Thermal Indices Working Group - Exercise Year 2005

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1. INTRODUCTION

The Thermal Indices WG conducted over last years interlaboratory exercises with the aim of improving the reproducibility and comparability of spectral fluorescence microscopy.

Last exercises included, besides spectral fluorescence measurements, other maturity parameters such as vitrinite reflectance, VIRF and some parameters derived from organic geochemistry in order to check the correlations and deviations among them.

A sample from the Irati Formation collected from the lower oil shale seam of the Petrosix Quarry (São Mateus do Sul, Paraná state, Brazil) was analyzed in the Round Robin Exercise of 2004 and results were presented at the 56th ICCP Meeting in Budapest. At this meeting, it was agreed that the WG would analyse samples (Posidonia shale (PS) and Asturias carbonaceous shale (CS)) previously analysed for the Qualifying by the Vitrinite Reflectance WG (Table 1).

- Summary from Borrego *et al.* 2006

> ***Carbonaceous shale.*** *... Most of the profiles are placed in the same range of vitrinite classes ... This indicates that the participants took readings in the same type of particles...* ***The group mean was R_o=0.70% and the group standard deviation 0.0456***.
>
> ***Posidonia shale.*** *The normalized histograms of sample PS were more complex than those of sample CS. The shape of the curves indicated more vitrinite classes in the histograms although most of them showed clear modal values. The standard deviations for the individual distributions were higher than in sample CS but still under 0.08 for 70% of participants.* ***The group mean for the sample was R_o=0.37 % and the standard deviation was higher than in sample CS (σ = 0.0658)***. *The higher standard deviation of the group and the differences in the distribution shapes and positions between participants indicate higher complexity of PS compared to CS...*

Table 1: Sample origin, geological age and suggested depositional environment (Borrego et al. 2006)

	Shale	*Country*	*Age*	*Origin*
CS	Asturian Central Coal Basin	Spain	Carboniferous	Terrestrial
PS	Posidonia	Germany	Jurassic	Marine

2. RESULTS OF ROUND ROBIN EXERCISE 2005

The results on spectral fluorescence measurements, VIRF and organic geochemistry presented in this report are based on data provided by 13 participants (Table 2).

Table 2: List of participants and associated laboratories

Participant	*Institution*	*Country*
Carla Viviane **A**raujo/ Silvana Maria Barbanti / Taíssa Menezes	PETROBRAS R&D Center	Brazil
Angeles Gomez **B**orrego	INCAR	Spain
James **H**ower	University of Kentucky/ Center for Applied Energy Research	USA
Wolfgang **K**alkreuth	Federal University of Rio Grande do Sul -UFRGS	Brazil
Ralf **L**ittke/ Jan Schwarzbauer	RWTH Aachen University	Germany
João Graciano **M**endonça Filho	Federal University of Rio de Janeiro - UFRJ	Brazil
Jane **N**ewman/ Nick Moore	Newman Energy Research Ltd	New Zealand
Kathrin **R**eimer/ Petra David	TNO - Utrecht	The Netherlands

2.1 Spectral Fluorescence Measurements

Five participants provided results on spectral fluorescence measurements. Spectral data provided by these participants were corrected with the correction function from the calibrated common lamp source (Baranger *et al.* 1990). Two participants analysed the samples in the same system.

Participants were asked to make the measurements on both alginites and sporinites. All five participants provided spectral curves for alginites of the Posidonia sample.

For the Asturias sample two participants provided curves for sporinite, one participant for alginite and two participants reported that the spectral curves were not meaningful because no appropriate object for measurement was found.

Asturias Carbonaceous Shale

Sporinite and alginite are not abundant in the Asturias CS sample. In addition to this feature the subjects for measurements are usually very thin, this is probably the reason why two participants did not provide results for this sample. Figure 1 presents the spectral curve obtained for alginite by participant A and Figure 2 present the curves from participants B and H for sporinite. The correlation among the curves for sporinite is good and both trends to present a secondary peak that is a characteristic feature for sporinite fluorescence spectra in the range of a High Volatile Bituminous A-C rank. The same feature was observed in the sporinite from Irati sample analysed last year for this WG. Parameters obtained for both alginite and sporinite are summarized in Tables 3 and 4.

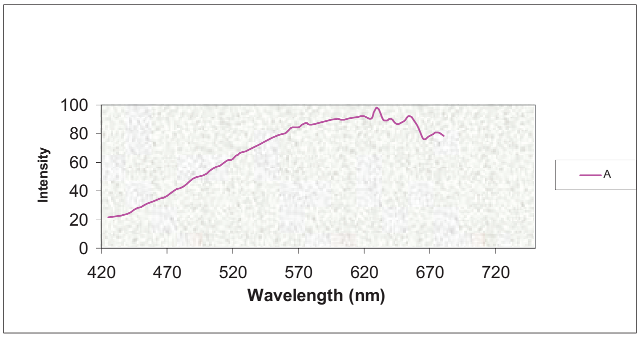

Figure 1 - Spectral curve for alginite provided by participant A

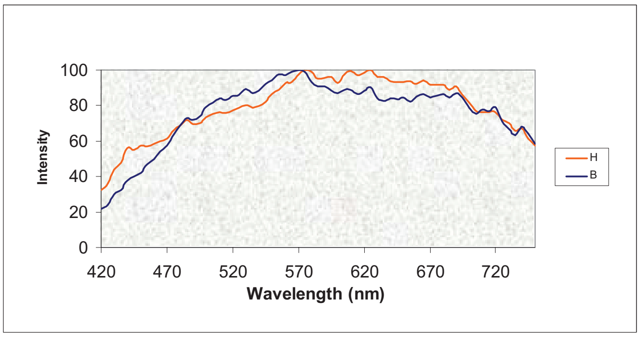

Figure 2 - Spectral curve for sporinites provided by participants H and B

Table 3: Spectral fluorescence parameters obtained for the alginite

Participant	***λmax (nm)***	***Q (I650/I500)***	***Q max (Imax/ I500)***
A	630	1.7	1.88

Table 4: Spectral fluorescence parameters obtained for the sporinite

Participant	***λmax (nm)***	***Q (I650/I500)***	***Q max (Imax/ I500)***
B	570	1.07	1.26
H	575/625	1.27	1.36

Posidonia Shale

Figure 3 presents fluorescence spectral curves of telalginite (tasmanites) provided by four participants. The correlation among these curves is very good, with λmax ranging from 510nm to 535nm and with excellent agreement in the determination of the Qmax values (1.01 - 1.03, Table 5).

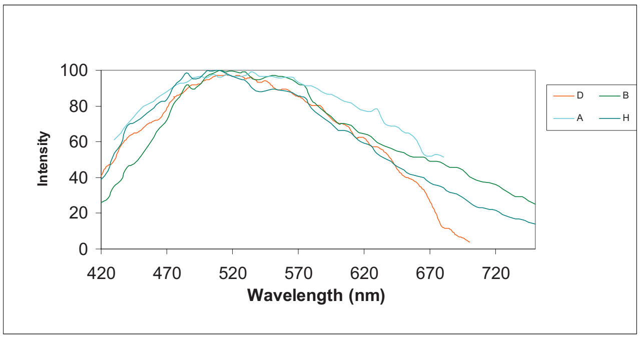

Figure 3 - Spectral curve for telalginite provided by four participants

Table 5: Spectral fluorescence parameters obtained for the telaginite

Participant	***λmax (nm)***	***Q (I650/I500)***	***Q max (Imax/ I500)***
A	535	0.68	1.03
B	510	0.55	1.03
C 1.1/1	550	0.82	1.43
C 1.1/4	595	0.96	1.46
C 1.1/5	570	0.71	1.22
C 1.1/12	560	0.81	1.40
D	515	0.43	1.03
H	510	0.45	1.01

Figure 4 shows the same curves of Figure 3 and in addition four spectral curves provided by participant C. It is worth to mentioning that this participant provided 10 curves to characterize this alginite population. The four curves presented in Figure 4, from participant C, were considered representative of the ten curves provided by this participant. The spectral fluorescence curves and parameters provided by participant C present a shift in λmax values ranging from 550nm to 595nm in relation to those values provided by other participants (510 - 535 nm). This feature could be either a response to subject selection for measurements, but it seems to be more likely related to systems calibration or, for instance, the size of the measuring diaphragm. Table 5 summarizes the fluorescence parameters obtained by the five participants.

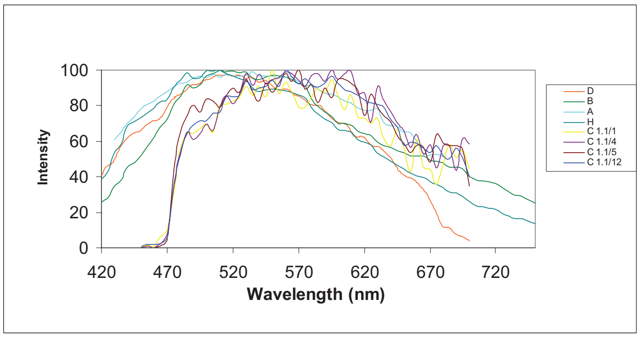

Figure 4 - Spectral curve for telalginite provided by five participants

2.2 VIRF

A report on VIRF results were provided by Jane Newman. In this report a brief summary of the results and interpretations based on VIRF is presented below:

*"... **The Asturias sample** contains abundant telovitrinite, none of which falls into the perhydrous field. Reflectance of subjects which have the appearance of vitrinite ranges from 0.62% to 0.92% Ro (random), and Ro (normal) calculated on all vitrinite is 0.82% (Figure 5). However a substantial population of subjects with reflectance above 0.82% exhibits uniformly low fluorescence and could, according to VIRF criteria, be classed with the inertinite group. This classification would reduce Ro (normal) to 0.74% (Figure 6)..."*

This second interpretation is closer to the actual values measured by participants in the WG (0.70%).

"The Posidonia sample produces a much more complex VIRF chart with more than one "vitrinite" population (Figure 7). The lower reflectance population has a distinctive granular texture and includes a significant perhydrous component. Similar complex charts have been obtained from shales ranging in age from Devonian to Early Cretaceous, and the low reflectance population is interpreted to represent a primitive vitrinite-like material which has reflectance up to 0.50% below Ro (normal). This material is provisionally entitled Population G, and was identified and discussed in the Irati Fm. sample (VIRF analysis of Irati Fm oil shale, Parana Basin, Brazil. Report for the ICCP Thermal Indices Working Group Exercise year 2004). *The average Ro (random) of Population G ... is approximately 0.30% whereas Ro (normal) calculated on the inferred normal vitrinite population is 0.69% (Ro random)...."*

The actual reflectance values measured were 0.37%, slightly higher than those derived for the population G, but significantly lower than those of the so called normal vitrinite population. No systematic presence of different vitrinite population was reported for this sample during vitrinite reflectance analysis by participants in the Qualifying for vitrinite reflectance WG.

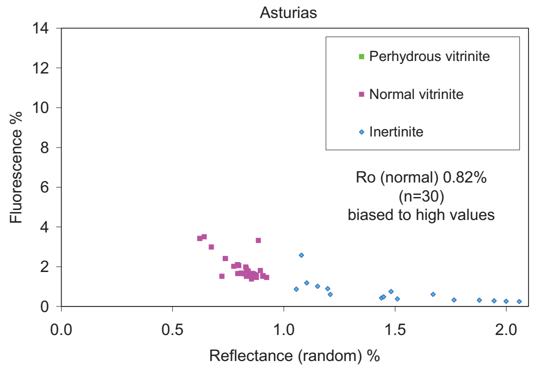

Figure 5 - VIRF chart for the Asturias sample. Maceral identifications are based on physical characteristics and are also compatible with chart interpretation based on VIRF criteria. However, an alternative VIRF interpretation is possible, as shown in Figure 6

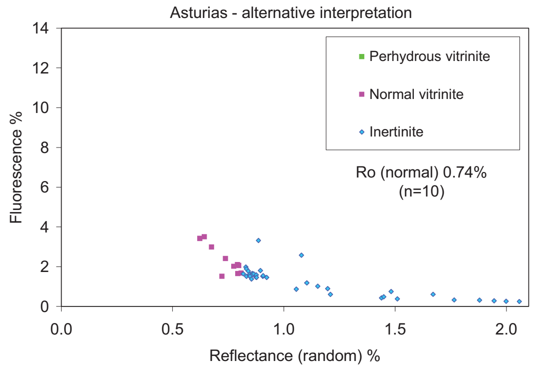

Figure 6 - Possible alternative interpretation of VIRF data for the Asturias sample. In this interpretation the subjects with reflectance above 0.81% reflectance, which (a) have relatively low fluorescence and (b) exhibit a low gradient relationship between reflectance and fluorescence, are assigned to the inertinite group …This results in Ro (normal) are 0.08% lower than in the Figure 5 interpretation

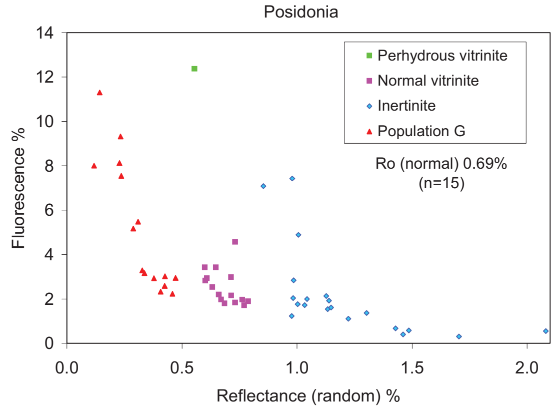

Figure 7 - VIRF chart for the Posidonia shale sample, showing distinct normal vitrinite and Population G populations

2.3 Organic Geochemistry

2.3.1 TOC/ Rock-Eval Pyrolysis/Ultimate and Proximate Analysis

Three participants provided results on bulk geochemistry (TOC/ Rock-Eval Pyrolysis) and one on ultimate/proximate analysis for Asturias CS and Posidonia shale samples (Tables 6 and 7). A good agreement between TOC values and wt.% C derived from ultimate analyses can be observed for both samples (Tables 6 and 7), although the carbon contents derived from ultimate analysis are slightly higher.

For the Rock-Eval pyrolysis data the best fit is presented by hydrocarbon source potential (S_2), hydrogen index (HI) and Tmax. The hydrocarbon source potential (S_2) and hydrogen index (HI) properly characterize the different type of organic matter of each sample and the Tmax point out the lower maturation of Posidonia shale sample in relation to the Asturias CS sample.

Table 6: Results on TOC, Rock-Eval Pyrolysis,Ultimate and Proximate Analyses for Asturias CS sample (ultimate and proximate analyses results in wt%)

	Participant			
	C	F	H	E
TOC (wt%)	8.4	7.9	7.9	-
S_1 (mgHC/grock)	0.62	0.38	0.23	-
S_2 (mgHC/grock)	13.08	10.45	12.62	-
S_3 (mgCO_2/grock)	0.22	0.69	0.49	-
HI (mgHC/gTOC)	165	132	160	-
OI (mgCO_2/gTOC)	2	9	6	-
Tmax (˚C)	436	439	434	-
C	-	-	-	8.71
H	-	-	-	1.45
N	-	-	-	0.31
S	-	-	-	1.12
O	-	-	-	6.59
Ash	-	-	-	81.82
Moisture	-	-	-	2.05

Table 7: Results on TOC, Rock-Eval Pyrolysis,Ultimate and Proximate Analyses for Posidonia shale sample (ultimate and proximate analyses results in wt%))

	Participant			
	C	F	H	E
TOC (wt%)	14.1	12.6	12.9	-
S$_1$ (mgHC/grock)	5.82	4.43	3.92	-
S$_2$ (mgHC/grock)	92.12	90.33	93.77	-
S$_3$ (mgCO$_2$/grock)	0.44	1.1	0.37	-
HI (mgHC/gTOC)	655	718	727	-
OI (mgCO$_2$/gTOC)	3	9	3	-
Tmax (°C)	426	428	425	-
C	-	-	-	15.49
H	-	-	-	1.97
N	-	-	-	0.31
S	-	-	-	4.00
O	-	-	-	7.41
Ash	-	-	-	70.82
Moisture	-	-	-	2.42

2.3.2 Gas chromatography and mass spectrometry

n-alkanes and isoprenoids

Pristane/*n*-C$_{17}$ and phytane/*n*-C$_{18}$ ratios decrease with increasing thermal maturity as more *n*-paraffins are generated from kerogen by craking (Tissot *el al.*, 1971 *in* Peters & Moldowan, 1993). The pristane/phytane ratio changes by thermal evolution in coal, and this can be extended to kerogens of comparable composition. Brown and subbituminous coals have moderate pristane:phytane ratios (1 to 7) whereas high volatile bituminous coals have higher values (7 to 15, Tissot & Welte, 1984).

The carbon preference index (CPI) was proposed as a maturity parameter based on the progressive change of the distribution of long-chain *n*-alkanes during maturation (Bray and Evans, 1961 *in* Tissot & Welte, 1984). Thermal degradation of kerogen during catagenesis generates new alkanes without predominance. Nevertheless, the CPI values are influenced by the type of organic matter and by the degree of maturity (Tissot & Welte, 1984). Despite the various limitations of this index it can be considered as a qualitative indicator and be used in association with another independent index. CPI values above 1.5 always refer to relatively immature samples (Tissot & Welte, 1984).

Figures 8 and 9 present a general GC profile for the studied samples. Tables 8 and 9 summarize some ratios derived from GC analyses provided by participants, except participant G that provided results based on m/z 85 monitoring and total ion chromatogram.

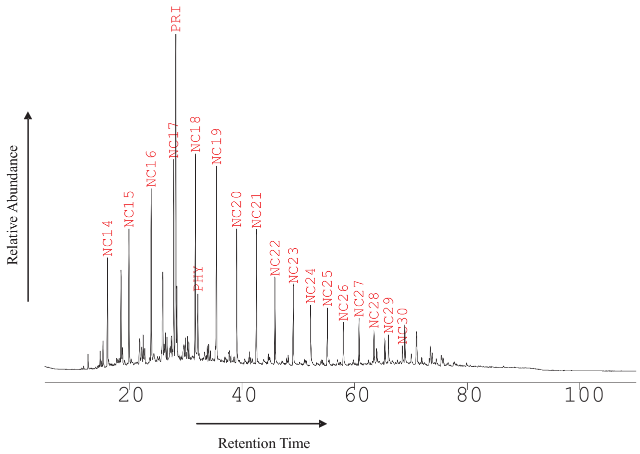

Figure 8- Aliphatic hydrocarbon distribution for Asturias CS sample for illustration

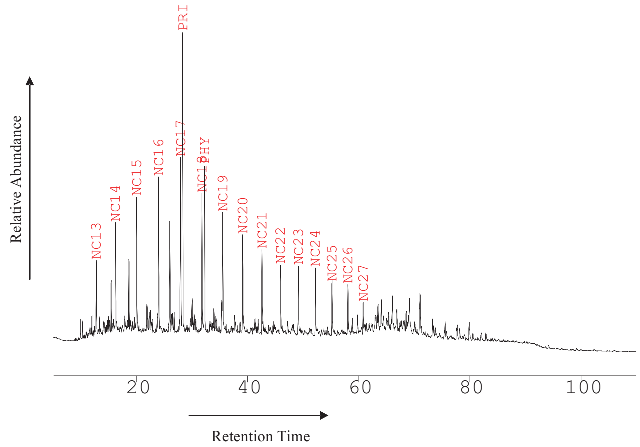

Figure 9- Aliphatic hydrocarbon distribution for Posidonia shale sample for illustration

The Pr/Ph ratios for the Asturias CS sample (Table 8) are generally high compared to Pr/Ph ratios for the Posidonia shale sample (Table 9). For the Asturias CS sample some differences can be detected between participants as shown by the low

Pr/Ph and phytane/*n*-C_{18} ratios reported by participant F (Table 8). Pr/Ph ratio up to 5.6, for the Asturias sample, is lower than what would be expected based on the group mean Ro of 0.70% obtained for the Qualifying for Vitrinite Reflectance WG.

CPI indices, for the Asturias sample, are mostly lower than 1.5 (except for some ratios provided by participant G). This would indicate a relatively high maturity in agreement with the group mean Ro of 0.70% obtained for the Qualifying for Vitrinite Reflectance WG. Nevertheless, the Pr/Ph ratio is lower than expected for this vitrinite reflectance.

The correlation of ratios among four different participants, for the Posidonia shale sample, is reasonably good (Table 9). It is worth to mention that the CPI indices are mostly lower than 1.5 like in Asturias CS sample despite the lower mean group vitrinite reflectance of the Posidonia shale. The ratios involving the *n*-alkanes of medium boiling point were more similar.

Table 8: Results from GC analyses for the Asturias CS sample

	Participant			
	C	F	G*	H
Pr/Ph	4.07	3.20	5.25	5.64
Pr/n-C_{17}	2.12	2.18	2.0	2.12
Ph/n-C_{18}	0.51	0.11	0.4	0.4
CPI (22-32)	1.14	0.98	-	1.01
CPI (24-32)	1.17	1.20	-	0.98
CPI (26-32)	1.3	1.38	-	0.67
CPI (26-30)	1.17	0.99	3.03	1.02
CPI (26-28)	1.26	0.99	9.16	1.08
CPI (28-30)	0.99	0.98	1.17	0.94
CPI (20-22)	1.19	0.43	1.11	1.19

* from the m/z 85

Table 9: Results from GC analyses for the Posidonia shale sample

	Participant			
	C	F	G*	H
Pr/Ph	1.68	1.47	1.42	1.73
Pr/n-C_{17}	1.86	2.07	2.15	1.96
Ph/n-C_{18}	1.61	1.13	1.44	1.55
CPI (22-32)	1.02	1.29	1.52	1.04
CPI (24-32)	1.03	1.48	1.6	1.05
CPI (26-32)	1.15	1.95	1.60	-
CPI (26-30)	1.13	1.20	1.64	1.18
CPI (26-28)	1.31	0.75	1.18	1.18
CPI (28-30)	0.94	1.95	1.89	-
CPI (20-22)	0.91	0.90	1.01	1.01

* from the Total Ion Chromatogram (TIC)

Terpanes

Figures 10 and 11 present the distribution of terpanes illustrating the range considered for the biomarker ratios presented on Tables 10 and 11.

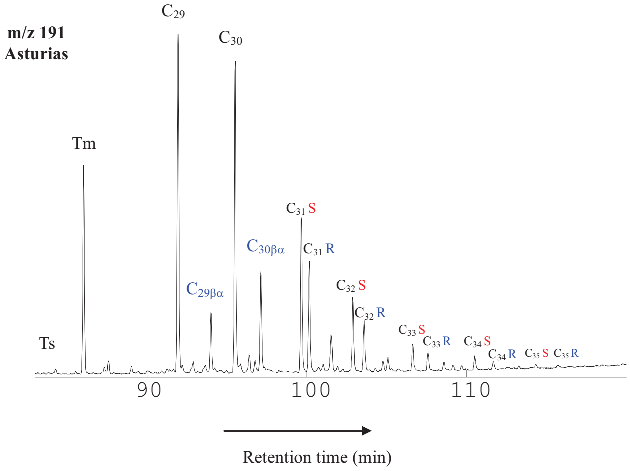

Figure 10- Mass chromatogram, m/z 191, showing terpane distribution for Asturias CS sample. A detail of the range considered for the ratios presented on Table 10

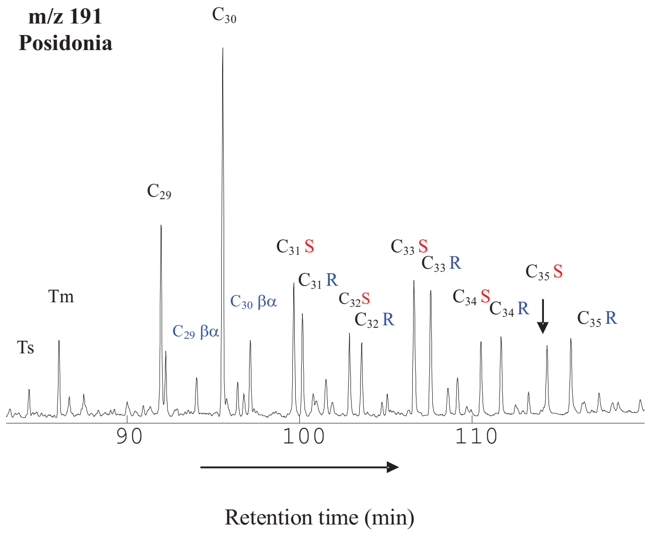

Figure 11- Mass chromatogram, m/z 191, showing terpane distribution for the Posidonia shale sample. A detail of the range considered for the ratios presented on Table 11

The correlation between the results on terpane distribution is good (Table 10), particularly between participants F and H. The best correlations were obtained for homohopanes from C_{31} to C_{33} S/(S+R) ratios. Ts/(Ts+Tm) ratio is both maturity and source dependent (Peters & Moldowan, 1993). The values obtained for this ratio (0.03-0.15; Table 10) seems to be anomalously low for the Asturias CS.

The isomerization of the biologically more abundant R isomer into the thermally more stable S isomer for homohopanes reaches its thermal equilibrium stage at ca. 0.6% VRE, with S/(S+R) ratios of ca. 0.6. The Asturias CS shale extract shows S/(S+R) ratios mostly around 0.6 for C_{31}-C_{33} homohopanes (Table 10), which point out that it already reached the equilibrium.

Ts/(Ts+Tm) ratios for the Posidonia shale sample are low (0.14 to 0.39, Table 11) but higher than those for the Asturias CS sample. As it was observed in the Asturias CS sample the best correlations were achieved for the homohopanes C_{31} - C_{33} S/(S+R) ratios. The extracts of the Posidonia shale sample show S/(S+R) ratios ranging from 0.31 to 0.64. For the C_{32} homohopane, the average value around 0.53 (except for participant G), point out that the extract from this sample is close to the equilibrium.

Table 10: Terpane maturity parameters for the Asturias CS sample

Ratios	***Participant***		
	C	F	H
Ts/Ts+Tm	0.15	0.03	0.02
Tm/C_{27}β	n.d.	n.d.	n.d.
C_{29} αβ/(αβ+βα)	n.d.	0.85	0.85
C_{30} αβ/(αβ+βα)	n.d.	0.75	0.76
C_{31}αβS/(22S+22R)	0.58	0.59	0.58
C_{32}αβS/(22S+22R)	0.60	0.58	0.59
C_{33}αβS/(22S+22R)	0.52	0.59	0.59
Homohopanes/ C_{30} αβ	1.16	1.5	1.47
C_{27} hopanes/ C_{30} αβ	1.47	0.73	0.68
C_{31} αβ hopanes/ C_{30} αβ	0.46	0.83	0.84

G participant reported a severe contamination by phthalate for Asturias sample, n.d.: not detected

Table 11: Terpane maturity parameters for the Posidonia shale sample

Ratios	***Participant***			
	C	F	G	H
Ts/Ts+Tm	0.39	0.28	0.14	0.27
Tm/C_{27}β	n.d.	n.d.	0.12	n.d.
C_{29} αβ/(αβ+βα)	n.d.	0.83	0.87	0.84
C_{30} αβ/(αβ+βα)	n.d.	0.81	0.81	0.83
C_{31}αβS/(22S+22R)	0.57	0.54	0.45	0.57
C_{32}αβS/(22S+22R)	0.54	0.52	0.64	0.53
C_{33}αβS/(22S+22R)	0.57	0.47	0.31	0.52
Homohopanes/ C_{30} αβ	1.16	2.41	1.55	2.56
C_{27} hopanes/ C_{30} αβ	0.61	0.37	0.26	0.29
C_{31} αβ hopanes/ C_{30} αβ	0.49	0.66	0.54	0.64

Steranes

Three participants provided results from sterane analyses of the Asturias CS sample and 4 participants for the Posidonia shale sample. Participant H provides results based on MRM-GC-MS technique, besides the results based on selective ion monitoring analyses. Biomarker ratios provided by MRM-GC-MS analysis were considered for maturity evaluation when available since they are more precise due to the monitoring of specific transitions from molecular ions to the diagnostic ions. Figures 12 and 13 present the distribution of the steranes, for illustration, with a detail on the range considered for the ratios presented on Tables 12 and 13.

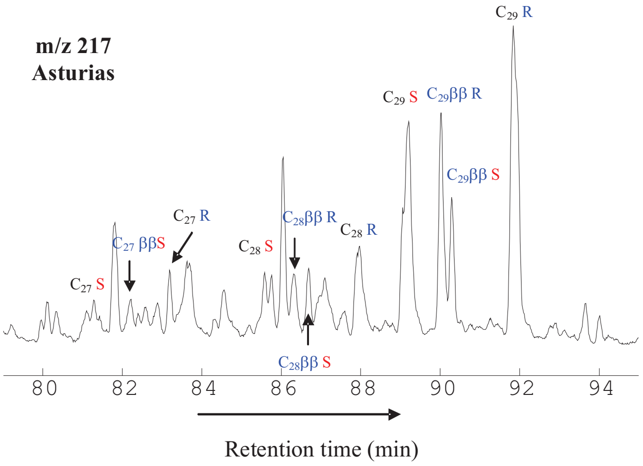

Figure 12- Mass chromatogram, m/z 217, showing the distribution of steranes for the Asturias CS sample. A detail of the range considered for the ratios presented on Table 12

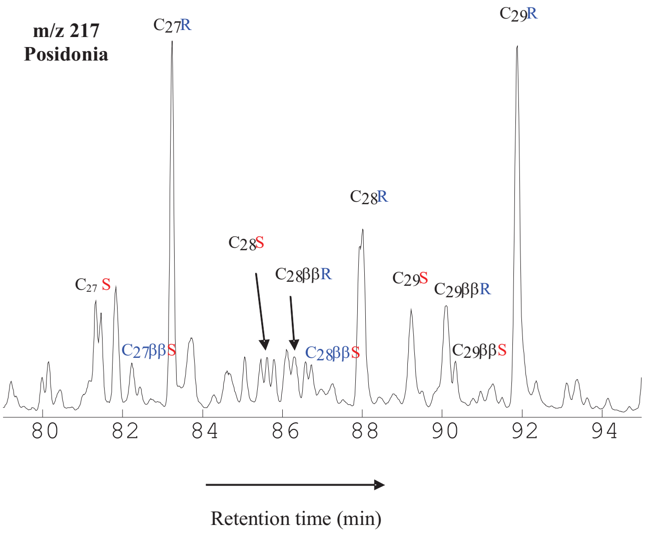

Figure 13- Mass chromatogram, m/z 217, showing the distribution of steranes for Posidonia shale sample. A detail of the range considered for the ratios presented on Table 12

The level of agreement among the sterane ratios is lower than for the terpane analyses. Low correlation of ratios could be related to differences on analytical procedures or on calculations.

The commonly occurring series from C_{27} to C_{29} ααα and αββ steranes were detected. There is a predominance of C_{29} steranes in the Asturias sample (Table 12) that can be related to the higher plant input. The Posidonia sample presents a predominance of C_{27} and C_{29} steranes (Table 13), which is consistent with algal and higher plant input.

Biologically more abundant R isomers on C-20 position isomerise into the thermally more stable S configuration with thermal maturation, and αα (14β, 17β (H)) isomers are isomerized to thermally more stable ββ (14β, 17β (H)) isomers (Mackenzie *et al*., 1982a, Mackenzie *et al*., 1982b, Mackenzie & Mckenzie, 1983). In the Asturias sample the C_{29} ααα 20S/(20S+20R) ratio, ranging from 0.44 to 0.52, is close to the empirical endpoint, ie. ca. 0.54 for the ratio S/(S+R), equivalent to ca. 0.9% VRE. In the Posidonia shale sample this ratio ranges from 0.25 to 0.38 and do not reach the empirical endpoint (ca. 0.54), pointing out the lower maturation of Posidonia compared to the Asturias CS sample. The isomerization ratio of the C_{29} ββ/(ββ+αα) ranges from 0.32 to 0.38 for the Asturias CS sample and from 0.16 to 0.32 for the Posidonia shale sample. In both samples these ratios are far from the empirical endpoint that is 0.7, equivalent to ca. 1% VRE (Peters & Moldowan, 1993).

An estimation of VRE from the C_{29} S/R ratio based on a relationship published by Sofer *et al.* (1993) is also provided (Tables 12 and 13). Some of the VRE for Asturias CS sample correlates to 0.70%, that is, the mean group vitrinite reflectance achieved by the Qualifying for vitrinite reflectance WG. On the other hand, the range of VRE for the Posidonia shale sample (0.52% to 0.66%) is significantly higher than the 0.37% achieved by the Qualifying for vitrinite reflectance WG.

Table 12: Sterane maturity parameters for the Asturias CS sample

Ratios	***Participant***			
	C	F	H	H^*
C_{27} steranes (%total C_{27} to C_{29} regular steranes)	15	19	17	
C_{28} steranes (%total C_{27} to C_{29} regular steranes)	40	20	20	
C_{29} steranes (%total C_{27} to C_{29} regular steranes)	43	61	63	
C_{27} ααα 20S/(20S+20R)	0.80	0.50	0.35	0.37
C_{28} ααα 20S/(20S+20R)	0.53	0.24	0.41	0.44
C_{29} ααα 20S/(20S+20R)	0.44	0.50	0.41	0.52
C_{29} ααα 20S/20R	0.79	0.99	0.69	1.07
VR equivalent (Sofer *et.al*,1993)	0.75	0.75	0.70	0.89
C_{27}αββ/(αββ+αααα)	0.26	n.d.	0.59	0.37
C_{28}αββ/(αββ+αααα)	0.26	0.42	0.45	0.42
C_{29}αββ/(αββ+αααα)	0.32	0.34	0.40	0.38

G participant reported a severe contamination by phthalate for Asturias sample;
n.d.: not detected
* MRM-GC-MS (metastable reaction monitoring)

Table 13: Maturity related steranes parameters for the Posidonia shale Sample

Ratios	***Participant***				
	C	F	G	H	H^*
C_{27} steranes (%total C_{27} to C_{29} regular steranes)	39	37	30	40	
C_{28} steranes (%total C_{27} to C_{29} regular steranes)	34	24	20	21	
C_{29} steranes (%total C_{27} to C_{29} regular steranes)	31	39	50	39	
C_{27} ααα 20S/(20S+20R)	0.40	0.37	0.43	0.20	0.23
C_{28} ααα 20S/(20S+20R)	0.35	0.10	-	0.23	0.21
C_{29} ααα 20S/(20S+20R)	0.36	0.28	0.38	0.22	0.25
C_{29} ααα 20S/20R	0.56	0.39	0.61	0.27	0.33
VR equivalent (Sofer *et.al*,1993)	0.63	0.56	0.66	0.49	0.52
C_{27}αββ/(αββ+αααα)	0.18	n.d	-	0.25	0.17
C_{28}αββ/(αββ+αααα)	0.36	0.27	-	0.29	0.19
C_{29}αββ/(αββ+αααα)	0.32	0.26	-	0.25	0.16

n.d.: not detected
* MRM-GC-MS (metastable reaction monitoring)

Aromatic hydrocarbons - Methylphenanthrene Index

The methylphenanthrene index is based on the distribution of phenanthrene and three or four of its methyl homologs which shows a progressive change during maturation (Radke *et al.*, 1982a, *in* Tissot & Welte, 1984). The increase of relative abundance of 2- and 3-methylphenanthrene during maturation can be explained on the basis of rearrangement reactions, which, at higher temperatures, favor these thermodynamically more stable isomers (Tissot & Welte, 1984).

The Methylphenanthrene index MPI 1 is defined as follows:

- MPI1=(1.5*(3MP+2MP))/(PHEN+9MP+1MP);

A similar ratio, Methylphenanthrene index MPI 2, may be used as controls means or as a substitute for MPI1:

- MPI2=(3*(2MP))/(PHEN+9MP+1MP);

Table 14: Maturity related methyphenanthrene parameters for the Asturias CS sample

Ratios	***Participant***			
	C	F	G	H
MPI 1	0.79	0.34	0.78	0.73
MPI 2	0.26	0.37	0.87	0.88

Table 15: Maturity related methyphenanthrene parameters for the Posidonia shale sample

Ratios	***Participant***			
	C	F	G	H
MPI 1	0.56	0.17	0.52	0.49
MPI 2	0.18	0.16	0.52	0.55

The numerical value of MPI2 is generally somewhat higher than of the MPI1. This difference reflects a slight predominance of 2- over 3-methylphenantrene which is common to the methylphenanthrene distribution (Tissot & Welte, 1984).

According to Peters & Moldowan (1993) several difficulties limit the use of methylphenantrene indices. Among them, the most relevant for this study is that samples with different maturities can show identical ratios.

Tables 14 and 15 summarize the methylphenanthrene indices provided by four participants. It is possible to observe that the MPI 1 ratios present a better correlation among participants than MPI 2. Results of participants G and H present a good correlation for both MPI1 and MPI2. The problem with the low correlation among results for MPI 2 may be, more likely, related to calculations.

MPI 1 ratios are, in general, higher for the Asturias CS sample than for the Posidonia shale sample, reflecting the higher maturation level of the Asturias CS sample.

It is worth to mentioning that previous exercises of the Thermal Indices WG did not include MPI parameters.

3. REMARKS AND DISCUSSION

- A good correlation among the spectral fluorescence curves and parameters for sporinites from the Asturias CS sample was observed. Participants reported to have problems in obtaining meaningful measurements due to the particular features of liptinite present in this sample. A very good correlation among spectral fluorescence curves and parameters was observed for the majority of participants for the Posidonia shale sample.

- VIRF analysis provided two possible interpretations for Ro (normal) to the Asturias CS sample. The Ro (normal) of 0.74% derived from the alternative interpretation present a good correlation with the group mean 0.70% Ro achieved by the Qualifying for vitrinite reflectance WG. For the Posidonia sample the VIRF chart is much more complex. A Population G was recognized in this sample presenting approximately 0.30% Ro whereas the Ro (normal) calculated on the inferred normal vitrinite is 0.69%.

Tmax from pyrolysis Rock-Eval present, in general, a good correlation, as well as the parameters derived from the GC analyses (*n*-alkanes and isoprenoids). For the terpane analyses the best correlations were presented by the homohopane (S/S+R) ratios for both samples. The ratios based on sterane analysis presented, in general, a better correlation for the Asturias sample. MPI 1 ratios are, in general, higher for the Asturias CS sample than for the Posidonia shale sample.

Some relevant observations have arisen from the results obtained by this exercise. Figures 14 and 15 summarize the distribution of some microscopic and chemical maturity parameters.

The parameters for the Asturias CS sample present a narrower dispersion (Figure 14) when compared to the Posidonia sample (Figure 15). There is a good correlation between the mean group Ro (random) 0.70%, alternative VIRF 0.74%, the rank range based on sporinite λmax and some isomerization ratios (VRE from the steranes C_{29} $\alpha\alpha\alpha$ *S/R* ratio and C_{29} $\alpha\alpha\alpha$ 20*S*/(20S+ 20R) ratio). Tmax from pyrolysis Rock-Eval indicates a slightly lower maturation level, whereas fluorescence parameters derived from alginite tends to point out a slightly higher maturation.

The correlation among different maturity parameters for the Posidonia shale sample, present a much more complex scenario (Figure 15). The higher complexity for maturation evaluation, presented by Posidonia sample, in comparison to the Asturias sample, was previously observed by the Qualifying for vitrinite reflectance WG exercise and VIRF analysis. A general good agreement of chemical maturity parameters, including Tmax from Rock-Eval pyrolysis, point out a higher maturation level for the Posidonia sample than the 0.37% Ro random, suggesting that this value may be suppressed. It is worth to mentioning the good correlation between the mean group Ro (random) of 0.37% and spectral fluorescence parameters provided by some participants. In this case, spectral fluorescence parameters do not point out suppression. The same behaviour was previously observed by the Thermal Indices WG for the Alpha sample study in 2002. The vitrinite population G identified by the VIRF study, as not true vitrinite, is probably included on the particles measured by the Qualifying vitrinite for reflectance WG, which yielded a group mean Ro (random) of 0.37%. VIRF Ro (normal) 0.69% is based on a population which was not registered as vitrinite by the Qualifying for vitrinite reflectance WG, and provides some support for the various geochemical parameters which suggest the Posidonia shale has higher maturity than Ro (random) 0.37%.

REFERENCES

Baranger, R; Martinez, L.; Pittion, J-l and Pouleau, J. (1990) A new calibration procedure for fluorescence measurements of sedimentary organic matter. *Org.Geochem.* **17**, 467-475.

Borrego, A. G.; Araujo C.V.;. Balke, A ; Cardott, B.; Cook, A.; David, P.; Flores, D.; Hámor-Vidó, M.; Hiltmann, W.; Kalkreuth, W.; Koch, J.; Kommeren, K.; Kus, J.; Ligouis, B.; Marques, M.; Mendonça Filho, J. G.; Misz, M.; Oliveira, L.; Pickel, W.; Reimer, K.; Ranasinghe, P.;. Suárez-Ruiz, I and Vieth, A. (2006) Influence of particle and surface quality on the vitrinite reflectance of dispersed organic matter: Comparative exercise using data from the qualifying system for reflectance analysis working group of ICCP, *in press*.

Mackenzie, A.S., Brassel, S.C., Eglinton, G., and Maxwell, J.R. (1982a). Chemical fossils: the geological fate of steroids. *Science*, **217**, 491-504.

Mackenzie, A.S., Lamb,N.A. and Maxwell, J.R. (1982b). Steroid hydrocarbons and thermal history of sediments. *Nature*, **295**, 223-226.

Mackenzie, A.S. and Mckenzie, D. (1983). Isomerization and aromatization of hydrocarbons in sedimentary basins formed by extension. *Geology Magazine*, **120**, 417-470.

Mukhopadhyay P.K. (1994). Vitrinite Reflectance as Maturity Parameter. Petrographic and Molecular Characterization and its Applications to Basin Modeling. *In:* Muklhopadhyay and Dow (eds.) *Vitrinite Reflectance as a Maturity Parameter. Applications and Limitations*. American Chemical Society, Washington. 1-24.

Peters, K.E. and Moldowan, J.M. (1993). *The biomarker guide. Interpreting molecular fossils in petroleum and ancient sediments*. Prentice Hall, Englewood Cliffs, N. J., 363 pp.

Sofer, Z., Regan, D. R., Muller, D.S. (1993). Sterane isomerization ratios of oils as maturity indicators and their use as an exploration tool, Neuquen basin, Argentina. *XII Congreso Geológico Argentino y II Congreso de Exploración de Hidrocarburos Actas I*, 407-411.

Tissot, B.P. and Welte, D.H. (1984). *Petroleum formation and occurrence.* Springer-Verlag Berlin, Heildelberg, New York, 699 pp.

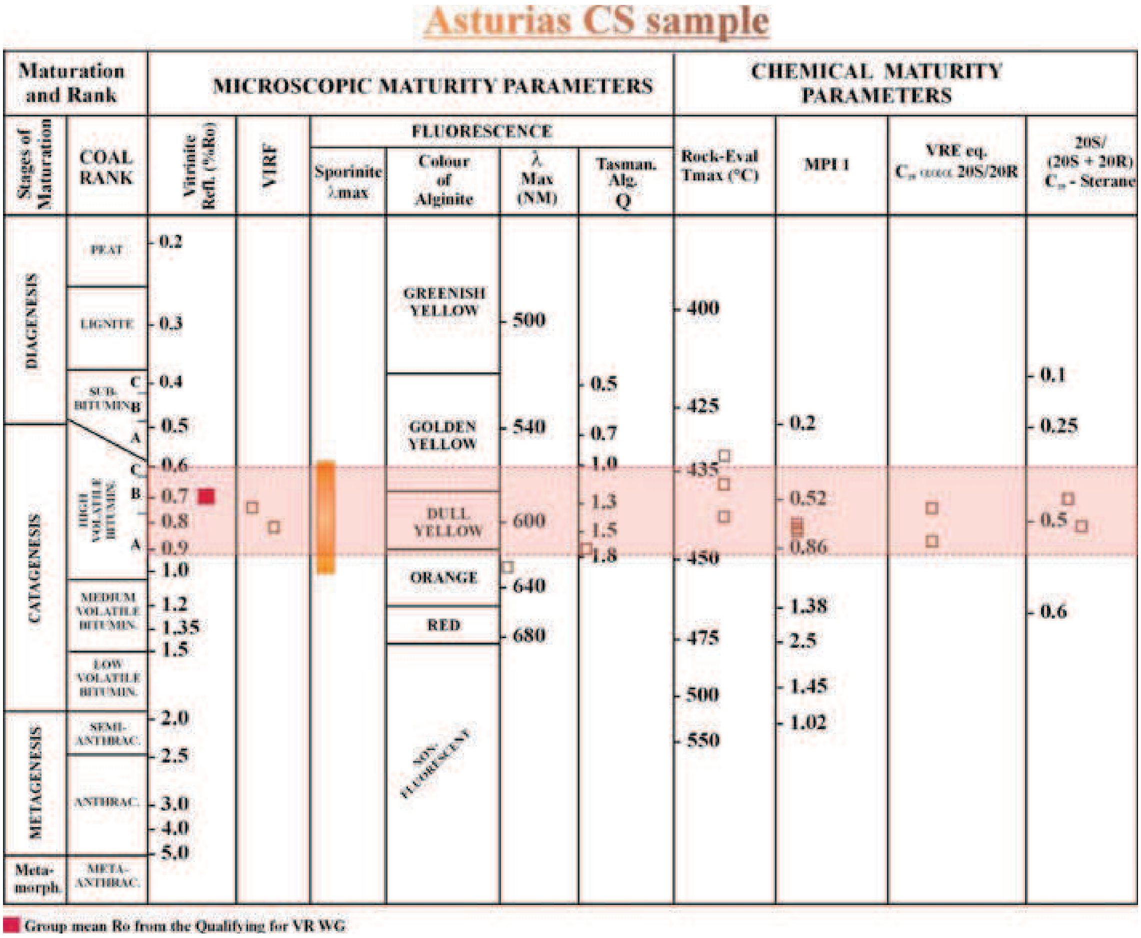

Figure 14: Correlation of microscopic and chemical maturation parameters chart from Asturias CS sample (modified from Mukhopadhyay, 1994)

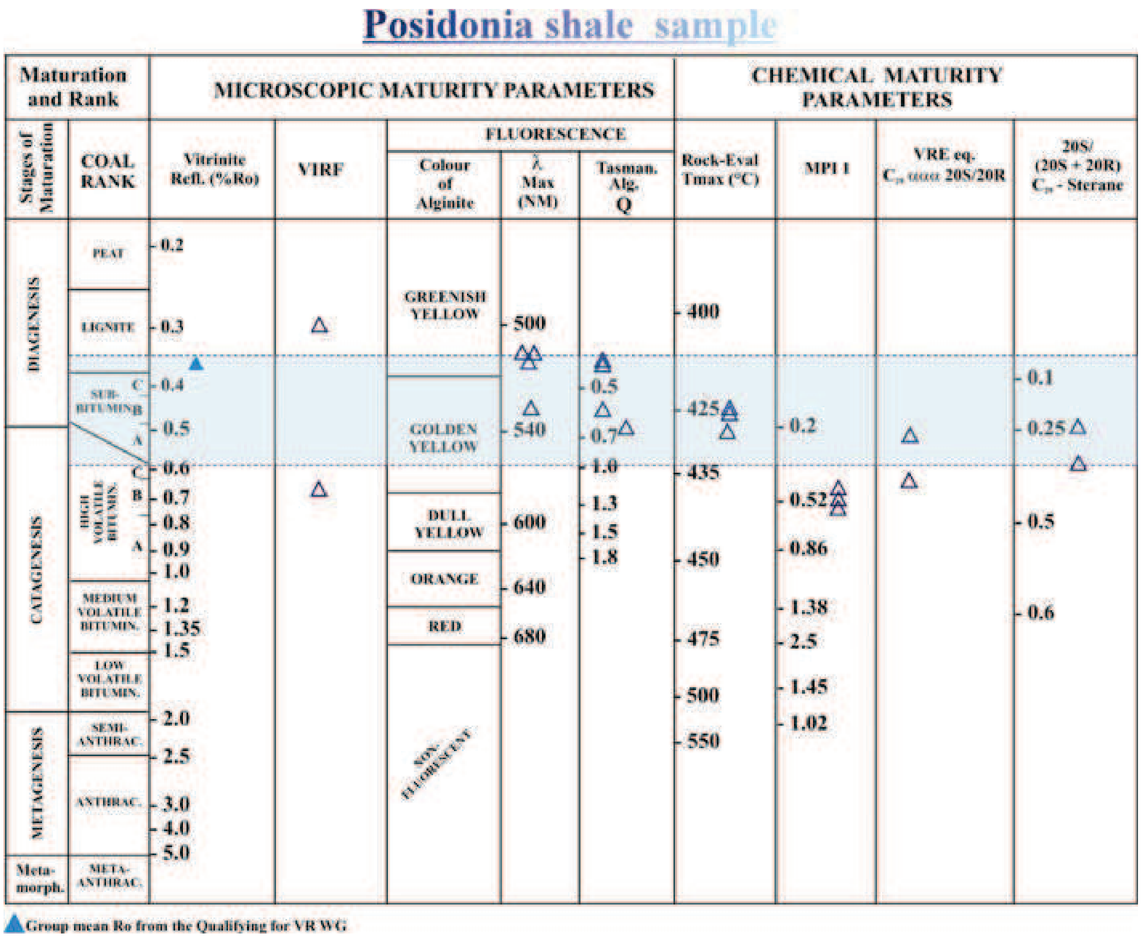

Figure 15: Correlation of microscopic and chemical maturation parameters chart from Posidonia shale sample (modified from Mukhopadhyay, 1994)

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Know Your Coal Petrologist #20

Two eminent members of ICCP are out enjoying an evening river cruise at the 2003 Utrecht meeting. The same cruise was also the location of the photos for KYCP #18 and #19. Answer page 39.