Rockall Studies Group

RSG Project 99/3

Thermal Maturation Report on Shallow Borehole Cores:

16/28-Sb01

83/20-Sb01

83/24-Sb02

by

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Summary Conclusions

Borehole 16/28-Sb01 has yielded very little information on indigenous maturation levels. Vitrinite reflectance and spore colour/fluorescence determinations have provided information on the maturity of reworked Carboniferous sources. Generally two sources for the reworked material can be proposed with slightly different maturation levels, both being mature with regards to hydrocarbon generation.

In borehole 83/20-Sb01, a probably indigenous Jurassic vitrinite population with a mean random reflectance (R_r) of around 0.3% has been found which can be interpreted as immature with regards to hydrocarbon generation. However, illite crystallinity suggests higher, mature grades, which would correlate with one of the 'reworked' vitrinite populations. Several mature sources of Carboniferous and Jurassic age are suggested.

Borehole 83/24-Sb02 contains a probably indigenous Carboniferous vitrinite population with a mean random reflectance (R_r) of around 2.4%. Illite crystallinity suggests lower anchizonal conditions. Thus, the maturity can be described as mature to over-mature with regards to hydrocarbon generation.

Two new methods to assess maturation levels have been attempted in this study. The use of organic microforaminiferal linings for palynomorph colour and fluorescence has been found of limited relevance in this investigation since foram calibration has not yet been established with the 'standard' vitrinite reflectance scale.

Illite crystallite size determinations have shown that sizes generally increase with age. The data also suggested a fault zone within borehole 83/24-Sb02 at 68.95m of depth. More data needs to be collected to enable a more detailed interpretation.

Contents

Introduction

Seventeen samples were collected from three different cores drilled in the Rockall Trough margins (Table 1). All samples were processed for clay minerals studies. Thirteen samples were processed for organic matter of which three proved barren. The other ten were mounted on slides for palynomorph colour/fluorescence and as resin blocks for vitrinite reflectance measurements.

Borehole No.	Depth (m)	CSA No.	Lithology
16/28-Sb01	88.9	12117	Grey mudstone
16/28-Sb01	101.9	12116	Grey mudstone
16/28-Sb01	130	12115	Grey mudstone
16/28-Sb01	147.06	12113	Sandstone
16/28-Sb01	147.2	12112	Sandstone
16/28-Sb01	147.35	12114	Basalt
83/20-Sb01	97.55	12111	Marl
83/20-Sb01	107.63	12110	Greensand
83/20-Sb01	107.8	12109	Greensand, more muddy
83/20-Sb01	127.97	12108	Greensand, more muddy
83/20-Sb01	176.5	12106	Grey siltstone
83/20-Sb01	176.7	12107	Grey siltstone
83/24-Sb02	67.91	12105	Red mudstone
83/24-Sb02	68.95	12104	Tectonically deformed siltstone
83/24-Sb02	71.18	12103	Grey siltstone
83/24-Sb02	71.36	12101	Grey siltstone
83/24-Sb02	71.47	12102	Grey siltstone

Table 1. List of samples, project 99/3, sampled 23/05/2000.

Maturation indicators I: Organic Matter

A preliminary check on organic matter was carried out for all samples processed for organic matter. Only three samples proved completely barren in this first check. Additionally, all samples were tested for $CaCO_3$ content. Except for sample no. 12101-12103, all samples showed the presence of $CaCO_3$.

Samples no. 12106 and 12107 contained large amounts pyrite that was handpicked and removed to enable easier preparation of vitrinite blocks.

Borehole	Sample no.	CO_3 present	Preliminary check	Slide	Vitrinite block
16/28-Sb01	12117	+	+	+	+
	12116	+	+	+	+
	12115	+	+	+	+
83/20-sB01	12111	+	Barren	-	-
	12110	+	+	+	+(none)
	12109	+	+	+	+(very little)
	12108	+	+	+	+(very little)
	12106	+	+ (pyrite rich)	+	+
	12107	+	+ (pyrite rich)	+	+
83/24-Sb02	12104	+	Barren	-	-
	12103	-	Barren	-	-
	12101	-	+	+	+
	12102	-	+	+	+

Table 2. Preparation list for organic matter; preliminary check list on $CaCO_3$ and palynomorphs.

Vitrinite reflectance - method

Organic residue was extracted by dissolving the samples with 40% hydrofluoric acid. The dried residue was mounted onto a block using an epoxy resin. Mean random vitrinite reflectance (R_r) was measured from polished blocks under a Leitz MPV-1 compact microscope/photometer. The standards used were glass (Leitz No. 998) with a reflectance of 1.23%R_r in oil, cubic zirconia (McCrone No. 319) with R_r of 3.28% in oil, and silicon carbide (McCrone No. 339) with a reflectance of 7.54% in oil. The actual measurements were made in non-polarised light. Mean and standard deviation were calculated and the data were plotted in histograms.

Palynomorph colour and fluorescence (Colour image analysis)

Palynomorph fluorescence was observed using a Leitz Dialux 20 binocular microscope. An incident fluorescent tube (Ploemopak 2.4) and a violet and blue +12 filter block with a band of 390-490 nm have been attached to the microscope to determine the fluorescence of specimens.

Colour image analysis using a Leica Q500IW imaging workstation and Qwin software made it possible to quantify palynomorph colour. The image was taken by a JVC TK-C1380E colour video camera attached to a Leitz Dialux 20 transmitted light microscope. Mean RGB (Red Green Blue) values were interpreted following Yule *et al.* (1998). With increasing maturity, Red and Green intensities decrease.

Maturation indicators II: Clays

The <2µm fraction was separated for XRD measurements using the common Atterberg cylinder method. All samples were treated with 1 M NaCl solution prior to PVP-10 (polyvinylpyrrolidone) treatment (Eberl *et al.* 1998). Four slides were prepared for each sample, air-dried, glycolated with ethylene glycol, Na-saturated and PVP-treated. Hence, four scans were carried out for each sample.

Most of the samples contained smectite to such a degree that it was impossible to measure the Kübler Index of the illite 001 peak. The Kübler Index was determined for samples 12101 - 12107 based on air-dried and ethylene glyocl treated scans. The Kübler Index is measured as the full width of half maximum peak height. It is commonly considered as a measure of clay crystallinity which is believed to increase with increasing grade of metamorphism. Illite crystallinity was calculated from the illite 001 peak at 10Å. The values were converted to CIS (crystallinity index standards) values (Warr & Rice 1994).

The Scherrer equation was used to calculate illite stack sizes from the Kübler Index. Fundamental particle sizes of illite were calculated using MudMaster, a program developed by Eberl *et al.* (1996). This allows the calculation of size distributions from the illite 001 peak of XRD scans. PVP treatment ensures the disarticulation of the illite stacks. The 'best mean' is used to compare the different particle size distributions of the various samples.

Kaolinite has been found to be present up to vitrinite reflectance (R_r) values of 1.9%-2.1% (Frey & Robinson 1999).

Borehole 16/28-Sb01

Samples 12115-12117 contain bitumen-like material, algae, inertinite, vitrinite and palynomorphs. All samples show at least two populations of vitrinite (Appendix 1). Spore colour image analyses have shown that Carboniferous, non-fluorescent spores (Appendix 2) are present in sample 12116 which can probably be correlated with the vitrinite population at 1.3%R_r, a value that marks the fluorescence threshold. Another Carboniferous, but fluorescent spore (Appendix 2) most likely represents the 0.8%R_r population. Tertiary dinoflagellates fluoresce brightly and are usually lighter in colour than spores (Appendix 2).

Samples no. 12113 and 12112 did not yield any clay minerals, either in the <2µm fraction or in the bulk sample. They seem to consist only of quartz, feldspar and (probably as cement) calcite. Sample no. 12114 was taken from the basalt below the sandstone (sample no. 12112 and 12113). It showed pure smectite in the XRD trace. The relationship between the sandstone and the basalt is unclear as no maturation determination could be made of the sandstone. Thus, it cannot be determined from these measurements whether the sill intruded the sandstone or whether the sandstone was deposited on top of the igneous body.

The <2µm fraction of the three upper samples from this core contained mainly smectite, illlite and kaolinite. The high amount of smectite made it impossible to measure the illite crystallinity. Kaolinite could indicate maturation levels below 2.2%R_r. Fundamental particle sizes of illite are fairly small, around 4nm (Appendix 3).

Borehole 83/20-Sb01

Sample no. 12111, a marl, yielded very little clay minerals and no organic material. Thus, no measurements were possible.

Samples no. 12110 to 12108 contained very little vitrinite. Overall, only three readings were taken (*c.* 1.3%R_r). It is likely that these are from reworked material.

The three greensand samples showed a relative high amount of smectite as well as kaolinite and illite. Illite crystallinity determinations were impossible due to the high amount of smectite. Illite fundamental particle sizes were similar to sizes of the Tertiary from borehole 16/28-Sb01, *c.* 4 nm (Appendix 3).

Grey siltstones (sample no. 12106 + 12107) were sampled from depths of around 176m. They yielded probably about three vitrinite populations (Appendix 1). A population with a reflectance of around 0.9%R_r may correlate with fluorescent spores of Jurassic age that is similar in colour to the Carboniferous, fluorescent spores in the Tertiary mudstones of borehole 16/28-Sb01 (Appendix 2).

A second population of vitrinite can be identified around 1.3%R_r. Carboniferous, non-fluorescent spores have been found to accompany this. Other spores (Jurassic and Caroniferous) show similar colour characteristics but do fluoresce (Appendix 2). This can be explained either by the fact that the fluorescence threshold is around 1.3%R_r. Or, that these spores have very thick walls and thus display darker colours than thinner walls spores of the same maturation level.

Jurassic dinoflagellates show generally lighter colours than the spores. At least some of them are significantly darker than the Tertiary dinoflagellates found in the Tertiary mudstones in borehole 16/28-Sb01 (Appendix 2).

A third population of vitrinite can be distinguished with a reflectance of around 0.3%R_r. As this is clearly the indigenous population, the other two vitrinite populations plus the associated palynomorphs are considered reworked.

The clay mineralogy of these siltstones is still dominated by kaolinite and illite. However, the lesser amount of smectite made it possible to measure illite crystallinity (Appendix 3). Generally, illite crystallinity values of around 0.6 $\Delta°2\theta$ suggest upper diagenetic conditions. Correlated with vitrinite reflectance, the values correspond to *c.*

1.2%R_r, but definitely not lower than 0.7%R_r. Fundamental particle sizes are larger (around 5nm) than for the Tertiary and the greensands in this borehole (Appendix 3).

Borehole 83/24-Sb02

Siltstones from depths of 71m (sample no. 12101 + 12102) yielded one vitrinite population with a reflectance of c. 2.4%R_r (Appendix 1). The samples contained quite a lot of woody material. Carboniferous spores have been found which are generally dark in colour and non fluorescing (Appendix 2).

Clay mineralogy is dominated by chlorite and illite. Illite crystallinity values of between 0.4 to 0.64 $\Delta°2\theta$ indicate upper diagenetic conditions for all samples taken from depths of 68m to 71m. Glycolated values show a definite difference between the upper three samples and the lower two samples. Fundamental particle sizes of around 5 nm for two of the samples (sample no. 12105 + 12103) are similar values for samples 12106 and 12107 from borehole 83/20-Sb01. One value (sample no. 12104) is higher and seems to show the thickening of crystallites due to tectonic influence. The lowest two samples (12101 + 12102) yielded larger fundamental particle sizes of around 6 nm. (Appendix 3)

References

Eberl, D.D. , Drits, V.A., Srodon, J. and Nüesch, R. (1996) MudMaster: a program for calculating crystallite size distributions and strain from the shapes of x-ray diffraction peaks. U.S. Geological Survey, Open-File Report 96-171. Boulder, Colorado (USA).

Eberl , D.D., Drits, V.A. and Srodon, J. (1998) Deducing growth mechanisms for minerals from the shapes of crystal size distributions. *American Journal of Science*, **298**, 499-533.

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Warr, L.N. and Rice, A.H.N. (1994) Interlaboratory standardization and calibration of clay mineral crystallinity and crystallite size data. *Journal of metamorphic Geology*, **12**, 141-152.

Yule, B., Roberts, S., Marshall, J.E.A. and Milton, J.A. (1998) Quantitative spore colour measurement using colour image analysis. *Organic Geochemistry*, **28**, 139-149.

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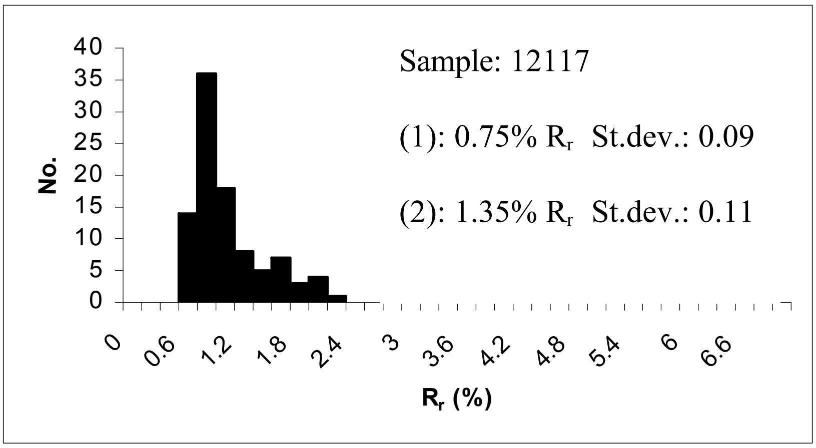
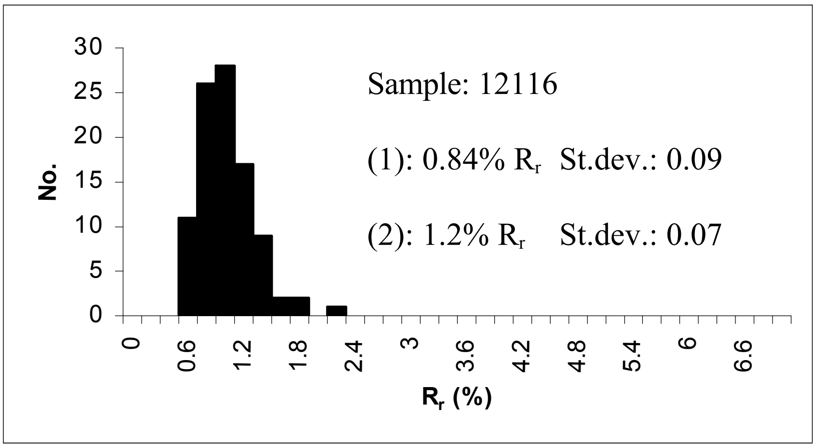
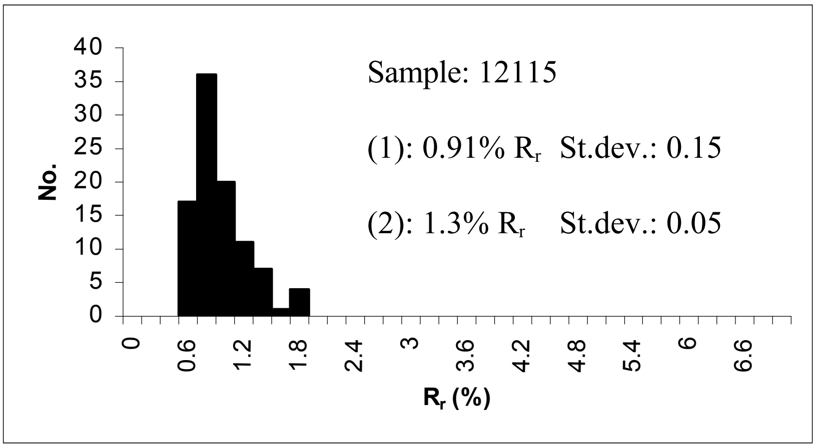
Appendix 1 - Vitrinite reflectance

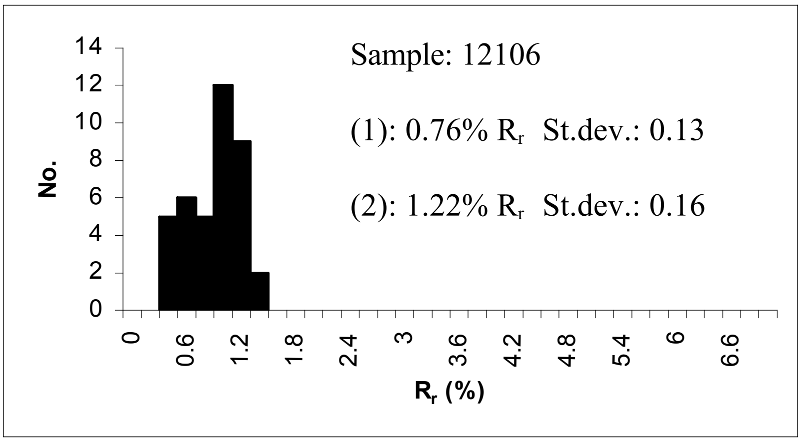
Borehole 16/28-Sb01

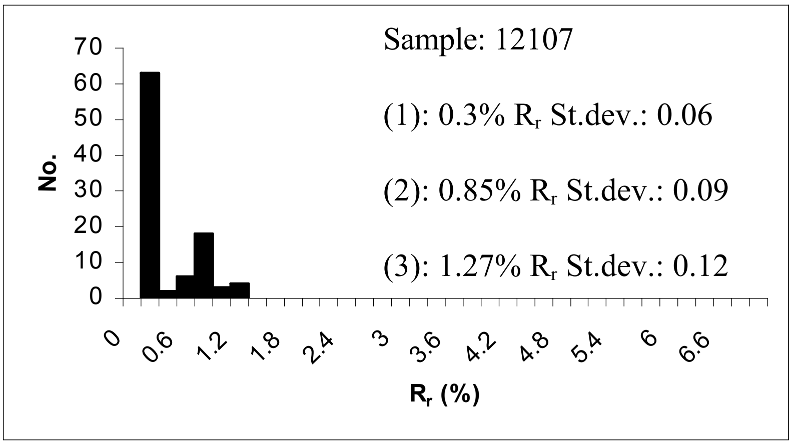






Borehole 83/20-Sb01





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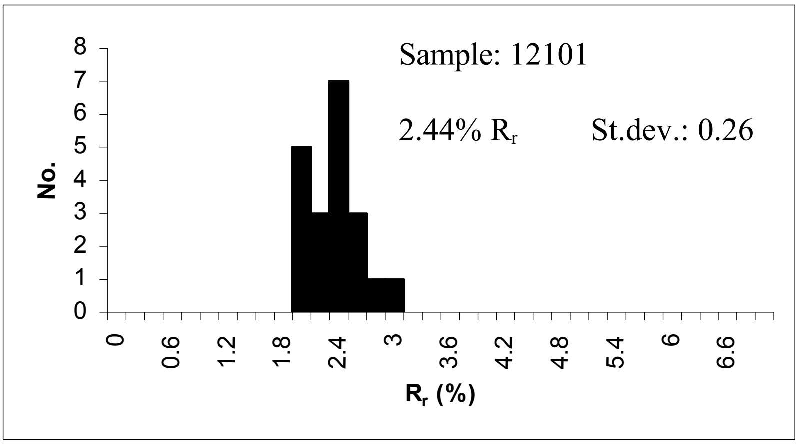
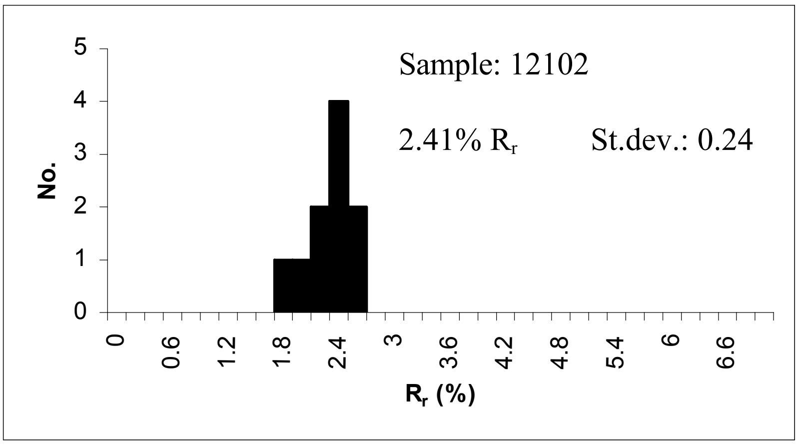
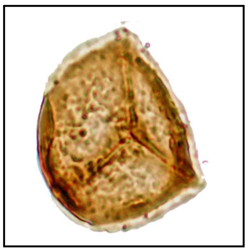




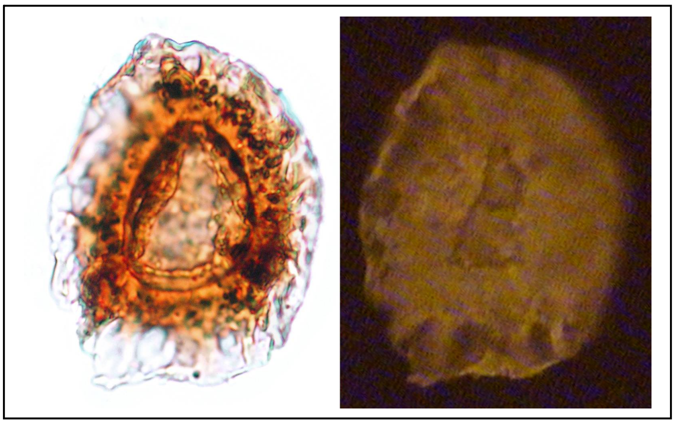
Appendix 2 - Palynomorph colour and fluorescence
(Representative palynomorph photographs x 1000, unless stated otherwise)

Borehole 16/28-Sb01

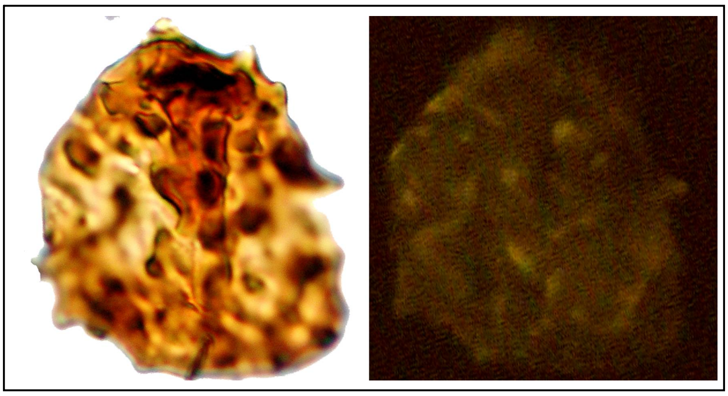
Sample: 12116



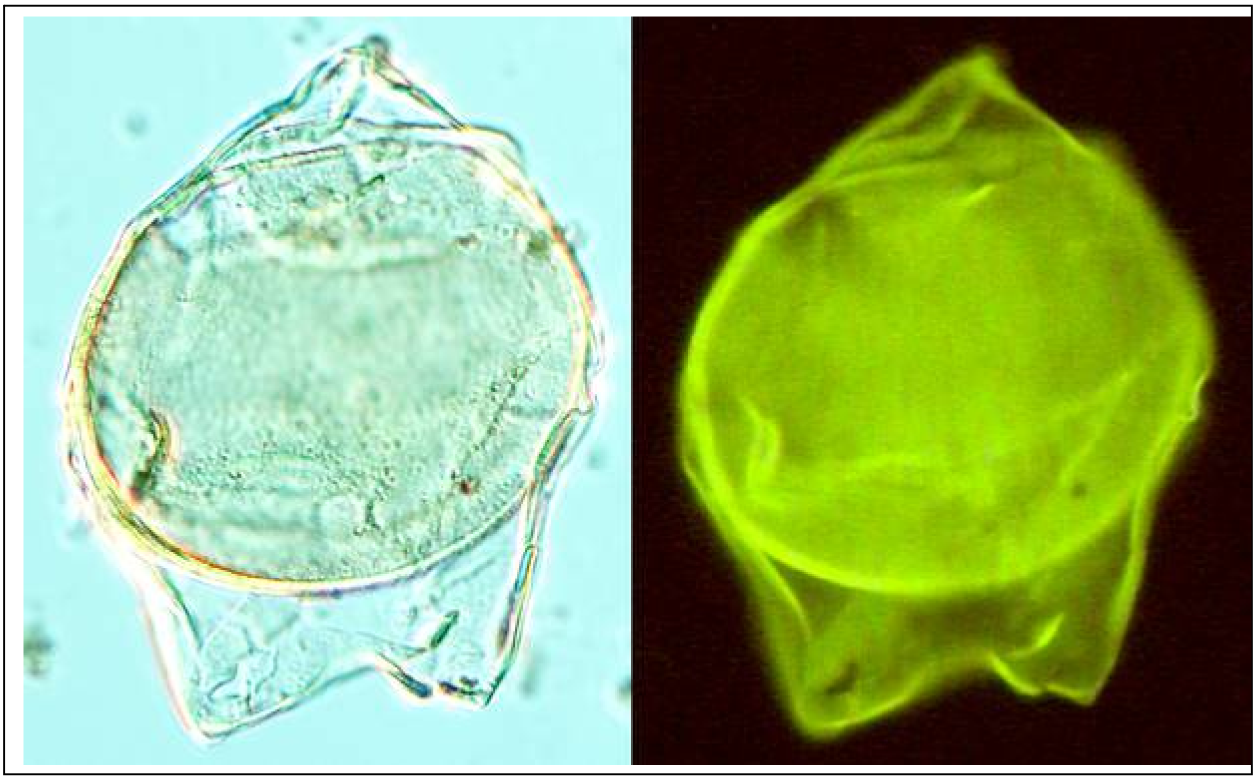
Lycospora pusilla
(Carboniferous)
non-fluorescent



Radiizonates sp.
Carboniferous
fluorescent



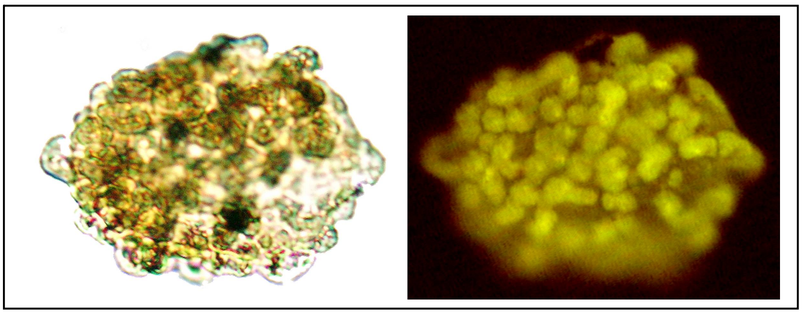
Raistrickia fulva
(Carb.: Westphalian A)
slightly fluorescent



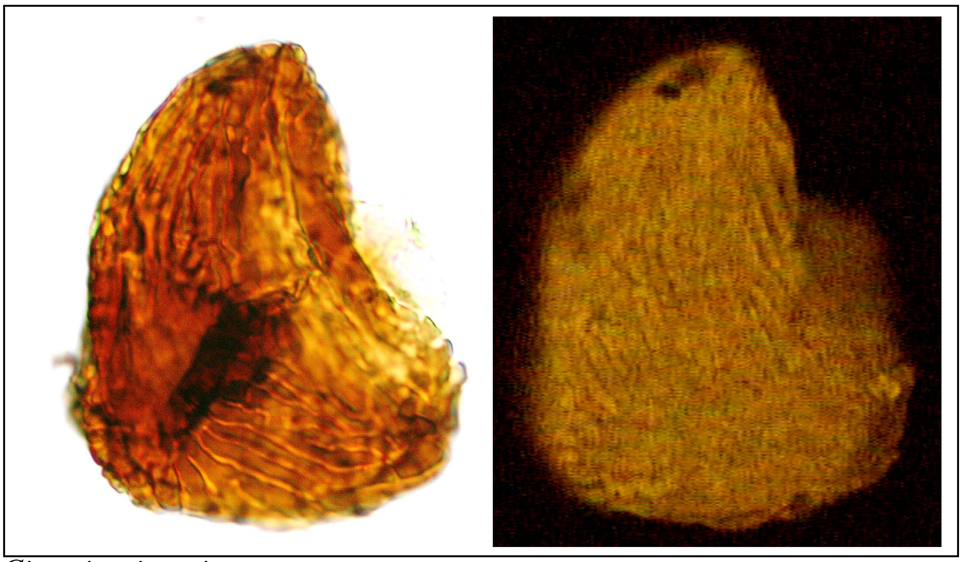
Deflandrea oebisfeldensis
Tertiary
fluorescent

Borehole 83/20-Sb01

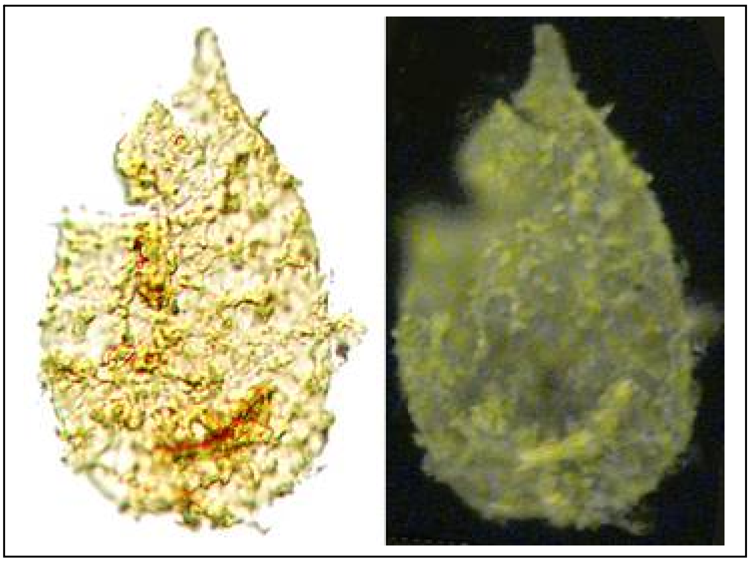
Sample: 12107



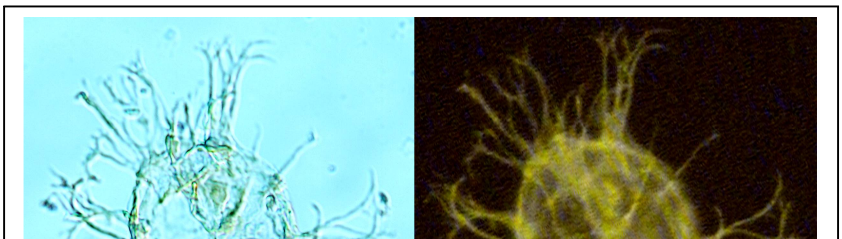
Cerebropollenites sp.
Jurassic
fluorescent



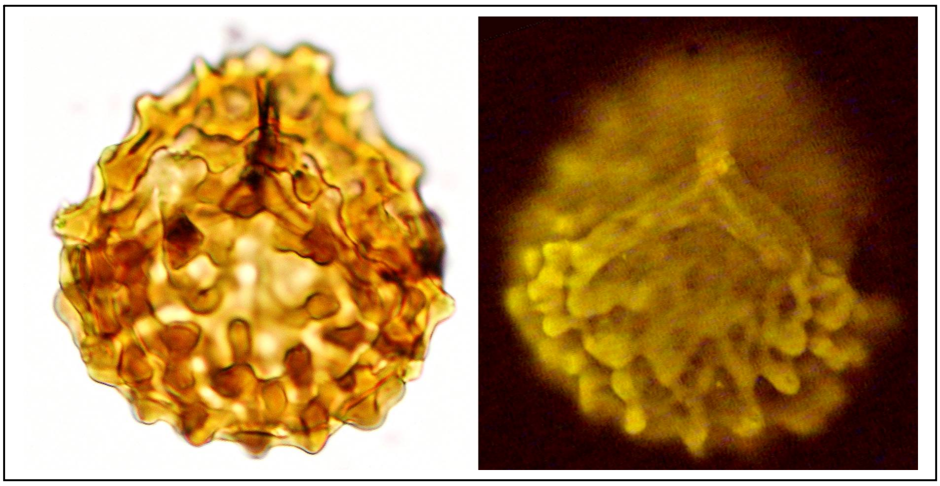
Cicatricosisporites
Jurassic - Cretaceous
Fluorescent



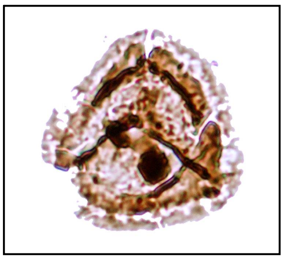
Gochteodinia mutabilis
Jurassic
fluorescent



Systematosphora aerolata
Jurassic
fluorescent
(x 500)



Raistrickia sp.
Carboniferous
fluorescent

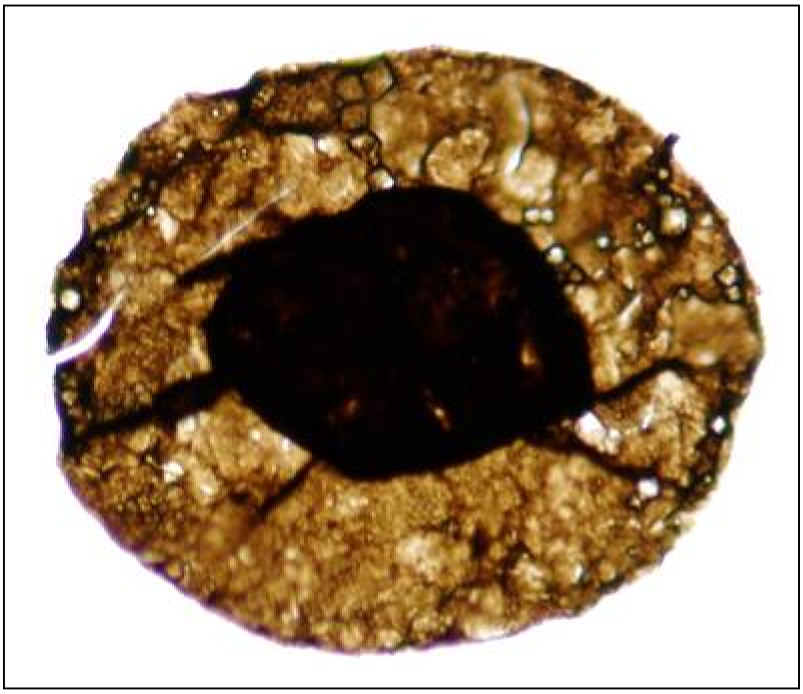


Lycospora pusilla
Carboniferous
non-fluorescent

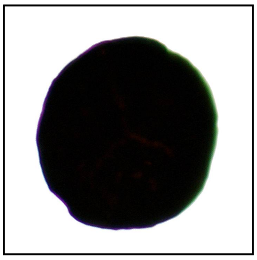
Borehole 83/24-Sb02

Sample: 12101

Calamospora sp.
Carboniferous
non-fluorescent



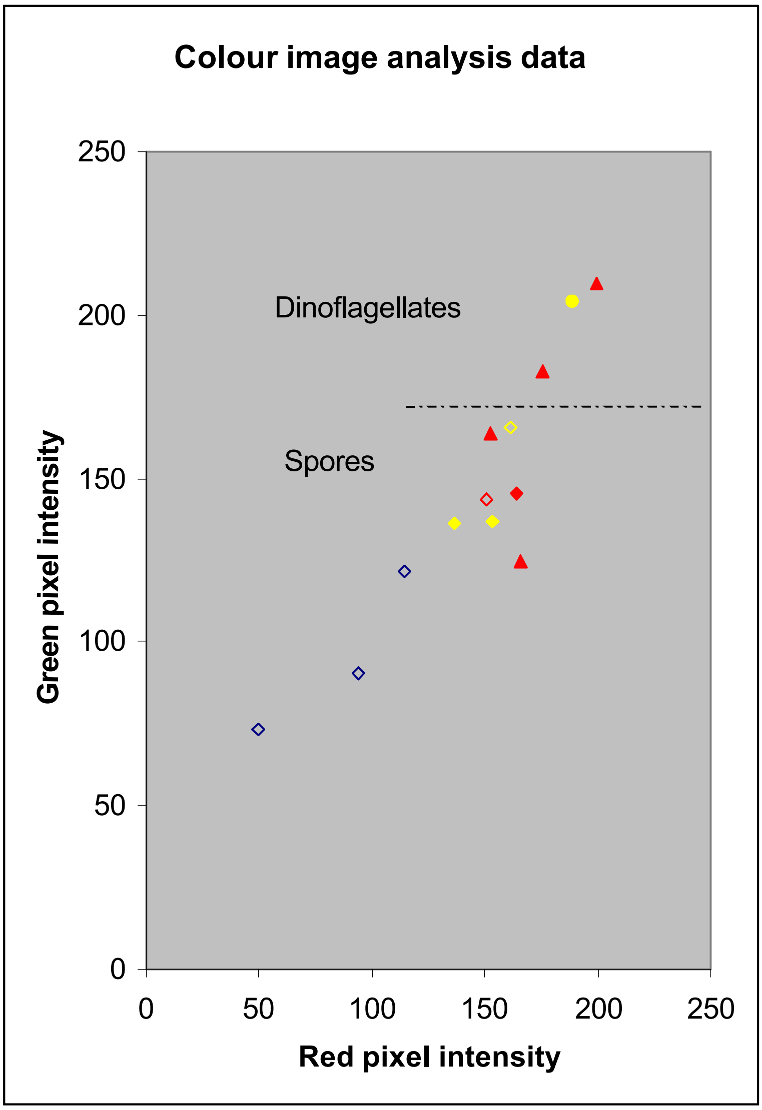
Florinites sp.
Carboniferous
non-fluorescent



Punctatisporites sp.
Carboniferous
non-fluorescent

Colour image analysis

Sample no.	Palynomorph	Age	Mean Red	Mean Green	Mean Blue
12116	*Lycospora pusilla*	Caboniferous	161.121	165.95	103.17
12116	*Radiizonates* sp.	Carboniferous	136.436	136.224	93.377
12116	*Raistrickia fulva*	Carboniferous	153.724	137.001	54.219
12116	*Deflandrea oebisfeldensis*	Tertiary	188.51	203.871	150.874
12107	*Lycospora pusilla*	Carboniferous	150.462	143.363	96.702
12107	*Raistrickia* sp.	Carboniferous	164.289	145.747	93.314
12107	*Cerebropollenites* sp.	Jurassic	152.214	163.51	108.553
12107	*Cicatricosisporites* sp.	Jurassic	165.8	124.487	56.745
12107	*Gochteodinia mutabilis*	Jurassic	175.752	782.665	140.394
12107	*Systematosphora aerolata*	Jurassic	199.325	209.888	162.656
12101	*Florinites* sp.	Carboniferous	93.742	90.399	69.979
12101	*Calamospora* sp.	Carboniferous	114.479	121.846	90.026
12101	*Punctatisporites* sp.	Carboniferous	49.472	73.139	62.351



Red - sample no. 12107; blue - sample no. 12101; yellow - sample no. 12116; diamonds - Carboniferous; triangles - Jurassic; sphere - Tertiary; filled - fluorescent; open - non-fluorescent.

Appendix 3 - Clay analysis

Borehole	Sample	IC (air-dried) Δ°2θ	KI (glycolated) Δ°2θ	KI (na-saturated) Δ°2θ	Fundamental particle sizes (nm)	Stack sizes (nm)
16/28-Sb01	12117	-	-	-	3.9	-
16/28-Sb01	12116	-	-	-	3.7	-
16/28-Sb01	12115	-	-	-	3.8	-
83/20-Sb01	12110	-	-	-	3.9	-
83/20-Sb01	12109	-	-	-	3.9	-
83/20-Sb01	12108	-	-	-	3.8	-
83/20-Sb01	12106	0.62	0.35	0.33	4.9	15
83/20-Sb01	12107	(0.19)	(0.14)	0.45	4.8	(69)
83/24-Sb02	12105	0.64	0.53	0.61	4.7	14
83/24-Sb02	12104	0.47	0.43	0.54	8.3	20
83/24-Sb02	12103	0.4	0.49	0.42	4.5	25
83/24-Sb02	12101	0.46	0.36	0.47	5.7	21
83/24-Sb02	12102	0.53	0.33	0.53	5.5	18

IC = Illite crystallinity corrected to CIS values; KI = Kübler Index corrected to CIS values; Fundamental particle sizes calculated with MudMaster ('Best Mean'); Stack sizes calculated using the Scherrer equation: $N = \frac{K\lambda}{\beta d \cos\theta}$.

Summary table

Borehole no.	Depth (m)	Sample no.	Illite crystallinity ($\Delta°2\theta$)	Vitrinite reflectance ($\%R_r$)
16/28-Sb01	88.9	12117	-	(0.75)/(1.35)
16/28-Sb01	101.9	12116	-	(0.84)/(1.2)
16/28-Sb01	130	12115	-	(0.91)/(1.3)
16/28-Sb01	147.06	12113	-	-
16/28-Sb01	147.2	12112	-	-
16/28-Sb01	147.35	12114	-	-
83/20-Sb01	97.55	12111	-	-
83/20-Sb01	107.63	12110	-	(1.28)
83/20-Sb01	107.8	12109	-	(1.32)
83/20-Sb01	127.97	12108	-	-
83/20-Sb01	176.5	12106	0.62	(0.76)/(1.22)
83/20-Sb01	176.7	12107	(0.19)	0.3/(0.85)/(1.27)
83/24-Sb02	67.91	12105	0.64	-
83/24-Sb02	68.95	12104	0.47	-
83/24-Sb02	71.18	12103	0.4	-
83/24-Sb02	71.36	12101	0.46	2.44
83/24-Sb02	71.47	12102	0.53	2.41

Vitrinite reflectance values in brackets are probably reworked. IC value in brackets is probably erroneous (cf. Na-saturated value in Appendix 3).

"This Project, including data and survey results acquired for the purpose, has been undertaken on behalf of the Rockall Studies Group (RSG) of the Irish Petroleum Infrastructure Programme Group 2 which was established by the Petroleum Affairs Division of the Department of the Marine and Natural Resources on 4 June, 1997 iin conjunction with the award of exploration licences under the Rockall Trough Frontier Licensing Round. The RSG comprises: Agip (UK) Ltd, Anadarko Ireland Company, ARCO Ireland Offshore Inc, BG Exploration & Production Ltd, Elf Petroleum Ireland BV, Enterprise Energy Ireland Ltd, Mobil Oil North Sea Ltd, Murphy Ireland Offshore Ltd, Shell EP Ireland B.V., Statoil Exploration (Ireland) Ltd, Total Oil Marine plc, Union Texas Petroleum Ltd and the Petroleum Affairs Division of the Department of the Marine and Natural Resources."