTURES, NORTH SEA – EVALUATION OF OPTICAL AND GEOCHEMICAL (ROCK EVAL, INFRARED SPECTROSCOPY) MATURITY PARAMETERS

W. Kalkreuth¹, M. Ade¹, G. Henz², H. Ganz³ and K. Kommeren⁴

¹Instituto de Geociências, UFRGS, Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil

²Petrobrás, E&P-BC, GEXP-GELAB, Av. Elias Agostinho, 665, 27913-350, Macaé, RJ, Brazil

³Shell UK. Exploration and Production, Shell-Mex House Strand, London, WC2R 0DX, U.K.

⁴Shell International Exploration and Production B.V., EPT-HM, Volmerlaan 8, 2280 AB Rijswijk, The Netherlands

ABSTRACT

The present study evaluates optical and chemical maturity parameters for a series of organic-rich source rocks (Kimmeridge Clay, Heather Shale, Pentland and Brent Coals) of the Central and Viking Graben structures, North Sea, covering a depth range from 1863 to 5064 m. The methods applied include Rock Eval pyrolysis, vitrinite reflectance, fluorescence spectroscopy, spore colouration indices, absorbance ratios and infrared spectroscopy. When considering depth/maturity relationships for the various maturity parameters Tmax values from Rock Eval show the highest correlation coefficients, followed by optical parameters such as vitrinite reflectance, spore colour indices and lambda max derived from spectral fluorescence analyses. The depth/maturity relationship for the absorbance ratio is less well defined. Correlation of maturity parameters with vitrinite reflectance shows that spore colour indices have the highest correlation coefficients, followed by Tmax values derived from concentrated kerogen. Estimated reflectance values based on spore colour indices are for most part of the section almost identical with measured vitrinite reflectances, whereas estimated reflectances based on infrared spectroscopy show quite a deviation from the measured values.

RESUMO

O presente estudo realiza uma avaliação dos parâmetros de maturação ótica e química de uma série de rochas geradoras de petróleo ricas em matéria orgânica (Kimmeridge Clay, Heather Shale, Pentland e Brent Coals) das estruturas Central e Viking Graben, no Mar do Norte, cobrindo uma profundidade de 1863 a 5064 m. Os métodos utilizados incluem pirólise Rock Eval, reflectância da vitrinite, espectroscopia fluorescente, índice de coloração dos esporos, taxas de absorção e espectroscopia de luz infravermelha. Quando se considera a relação profundidade/grau de maturação para os diversos parâmetros de maturação, os valores de Tmax de Rock Eval apresentam os coeficientes de correlação mais altos, seguidos por parâmetros óticos, tais como a reflectância da vitrinite, os índices de coloração dos esporos e o lambda max derivado das análises de fluorescência espectral. A relação profundidade/grau de maturação com as taxas de absorção é menos bem definida. A correlação dos parâmetros de maturação com a reflectância da vitrinite mostram que os índices de coloração dos esporos possuem os coeficientes de correlação mais altos, seguidos por valores de Tmax derivados da concentração de querogênio. Os valores de reflectância estimados baseados nos índices de coloração dos esporos são, para quase toda a seção, praticamente idênticos às reflectâncias da vitrinite medidas, enquanto as reflectâncias estimadas baseadas na espectroscopia de luz infravermelha mostram um significativo desvio dos valores medidos.

KEY WORDS: North Sea, Petroleum Source Rocks, Maturity Parameters

INTRODUCTION

In the present study 46 samples of organic-rich source rock intervals (Kimmeridge Clay, Heather Shale, Pentland and Brent coals) from the Central and Viking Graben areas, North Sea (Fig. 1), were analyzed for maturity. The Upper Jurassic Kimmeridge Clay is the prominent type II source rock of most oils in the North Sea (Fig. 2), whereas the underlying Heather Shale is regarded as a poor type II/IV source rock. In some parts of the basin Middle Jurassic Pentland and Brent coals are underlying the oil source rock sequences. Samples were obtained from cores and sidewall samples covering a depth range from 1863 to 5064 m and were prepared for a variety of optical and chemical analyses according to standardized procedures. The methods applied included optical analysis (vitrinite reflectance, spectral fluorescence, spore colouration index (SCI), photometric colour measurements of structureless organic matter (SOM) in translucent light), and Rock Eval pyrolysis on whole rock and isolated kerogens and infrared spectroscopy.

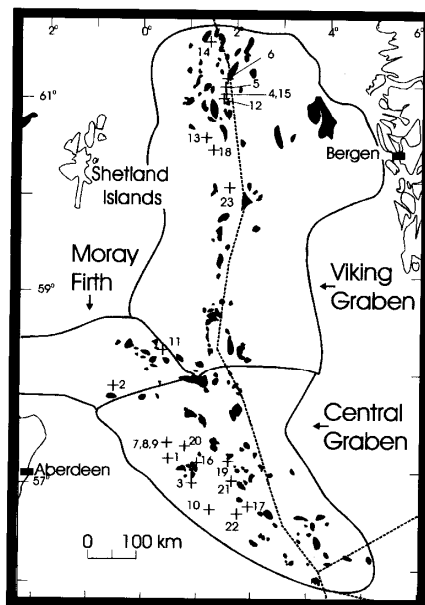


Fig. 1: Study area with outline of Central and Viking Graben in the North Sea and locations of wells used in the present study (for detailed sample information and depth interval analyzed see Table 1). Black areas indicate oil and gas pools.

SAMPLES AND ANALYTICAL PROCEDURES

The sample material comes from 23 wells (for locations see Fig. 1) and was split into representative portions to provide a) whole rock samples for Rock Eval Analyses, b) kerogen concentrates for incident light microscopy, Rock Eval pyrolysis and Infrared Spectroscopy and c) strewn slides for determination of spore colour indices.

Vitrinite Reflectances

Vitrinite reflectances were determined according to standardized procedures (Bustin et al., 1989). The results include analysis of 5 coals, in which vitrinite was found to be the predominant maceral, whereas the remainder of the vitrinite reflectances were obtained from dispersed organic matter, in which vitrinite particles constituted only a minor fraction of the organic components.

Rock Eval Pyrolysis

Rock Eval pyrolysis has become a routine and rapid tool in petroleum exploration to provide information on source rock quality and level of thermal maturity (Peters, 1986), although the pyrolysis data often show a wide scatter due to mineral matrix effects (Katz, 1983) and/or paucity of organic matter. In the present paper Rock Eval analyses were carried out on whole rock and kerogen concentrates (Rock Eval II), to evaluate the effect of mineral matter on T_{max} ($^{\circ}C$), the principal maturity parameter derived from Rock Eval.

Fluorescence Microscopy

Fluorescence microscopy has become an important tool in the evaluation of maturity and hydrocarbon generative potential of dispersed organic matter (DOM) based on the pioneering work by Jacob (1965), Ottenjann et al. (1974) and Gijzel (1981). This is in particular true for lithologies such as petroleum source rocks, which

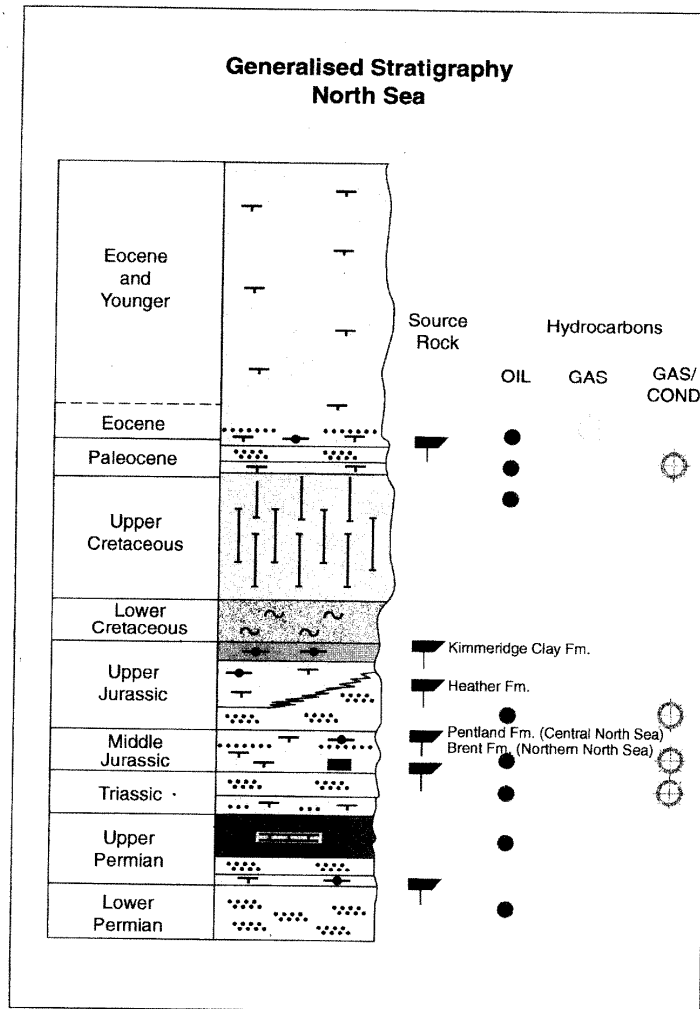


Fig. 2: Stratigraphic column of the study area showing intervals selected for analysis of thermal maturity (Kimmeridge Clay Fm., Heather Fm., Pentland Fm., Brent Fm.).

are characterized by the dominance of liptinitic amorphous and structured organic matter.

Fluorescence properties (intensity and colour) of the liptinic components are related to the level of maturity, with the fluorescence intensity decreasing with increase of maturity and the fluorescence colours changing from green-yellowish in immature samples to orange-brown in mature samples. The organic matter exhibits no visible fluorescence at maturity levels greater

than $\sim R_o > 1.35\%$. The changes in fluorescence intensity and colour have been the base for the development of quantitative methods to assess maturity level of the organic matter:

- Measurement of Fluorescence Intensity at 546 nm using blue-light excitation.
- Spectral Fluorescence Measurement. The organic matter is excited by UV-light and the spectral intensities are recorded over a wavelength range from 400-700 nm. From the

spectra two parameters are commonly used to describe the level of maturity: a) λ_{max} , which is the wavelength of highest fluorescence intensity and b) the Red/Green Quotient (Q), which is the ratio of fluorescence intensity at 650 nm over the intensity at 500 nm. Both parameters shift to higher wavelengths with increase in maturity.

In the present study spectral analysis was carried out using a MPV 3 Leitz microscope. The spectra were recorded using the program "Spectra", which records the fluorescence spectrum, the λ_{max} and Red/Green Quotient (Q) derived from the spectrum and a list showing the fluorescence intensities at increments of 1 nm over the wavelength interval selected.

Prior to the analysis of the organic matter the microscope and software was tested by using 3 Plexiglas standards of well-defined λ_{max} and Q values (Thompson-Rizer et al., 1987; Baranger et al., 1991). The results from the standards indicated good agreement with the data set established in the previous studies and indicated also very good reproducibility.

Within the organic fraction of the organic matter the maceral alginite was selected for measurement of fluorescence properties. This maceral usually has the highest fluorescence intensity of all liptinite macerals and has -as in the case of tasmanites algae - also a considerable size, which makes it particularly suitable for the recording of the in general low fluorescence intensities (Araujo et al., 1998). The algal material usually shows quite a variation in fluorescence intensity and colour within one sample related to varying degrees of degradation. The spectra produced in this study were obtained from the brightest fluorescing alginites, which are believed to be least effected by degradation. If not stated otherwise the spectra were averaged from 5 heterogeneous alginite bodies (acritarchs, dinoflagellates, botryococcus, tasmanites, algal debris). For correlation purposes spectra of tasmanites algae were measured separately in those samples, where this type of alginite was positively identified.

Spore Colouration Index

One of the first studies to use spore and pollen coloration as indicators of maturity was that of Gutjahr in 1966. He observed that the spore and pollen colours change from yellow to dark brown and black in relation to maturity, which he at the time called "carbonization".

The spore coloration scale used in this report is that of Robertson Research International Ltd. (1974), which was published by Fisher et al. (1980). This scale covers a range from 1 (uncoloured to glassy) for spores and pollen in the immature stage to 10 (black) indicating overmaturity. The changes in spore colour alteration normally show a linear relationship to temperature and depth of burial.

When correlating spore coloration index with vitrinite reflectance one has to make adjustments which take into account both the geological age of the samples under investigation and the time the strata has been exposed to the temperature (Triguís and Henz, 1987). In this report the estimated vitrinite reflectances were obtained from a correlation chart published by Fisher et al. (1980).

Photometric Colour Analysis of SOM

Structureless organic matter (SOM) shows a colour change from light to dark brown to eventually black with increasing maturity. This colour change is more or less similar to the decreasing translucency of sporomorphs, of which the chemical composition is comparable to SOM.

Theoretical Principles

Translucency (T) is defined as the intensity of light leaving (I_{sp}) divided by the intensity of light incident (I_{ref}) on a substance ($T = I_{sp}/I_{ref}$). The absorbance (A) is related to translucency as the negative logarithm of the translucency ($A = -\log T$). The absorbance can also be expressed as $A = t.c.e$, where t is the

length of the light path (thickness of the SOM), c is the concentration of absorbing compounds and e is the molar absorptivity. The two absorbency equations are known as Lambert-Beer's laws (Wolfard, unpublished report). The molar absorptivity e is specific for the substance involved, being dependant on both thickness and concentration of the absorbing compounds. Assuming e is constant, one can eliminate the thickness and concentration of the substance by using the ratio between the absorbance at two different wavelengths, A656 nm (red) divided by A497 nm (green). This technique, which is independent of thickness and concentration and which is known as the "photometric spore colour analysis" (Thronson and Aasgaard, 1990), was applied here to measure the absorbance ratio of SOM.

Measurement and equipment

An oil immersion objective and band pass filters of 497 and 656 nm were used to perform the absorption measurements on the SOM which was embedded in glycerin jelly and mounted on glass slides. The measurements were carried out with a Leitz Orthoplan microscope equipped with a MPV Compact photometer. The measurements were made in terms of translucency (T) and subsequently transformed to absorbance (A) using the equation:

$$A = \log(1/T) = -\log T$$

The translucency values were obtained by dividing the intensity of light measured on an object (SOM) by that measured on an empty spot in the surrounding embedding medium. The leaving (Insp.) and incident light (Inref) intensities at 497 and 656 nm were manually measured on exactly the same spot of SOM and a spot away from the periphery of the SOM particle. From these data the translucency (T) and absorbance ratio (A656/A497) per SOM spot were calculated. Finally the average absorbance ratio and standard deviation was calculated from about 30-35 SOM spots measured for each sample.

Infrared Spectroscopy

Thermal alteration of kerogen during burial and the changes taking place within its molecular structure are reflected by its infrared spectrum. The spectra typically display distinctive peaks at 2860 and 2930 cm^{-1} (CH_2 and CH_3 aliphatic groups), at 1710 cm^{-1} (carboxyl and carbonyl groups) and at 1630 cm^{-1} (aromatic C=C bands). Ganz (1986) and Ganz and Kalkreuth (1987, 1990) developed a "vitrinite reflectance equivalent grid" based on a large number of well defined samples of kerogen I, II and III of various maturity levels. The diagram makes use of the changes in relative ratios of intensities of aliphatic/aromatic bands (A-Factor) against the ratios of carbonyl and carboxyl/aromatic bands (C-Factor) to evaluate vitrinite reflectance equivalents (VRE).

RESULTS

The various maturity parameters are shown in Table 1, in which the samples are listed according to present depth. A graphical display of the results is given in Figs. 3-16.

Vitrinite Reflectances

Most of the samples yielded two clearly defined vitrinite populations (indigenous and reworked material). The values in Table 1 represent the "mode", in other words the mean values of the highest peaks within these two populations. The values range from 0.33 to 1.16 % Rrandom (Table 1). A graphical display of the vitrinite reflectance variations in relation to depths is shown in Fig. 3. Low and high reflecting vitrinite populations show essentially the same trend (Fig. 3), namely a slow increase in the depth interval 1800 - 3000 m, followed by a rapid increase at greater depth. Within the lower population (Fig. 3) there appears to be a wide range in vitrinite reflectances around the 4000 m depth level, suggesting differences in maturity in samples analyzed from that depth range.

The sample set comprised also 5 coal samples. The reflectance values for these coals

Table 1: Well and sample identification and maturity parameters listed according to depth (m).

Well	Depth (feet)	Depth (m)	Formation	Sample IR #	Imax (mm)	Q	Comments	SCI*	SCI**	Ro (%) from SCI	Ro (%) low	Ro (%) high	A-SOM	C-Factor	IR VRE	Sample IR #	Tmax (°C) rock	Tmax (°C) kerogen
1	6113.7	1863.46	Kim. Clay	7	511	0.84	alignite, undif.***	2.5-3.0	2.5	0.37-0.40	0.42	0.53	0.53	0.52	0.60	7	424	414
1	6124.3	1866.68	Kim. Clay	8	509	0.59	alignite, undif.***	2.5-3.0	3.0	0.37-0.40	0.42	0.53	0.69	0.47	0.60	8	424	414
2	6163.4	1878.60	Kim. Clay	14	567	0.75	alignite, undif.***	2.0-2.5	2.0	0.32-0.38	0.33	0.47	0.47	0.50	0.50	14	415	414
3	7561.3	2304.68	Kim. Clay	18	562	0.99	alignite, undif.***	3.0-3.5	3.5	0.38-0.42	0.33	0.47	0.46	0.48	0.52	18	423	421
3	7567.2	2306.48	Kim. Clay	19	570	0.97	tasmanites	3.5-4.0		0.42-0.47	0.33	0.47	0.43	0.50	0.50	19	427	424
4	8512.7	2594.67	Brent	29				4.0-4.5		0.47-0.50						29	428	
5	8678.7	2645.27	Kim. Clay	12	584	1.13	alignite, undif.***	3.5-4.0	3.5	0.42-0.47	0.37	0.52	0.49	0.45	0.60	12	424	421
5	8679.3	2645.45	Kim. Clay	13	570	1.22	alignite, undif.***	3.5-4.0	3.5	0.42-0.47	0.37	0.52	0.45	0.44	0.60	13	424	421
6	8707.5	2654.05	Brent	11a				3.5	3.5	0.42				0.26	0.75	11a	426	
6	8770.0	2673.10	Brent	11				3.5-4.0	4.0	0.42-0.47	0.57	0.57	0.57	0.33	0.67	11	425	
6	8775.0	2674.62	Brent	10				4.0-4.5	4.0	0.47-0.50	0.57	0.57	0.58	0.28	0.76	10	428	
6	8862.6	2701.32	Brent	9	575	1.39	coal, alignite, undif.***	3.5-4.0	3.5	0.42-0.47	0.52	0.52	0.31	0.31	0.75	9	428	431
7	9728.2	2965.16	Kim. Clay	1	546	0.95	alignite, undif.***	3.0-3.5	3.5	0.38-0.42	0.37	0.57	0.53	0.19	0.67	1	430	433
7	9753.4	2972.84	Heather	2	547	0.76	alignite, undif.***	3.0-3.5	3.0	0.38-0.42	0.37	0.57	0.54	0.30	0.67	2	431	432
7	9784.6	2982.35	Heather	3	538	0.77	alignite, undif.***	3.0-3.5	3.0	0.38-0.42	0.37	0.57	0.58	0.35	0.67	3	428	428
8	10245.6	3122.86	Heather	4	545	0.95	alignite, undif.***	3.5-4.0	3.5	0.42-0.47	0.37	0.57	0.51	0.30	0.67	4	432	432
9	10575.6	3223.44	Kim. Clay	5	570	1.05	alignite, undif.***	4.0-4.5	4.0	0.47-0.50	0.43	0.57	0.5	0.38	0.67	5	429	429
9	10517.9	3205.86	Kim. Clay	6	600	1.13	alignite, undif.***	4.0-4.5	4.0	0.47-0.50	0.47	0.57	0.51	0.45	0.67	6	427	427
10	10544.0	3213.81	Penland	26a	615	1.27	alignite, undif.***	0.45-5.0	4.5	0.50-0.54	0.53	0.57	0.62	0.27	0.79	26a	431	
10	10576.0	3223.56	Penland	26b	605	1.12	tasmanites	4.0-4.5		0.47-0.50			0.59	0.92	26b	431		
10	10586.0	3227.22	Kim/Heather	26c	604	1.16	alignite, undif.***			0.47-0.50				0.92	26c	431		
11	10709.0	3264.10	Kim. Clay	15a	625	1.37	alignite, undif.***	4.0-4.5	4.0	0.47-0.50	0.42	0.53	0.48	0.05	0.68	15a	428	
12	10770.1	3282.73	Kim. Clay	33	616	1.21	tasmanites	4.0-4.5	4.0	0.47-0.50	0.60	0.62	0.64	0.19	0.92	33	430	425
12	10836.8	3303.06	Kim. Clay	34	650	1.39	alignite, undif.***	4.0-4.5	4.0	0.47-0.50	0.60	0.62	0.51	0.28	0.80	34	427	427
12	10831.8	3301.53	Kim. Clay	34a	595	1.39	tasmanites	4.5-5.0	4.5	0.50-0.53	0.49	0.49	0.48	0.05	0.68	34a	432	
10	10892.8	3320.13	Penland	26	660	1.30	coal	4.5-5.0	4.5	0.50-0.53	0.57	0.57	0.48	0.05	0.68	26	430	
11	10918.1	3327.84	Heather/Kim	15	630	1.41	alignite, undif.***	3.5-4.0	3.5	0.42-0.47	0.52	0.62	0.54	0.30	0.68	15	428	427
13	11130.5	3392.58	Kim. Clay	35				4.0-4.4	4.0	0.47-0.50	0.57	0.57	0.59	0.30	0.68	35	435	440
13	11133.2	3393.40	Kim. Clay	36									0.66		36	435		

14	11466.0	3494.84	Kim. Clay	28				7.0-7.5	7.0	0.80-0.90	0.57	0.72	0.50		28	437	438	
15	11548.7	3520.04	Brent	31				5.0-5.5	5.5	0.55-0.58	0.63	0.63			31	435		
15	11551.3	3520.84	Brent	32			coal							0.07	0.77	31	437	
16	12693.9	3869.10	Kim. Clay	20			no fluorescence	7.0-7.5	7.5	0.80-0.90	0.57		0.65	0.22	0.86	20	443	
17	12782.0	3895.95	Kim. Clay	27b	655	1.32	tasmanites	5.5-6.0	5.5	0.58-0.62	0.67		0.56	0.26	0.70	27b	438	
18	12822.0	3938.63	Kim. Clay	37			no fluorescence	8.0-8.5	8.5	0.95-1.10	0.67		0.72		37	438	448	
18	12843.0	3945.03	Kim. Clay	38			no fluorescence				0.82	0.96			38	448	448	
18	12888.0	3958.74	Heather/Kim	39			no fluorescence	7.5-8.0	8.0	0.90-1.00	0.83	1.12	0.54	0.06	0.60	39	446	450
19	12946.2	3948.00	Kim. Clay	24	693	1.64	alginite, uninf.***	7.0-7.5	7.0	0.80-0.90	0.74	1.03	0.66		24	447	433	
19	12953.7	3948.29	Heather	25			no alginite	7.0-7.5	7.0	0.80-0.90	0.87	1.00	0.72		25	436	436	
20	13251.7	4039.12	Kim. Clay	16			no fluorescence	8.0-8.5	8.5	0.95-1.10	0.83		0.67	0.15	16		446	
17	13429.1	4093.19	Heather	27			no fluorescence	8.5-9.0	9.0	1.10-1.20	0.97	1.13	0.81	0.09	27	444		
21	13611.0	4148.63	Heather	22a	665	1.66	alginite, uninf.***	7.5-8.0	8.0	0.90-1.00	0.82	1.13	0.64		22a	441		
16	14374.0	4381.20	Penland	20a				8.5-9.0	8.5	1.10-1.20			0.63		20a	447		
22	14471.2	4410.62	Kim. Clay	23	700	1.67	alginite, uninf.***	8.5-9.0	9.0	1.10-1.20	0.97	1.14	0.72		23	442		
23	16613.0	5663.64	Kim. Clay	40			no fluorescence	8.5-9.0	8.5	1.10-1.20	0.93	1.16	0.67		40	451		

lmax (nm) = wavelength of highest fluorescence intensity; Q = Red/Green Quotient; *SCI = Range of Spore Colouration Indices; **predominant SCI; ***Spectra averaged from undifferentiated alginite; A SOM = absorbance ratio (A656/A497) determined on structureless organic matter; C-Factor = (1710 cm⁻¹ / 1710 cm⁻¹ +1630 cm⁻¹) determined by infrared spectroscopy; IR VRE=vitrinite reflectance equivalent estimated from infrared spectroscopy.

Tabla 2 - Correlation coefficients between vertical depth and the various maturity parameter

Ro (%) low pop.	Ro (%) high pop.	Lamda max(nm)	Q	SCI	Tmax (°C) kerogen	Tmax (°C) rock	A-ratio (SOM)	C-Fact. IR
0.86	0.87	0.85	0.80	0.86	0.93	0.85	0.61	0.82

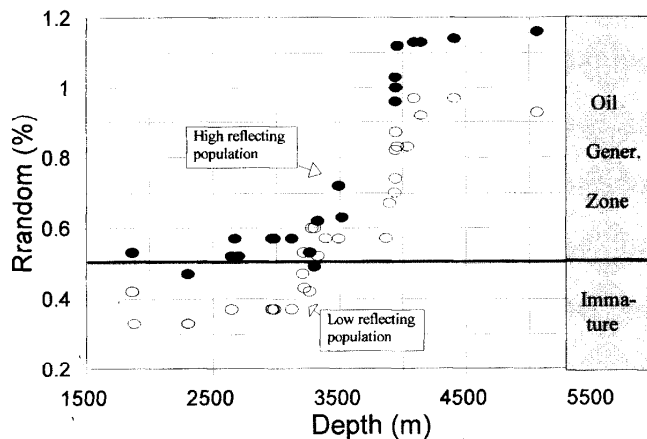


Fig. 3: Vitritine reflectance (Rrandom %) versus depth (m)

range from 0.52 to 0.63 % Rrandom (Table 1). The petrographic composition of the coals is quite different. Visual examination showed that samples IR-9 and IR-10 are characterized by the abundance of trimacerites (consisting of macerals of vitritine, inertinite, liptinite groups). In contrast, samples IR-26 and IR-31 consist almost entirely of vitritine, which explains the greasy luster and conchoidal fractures when examined macroscopically. Sample IR-34a is characterized by the abundance of detrital macerals of inertinite and vitritine groups, and has an extremely high content of sporinite.

When considering the lower vitritine population as primary maturity parameter (indigenous vitritine), the data set suggests, that strata are immature at depth less than 3250 m and are in the oil generation zone (moderately to highly mature) at greater depth levels (Fig. 3).

Rock Eval Analysis

Tmax (°C) values obtained from whole rock samples and kerogen concentrates are shown in Fig. 4. The values range from 414 (immature)

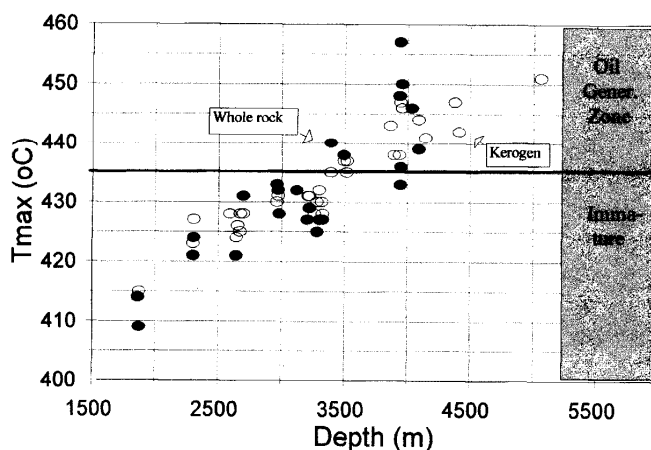


Fig. 4: Tmax (°C) versus depth (m)

to 451 (mature). It appears that Tmax values obtained from kerogen concentrates show a better correlation with depth than the Tmax values determined on whole rock samples. The threshold from immature to mature strata, considered to occur at a Tmax (°C) value of 435 (Fig. 4), is approximately at a depth of 3500 m, somewhat deeper than the threshold indicated by vitrinite reflectances (3250 m).

Fluorescence parameters (alginite macerals, undifferentiated)

The relationship between present day depth and fluorescence parameters derived from alginite macerals (undifferentiated) are shown in Figs. 5a (lmax) and 5b (Q). It appears that in ge-

neral both lmax and Q values increase with depth indicating a progressively higher maturity. From Table 1 it is also apparent that the fluorescence parameters in samples from one well taken at close depth range are consistent with only little variations in lmax and Q values (wells 3, 5, 9). However, it is obvious, that for similar depth levels at different locations there exist quite a variation in fluorescence parameters (Figs. 5a and 5b). This is in particular true for wells 1 and 2 (Table 1), which would indicate a somewhat higher maturity for the strata in well 2.

A similar pattern is apparent at the 3000 m depth level (Figs. 5a and 5b), where both lmax and Q values indicate relative low maturity in comparison with overlying and underlying strata.

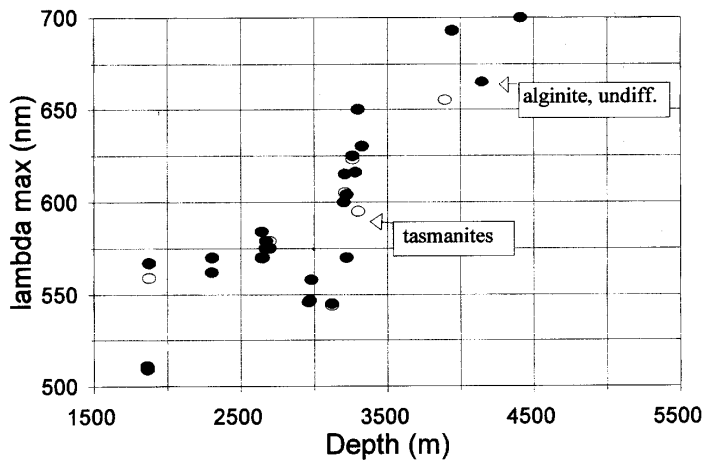


Fig. 5a: lmax (nm) determined on alginite versus depth (m)

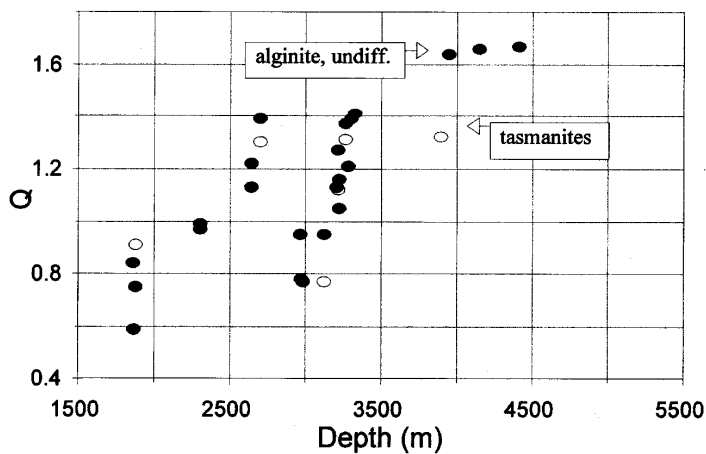


Fig. 5b: Red/Green Quotient (Q) determined on alginite versus depth (m)

This concerns strata in wells 7 and 9, which may be somewhat lower in maturity when considering the overall trends in Figures 5a and 5b.

Fluorescence parameters (tasmanites)

In 10 samples *tasmanites* type alginite was identified positively and the relationship between fluorescence parameters and depth was demonstrated in Figs. 5a and b. The I_{max} values range from 559 nm at 1878.60 m depth (well 2) to 655 nm at 3895.95 m depth (well 17). A relatively low value (544 nm) is shown for well 8 at a depth of 3122.86 m consistent with the low I_{max} value determined on other algal material from this well (Table 1 and Fig. 5a). A similar pattern is shown for the trend of Q values versus depth (Fig. 5b), indicating that the sample analyzed from this well may in fact represent a somewhat lower maturity level.

Spore Colouration Index

The Spore Colouration Index (SCI) values for the samples are summarized in Table 1. Each sample commonly yielded abundant spores with a wide variation in spore colours due to the presence of indigenous material, only little affected by degradation, the presence of degraded indigenous material and the presence of reworked material. From this wide distribution of colours a range of colour indices was selected for each

sample ranging from 2.0-2.5 in the relatively shallow samples (<2000 m) to 8.5-9.0 in samples at greater depth (> 4000 m). A graph showing the SCI/depth (m) relationships is shown in Fig. 6. From this figure it is apparent that there is only little change in SCI values in the depth interval 2500 to 3400 m. It is interesting to note that at 3000 m depth a somewhat lower SCI value corresponds to the low λ_{max} and Q values recorded by fluorescence microscopy.

Beyond 3500 m the SCI values increase rapidly with depth and indicate in places also significant differences in maturity in samples from similar depths intervals in different wells (Fig. 6). This is in particular true for samples from wells 15 and 17 (Table 1), where SCI values of 5.5 were recorded, whereas the regional SCI values in samples from similar depth at other locations are in the order of 7.0 to 8.5. At present time there is no explanation for these discrepancies, which may just show the limitations of this particular maturity parameter.

Photometric Colour Analysis of SOM

The absorbance ratios (A656/A497) range from 0.43 to 0.81 (Table 1). When plotted versus depth there is an overall trend apparent from low absorbance ratios at relatively shallow depth (Fig. 7) to higher values at greater depth, although a considerable scatter occurs for samples from si-

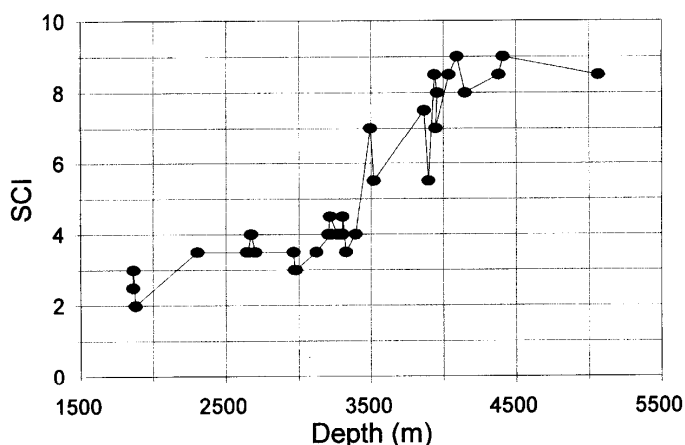


Fig. 6: Spore Colouration Index (SCI) versus depth (m)

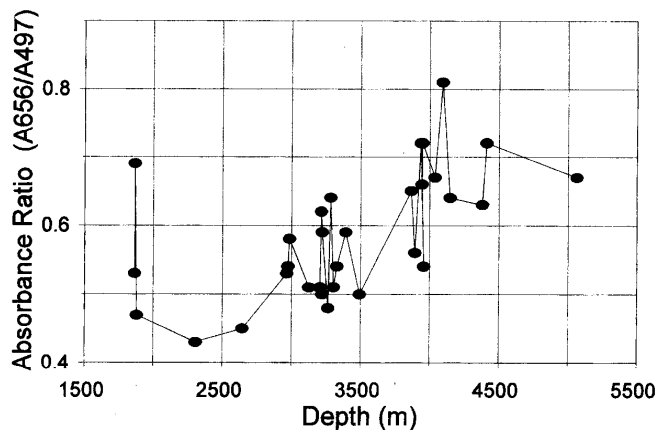


Fig. 7: Absorbance Ratio (A656/A497) determined on structureless organic matter (SOM) versus depth (m)

milar depth intervals. A rapid decline of the translucency of the SOM is observed at higher maturity levels (> 0.80% Rrandom). At present the photometric colour analysis method of measuring the absorbance/translucency of SOM in kerogen type II source rocks does not seem very promising and needs further testing.

IR Spectroscopy

Interpretation of maturity levels from IR spectroscopy is based on the changes in relative ratios of intensities of aliphatic/aromatic bands (A-Factor) against the ratios of carbonyl and carboxyl/aromatic bands (C-Factor). When considering the

changes in the C-Factor alone there is an overall trend to lower values with increasing depth (Fig. 8), however, a better assessment of maturity changes is obtained by using the "vitrinite reflectance equivalent grid (VRE)" (Fig. 9), based on Ganz (1986) and Ganz and Kalkreuth (1987, 1990), which provides at the same time information on maturity and type of organic matter. The vitrinite reflectance values derived from this diagram range from 0.52 to 1.00 VRE % (Table 1).

Correlation coefficients for the maturity parameters

Since the burial history in the study area is

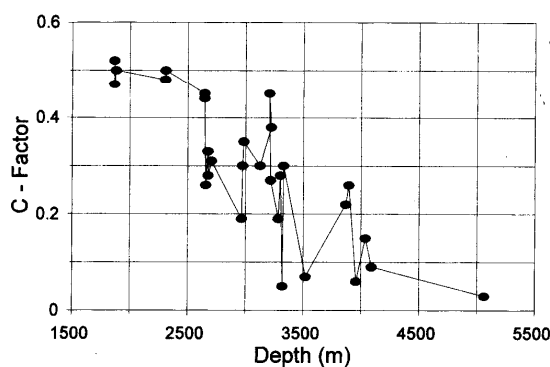


Fig. 8: C-Factor ($1710\text{ cm}^{-1} / 1710\text{ cm}^{-1} + 1630\text{ cm}^{-1}$) determined by infrared spectroscopy versus depth (m)

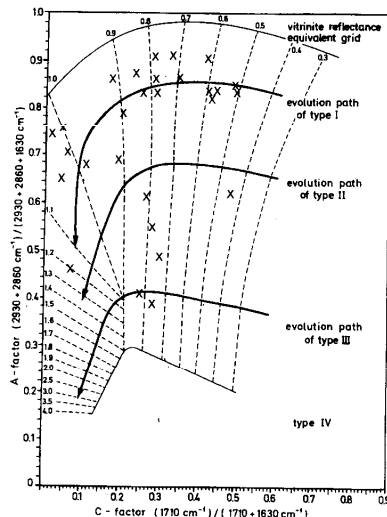


Fig. 9: Vitrinite reflectance equivalent grid based on A-Factor and C-Factor and position of samples analyzed in this study

relatively simple and present day burial is equivalent to maximum temperature, vitrinite reflectance measurements of the Pentland and Brent coal samples show a very good correlation with true vertical depth. Therefore true vertical depth data could effectively be used to evaluate the reliability of the different maturity tools on the samples of the oil prone Kimmeridge Clay source rock. From Table 2 it is apparent that Tmax (°C)

from Rock Eval analysis and vitrinite reflectance yield the highest overall correlation coefficients for the sample interval studied ($c = 0.93$ and 0.87 respectively), whereas the absorbance ratio derived from structureless organic matter has the lowest correlation coefficient ($c = 0.61$).

CORRELATION OF OPTICAL AND CHEMICAL (ROCK EVAL, INFRARED SPECTROSCOPY) MATURITY PARAMETERS

The following section discusses briefly the correlations between vitrinite reflectances (low reflecting population), which is considered to represent the indigenous or primary vitrinite population in the samples and the other maturity parameters applied in this study (based on linear regression profiles).

Vitrinite Reflectance versus Tmax (°C)

The correlation between vitrinite reflectance (Rrandom%) and Tmax-values determined on kerogen and whole rock samples is shown in Fig. 10. The data suggest a relatively high correlation of vitrinite reflectance with Tmax values determined on kerogen samples ($r=0.8440$), whereas the correlation with Rock

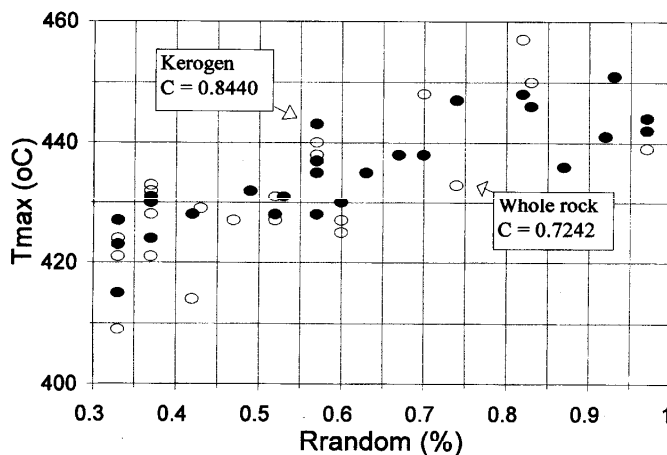


Fig. 10: Correlation of vitrinite reflectance (Random %) with Tmax (°C) from Rock Eval pyrolysis. c =correlation coefficient.

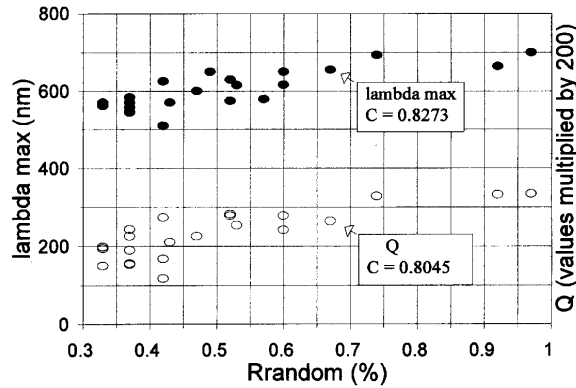


Fig. 11: Correlation of vitrinite reflectance (Rrandom %) with fluorescence maturity parameters (lambda max and Q). Note: Q-values have been multiplied by 200. c=correlation coefficient.

Eval data from whole rock samples is not as good (r=0.7242).

Vitrinite Reflectance versus Fluorescence Properties

The correlation between fluorescence properties of alginite (lambda max and Q) and vitrinite reflectances are shown in Figure 11. They show in samples < 0.5 % Rrandom large variations in lambda max and Q values for samples having same or similar vitrinite reflectance levels. At reflectances > 0.50 % Rrandom both vitrinite reflectance and fluorescence parameter, in particular lambda max

increase significantly (Fig. 11). The correlation coefficient is highest for vitrinite reflectance versus lambda max (c=0.8273) and is somewhat lower for Q (r=0.8045).

The results from this report are in agreement with earlier studies (Ottenjann, 1980), which indicated for lambda max values < 550nm reflectance levels of < 0.50 % Rrandom, whereas lambda max values of about 650 nm would indicate a vitrinite reflectance level of 1.0 % Rrandom.

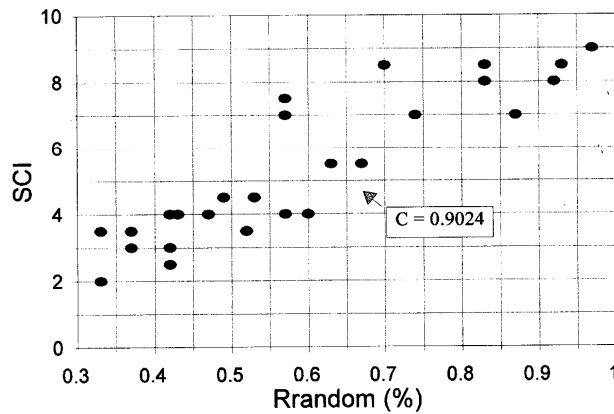


Fig. 12: Correlation of vitrinite reflectance (Rrandom %) with Spore Colouration Index (SCI). c=correlation coefficient.

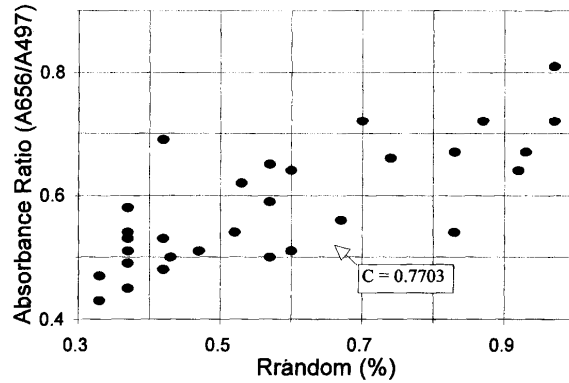


Fig. 13: Correlation of vitrinite reflectance (Rrandom %) with Absorbance Ratio (A656/ A497) determined on structureless organic matter. c=correlation coefficient.

Vitrinite Reflectance versus SCI

The correlation between spore colouration index and vitrinite reflectance is shown in Figure 12. It shows an almost linear relationship between the two parameters, except at higher SCI values, where for the same SCI values quite a spread of vitrinite reflectances is apparent (Fig. 12). This suggests that in that maturity range (Rrandom > 0.6 %) vitrinite reflectances are more sensitive to thermal alteration than spore colouration. However, the overall correlation coefficient is very good (r=0.9024).

Vitrinite Reflectance versus Absorbance Ratios

The correlation of vitrinite reflectance with absorbance ratios obtained from SOM is shown in Fig. 13. The overall trend is that of increasing absorbance ratios with increase in vitrinite reflectances. It is obvious that there exist a considerable spread in data, reflecting the poor relationship between absorbance ratio and depth as discussed earlier. Based on the data set of the present study a correlation coefficient of r=0.7703 was determined.

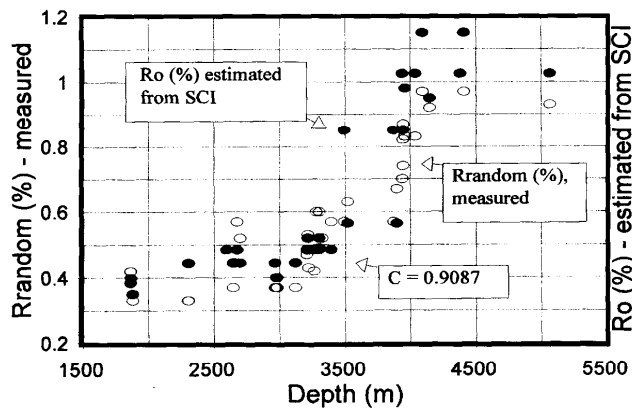


Fig. 14: Correlation of vitrinite reflectance (Rrandom %) with C-Factor ($1710\text{ cm}^{-1} / 1710\text{ cm}^{-1} + 1630\text{ cm}^{-1}$) derived from infrared spectroscopy. c=correlation coefficient.

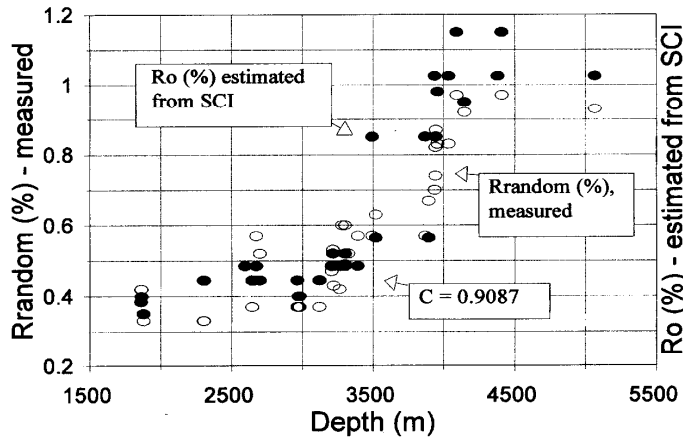


Fig. 15: Comparison of measured vitrinite reflectances (Rrandom %) and reflectances estimated from Spore Colouration Indices (SCI). c =correlation coefficient.

Vitrinite Reflectances versus C-Factor

The correlation of vitrinite reflectances with the C-Factor determined by infrared spectroscopy is shown in Fig. 14. There appears to be a rapid decline in C-Factor values in the early stages of maturity (low vitrinite reflectance levels), whereas at higher reflectances the C-Factor changes only slightly (Fig. 14). This observation is in agreement with the thermal kerogen evolution paths shown in Fig. 9, indicating a rapid decrease in C-Factor values at low and intermediate maturity levels, whereas at higher maturity levels the C-Factor values do not change

significantly. The overall correlation coefficient for the two maturity parameters is $r=0.7994$.

Comparison of measured vitrinite reflectances with reflectances estimated from spore colour indices (SCI) and infrared spectroscopy (VER)

The correlations between measured vitrinite reflectances and reflectance levels estimated from SCI are shown in Figs. 15. The two maturity parameter show over much of the section a parallel trend, with measured and estimated reflectances in many instances almost

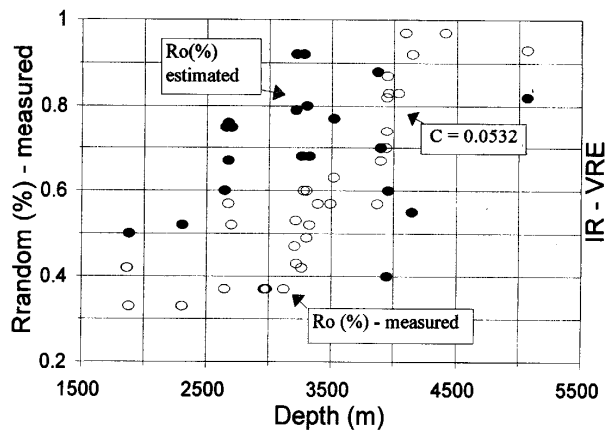


Fig 16: Comparison of measured vitrinite reflectances (Rrandom %) and reflectances estimated from the vitrinite reflectance equivalent grid, based on A- and C-Factors determined by infrared spectroscopy. c =correlation coefficient.

identical ($c=0.9087$). Some deviations are obvious at higher maturity level, where Ro-values estimated from SCI analysis indicate higher maturity levels when compared to measured vitrinite reflectances (Fig. 15). A similar relationship was observed earlier, when vitrinite reflectances were plotted against SCI values (Fig. 12), suggesting that vitrinite reflectance at higher maturity levels may be a better maturity parameter than SCI.

Comparison of measured vitrinite reflectances and Ro-values estimated from infrared spectroscopy are shown in Fig. 16. At lower maturity the estimated VRE values are consistently higher, whereas at higher maturity the trend is reverse, and VRE values suggest a lower maturity when compared to measured reflectance values. As a consequence the correlation coefficient between the two series of Ro-values is low ($r=0.0532$). The poor relationship between measured vitrinite reflectances and IR estimated vitrinite reflectances is at present time poorly understood but suggests that for the current sample set IR maturity estimations based on the *vitrinite reflectance equivalent grid* (Ganz and Kalkreuth, 1987, 1990) are not very reliable maturity parameters.

CONCLUSIONS

Maturity

Vitrinite reflectances and Tmax values from Rock Eval Pyrolysis suggest that the transition from immature to mature source rocks in the study area occurs at a depth range from 3250 – 3500 m. At greater depth (3500-5063 m) the maturity parameters suggest moderate to high maturity of the strata.

Maturity Parameters versus depth (m)

Evaluation of the maturity/depth relationships for the depth interval investigated (1863-5063 m) indicate highest correlation coefficients for Tmax values derived from kerogen concentrates ($r=0.93$), vitrinite reflectance ($c=0.87$

(high population) and $c=0.86$ (low population)) and Spore Colouration Indices ($r=0.86$). The Red/Green Quotient (Q) has slightly lower correlation coefficient ($c=0.80$). The absorbance Ratio derived from structureless organic matter in transmitted light shows the lowest correlation coefficient with depth ($r=0.61$). The C-Factor derived from infrared spectroscopy shows an intermediate correlation coefficient ($c=0.82$).

The study demonstrated also that fluorescence parameters (lambda max and Q) are in particular useful in maturity ranges where other maturity parameters such as the Spore Colouration Index (SCI) and vitrinite reflectances show only little variation.

Correlation of vitrinite reflectance with other maturity parameter

Evaluation of correlation coefficients between vitrinite reflectances and the other maturity parameters applied in this study indicated the best correlation between Spore Colour Indices and vitrinite reflectance ($r=0.9024$). This is followed by vitrinite reflectance versus Tmax values derived from kerogen ($r=0.8440$), whereas the relations between Tmax from whole rock analysis and vitrinite reflectance are less well defined ($r=0.7242$). The C-Factor derived from infrared spectroscopy shows an intermediate correlation coefficient ($c=0.7994$).

Amongst the optical maturity parameters I_{max} shows the highest correlation coefficient to vitrinite reflectance ($r=0.8273$), followed by Q ($r=0.8045$) and the absorbance ratio ($r=0.7703$).

Comparison of estimated vitrinite reflectances from Spore Colouration Indices and Infrared spectroscopy indicate a high correlation coefficient between measured and SCI derived reflectance values ($r=0.9087$), whereas the relationships between infrared spectroscopy derived reflectances and measured vitrinite reflectance values is rather poor for the sample set analyzed ($r=0.0532$).

Applicability of the maturity parameters

For routine assessment of large sample sets it is obvious that Rock Eval pyrolysis performed on whole rock samples provides fast and reliable results (correlation coefficient of $r = 0.82$ in this study). Rock Eval pyrolysis performed on kerogen concentrates from the same sample set resulted in a significant higher correlation coefficient ($r = 0.93$), but additional time-consuming and expensive sample preparation is needed to remove mineral matter by acid treatment and/or density fractionation processes.

Vitrinite reflectances determined on dispersed organic matter shows similar high correlation coefficients ($r = 0.86-87$), despite the known shortcomings of difficulties in identifying indigenous vitrinite particles, the possible suppression of vitrinite reflectance values in petroleum source rocks and the scarcity of vitrinite particles in certain lithologies, i.e. carbonates.

Spore Colouration Indices (SCI) show a good correlation with depth, but tend to overestimate slightly maturity levels at elevated maturity.

Fluorescence parameters are useful additional maturity parameters and are best applied at low to intermediate maturity levels. The method is limited by the fact that fluorescence intensities decrease rapidly at elevated maturity and disappears altogether at a maturity level equivalent to approximately 1.3 % Ro. The method is also dependent on the availability of suitable organic matter, i.e. alginite macerals.

Infrared spectroscopy derived maturity assessment based on the C-Factor shows an overall good relationship to depth ($r = 0.82$), the method, however, requires time-consuming kerogen isolation prior to analysis.

The absorbance ratio determined on structureless organic matter in transmitted light

mode shows a relatively large scatter of data in relation to depth, resulting in a low correlation coefficient ($r = 0.61$), when compared with the other maturity parameters. Unless this method can be improved significantly its use is recommended only if the other methods for maturity assessment are not available.

ACKNOWLEDGEMENTS

The manuscript benefited from critical reviews by Prof. M. Lemos de Sousa and Drs. M. Marques and L. Trindade and the authors gratefully acknowledge their contribution.

REFERENCES

- Araujo, C., Vieth-Redemann, A., Pradier, B., Kalkreuth, W., Hagemann, H., Hufnagel, W., Koch, M., Koch, J., Kuili, J., Laggoun-Defarge, F., Newman, J., Petersen, H., Spanic, D., Stasiuk, L., Suarez-Ruiz, I., Thompson-Rizer, C., Wang, J., Wilkins, R., 1998. ICCP Interlaboratory Exercise on the Application of Micro Spectral Fluorescence Measurements as Maturity Parameters. 6th Alago Meeting, Margarita Island, Venezuela, Oct. 18-21, 1998, CD ROM, 5 pages
- Baranger, R.; Martinez, L.; Pittion, J-L. and Pouleau, J. 1991. A new calibration procedure for fluorescence measurements of sedimentary organic matter. *Org.Geochem.* 17, 467-475.
- Bustin, M., Cameron, A., Grieve, D. and Kalkreuth, W. 1989. *Coal Petrology - Its Principles, Methods and Applications*, GAC, Short Course Notes, Vol 3, 230pp.
- Fisher, M., Barnard, P., Cooper, B. 1980. Organic maturation and hydrocarbon generation in the Mesozoic sediments of the Sverdrup basin, Arctic Canada. in: 4th International Palynology Conference, Lucknow, 1976-77, Vol. 2, 581-588
- Ganz, H. 1986. Organisch- und anorganisch-geochemische Untersuchungen an ägyptischen Schwarzschiefer/Phosphoritsequenzen - Methodenentwicklung

- und genetisches Modell. Berliner Geowissenschaftliche Abhandlungen, Reihe A/ Band 70, Verlag D. Reimer, Berlin, 113pp.
- Ganz, H. and Kalkreuth, W. 1987. Application of infrared spectroscopy for the classification of kerogen types and the evaluation of source rock and oil shale potentials, FUEL, 66, 5, 708-711
- Ganz, H. und Kalkreuth, W. 1990. The potential of infrared spectroscopy for the classification of kerogen, coal and bitumen, Erdöl und Kohle, 43, 3, 116-117
- Gijzel, P. 1981. Applications of the geomicrophotometry of kerogen, solid hydrocarbons and crude oils to petroleum exploration. in: Brooks, J. editor, Organic Maturation Studies and Fossil Fuel Exploration, Academic Press, London, 351-377
- Gutjahr, C. 1966. Carbonization measurements of pollen grains and spores and their application. Leidse Geol. Medd., No 38, 1-29
- Jacob, H. 1965. Neue Erkenntnisse auf dem Gebiet der Lumineszenzmikroskopie fossiler Brennstoffe. Fortschr. Geol. Rheinld. u. Westf., 12, 569-588
- Katz, B. 1983. Limitations of Rock Eval pyrolysis for typing organic matter. Organic Geochemistry, 4, 195-199
- Ottenjann, K., Teichmüller, M. and Wolf, M. 1974. Spektrale Fluoreszenzmessungen an Sporiniten mit Auflicht-Anregung, eine mikroskopische Methode zur Bestimmung des Inkohlungsgrades gering inkohlter Kohlen. Fortschr. Geol. Rheinld. u. Westf., 24, 1-36
- Ottenjann, K. 1980. Spektrale Fluoreszenz-Mikroskopie von Kohlen und Ölschiefen. Leitz-Mitteilungen, Wissenschaft und Technik, 7, 8, 262-272
- Peters, K. 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. AAPG Bulletin, 70, 318-329
- Pradier, B., Bertrand, P., Mertinex, L., Laggoun, F. and Pittion, J. 1988. Microfluorometry applied to organic diagenesis study. Organic Geochemistry, 13, 4-6, 1163-1167
- Robertson Research Group, North Wales. 1974. In-house manual of procedures in determination of spore colouration indices and kerogen typing. North Wales, 18pp.
- Thompson-Rizer, C. and Woods, R. 1987. Microspectrofluorescence measurements of coals and petroleum source rocks. International Journal of Coal Geology, 7, 85-104
- Trigüis, J. and Henz, G. 1987. A petrografia orgânica na pesquisa de petróleo. In: Congresso Brasileiro de Geoquímica, 1o, Sociedade Brasileira de Geoquímica - SBGq, Porto Alegre, Brasil, Vol. 2, 395-408
- Thronson, T. and Aasgard, K. 1990. Photometric spore colour analysis - an approach that is independent of species and wall-thickness. EP 91-1608
- Wolfard, A. Photometric sporomorph colour measurements, the A656/A495 ratio as a maturity tool - a pilot study. EP 91-1585