ICCP - Thermal Indices Working Group : Summary of the 2002 Round Robin Exercise

C. V. Araujo[1],
S. M. Barbanti[1],
V. C. Condé[1],
W. Kalkreuth[2],
A.C. Macedo[1],
J. Newman[3],
W. Pickel[4],
L. Stasiuk[5] and
H. Volk[4]

[1] PETROBRAS Research and Development Center, Brazil
[2] Federal University of Rio Grande do Sul - UFRGS, Brazil
[3] Newman Energy Research, New Zealand
[4] CSIRO, Australia
[5] Geological Survey of Canada, Canada

1. INTRODUCTION

History:

The Thermal Indices Working Group within ICCP (International Committee on Coal and Organic Petrology) conducted interlaboratory exercises over the last years with the aim of improving the reproducibility and comparability of spectral fluorescence microscopy. For this purpose a calibrated common lamp source (Baranger *et al.* 1991) was used by the laboratories to obtain a relative correction function. The first exercise consisted of the determination of spectral characteristics of *Tasmanites* algae in a series of increasing maturity samples from the Toarcian of the Paris Basin (Araujo *et al.* 1998).

From 1999 to 2001 the Thermal Indices Working Group determined spectral fluorescence properties and vitrinite reflectance on torbanite samples (1 - Alpha and 3 - Joadja) from Australia (Araujo *et al*, 2002). The results showed that the fluorescence spectra of the Alpha Torbanite exhibit two curves distinguishing two alginite populations with different fluorescence characteristics, one presenting a bluish-yellow fluorescence, and a second an orange-fluorescing algal population (Figs. 1a and 1b). Laboratories 1 and 3 characterized both populations and laboratory 2 supplied an average curve for this sample (Figure 1a and b, Table 1). The curve with the lower λmax is interpreted to represent the real maturation level of the sample. Spectral fluorescence parameters λmax, Q and Qmax, together with vitrinite reflectance (R_{random} (%)) are given in Table 1. The analyses of the Alpha Torbanite also included complementary spectral fluorescence measurements techniques such as VRF™ (Newman, 1997a; Newman, 1997b; Figure 2) and Fluorescence Alteration of Multiple Macerals - FAMM (Wilkins *et al*., 1995 and Pickel *et al*., 2001; Figure 3).

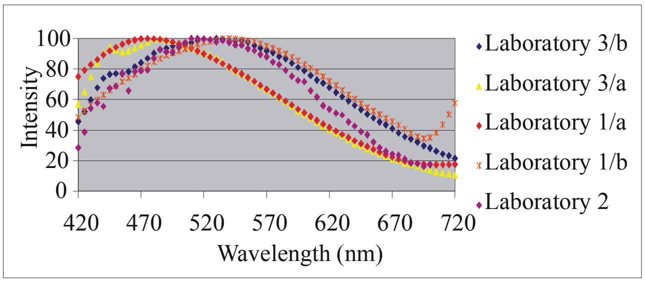


Figure 1a - *Spectral curves for Alpha Torbanite*

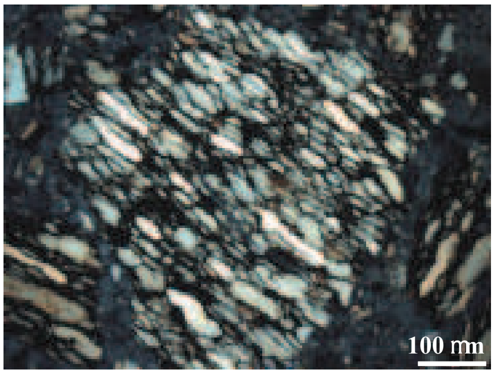


Figure 1b - *Alpha sample under ultraviolet irradiation*

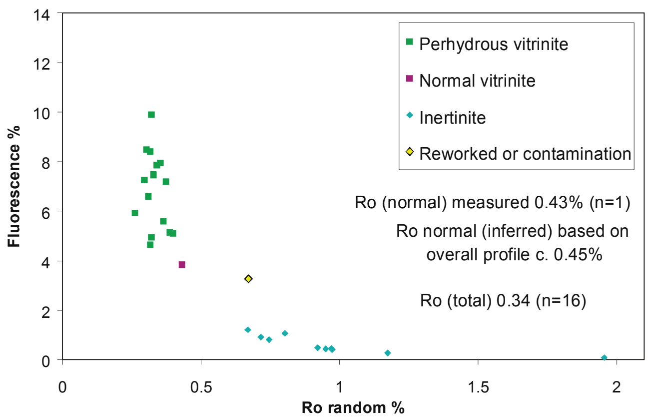


Figure 2 - *VRF™ plot for Alpha Torbanite illustrating relative positions of vitrinites and inertinite*

Table 1 - Fluorescence spectra parameters and vitrinite random reflectance obtained for Alpha Torbanite

Sample 1 (Alpha)							
Laboratory	1		2	3			5
Parameter	a	b		Axiophot II a	b	UMSP	
λmax (nm)	475	540	508	485	530	480	
Q	0.30	0.59	0.39	0.29	0.53	0.31	
Qmax	1.04	1.09	1.06	1.04	1.05	1.10	
n	10	10	10				
R_{random}(%)	0.29		0.29				0.31
S.D.	0.06		0.03				0.06
n	20		20				50

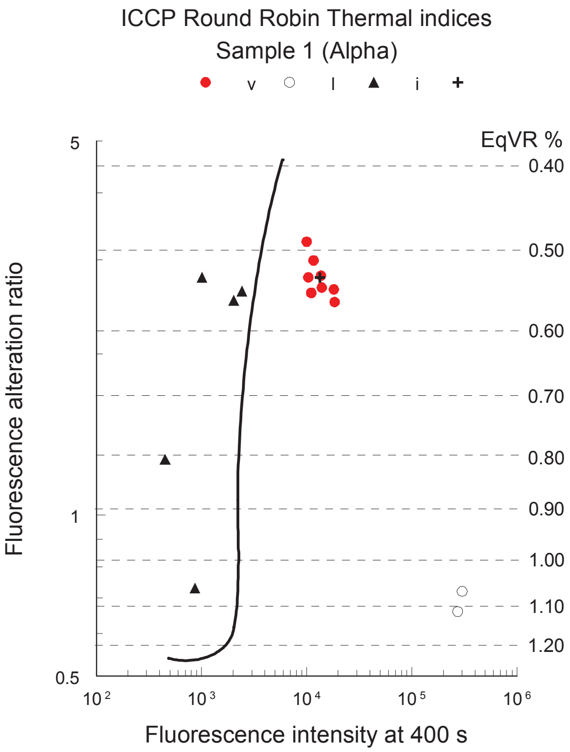


***Figure 3** - FAMM diagram for Alpha Torbanite red circles: vitrinite; blank circles: liptinite; triangles: inertinite*

Spectral curves and parameters provided by three different laboratories showed good correlations. Problems in the correlation of the results are related to the selection of the different populations present in the samples. Spectral fluorescence parameters and corresponding estimated vitrinite reflectance (VR) values for Alpha Torbanite indicate no suppression of vitrinite reflectance, while both VRF and FAMM data indicating that the vitrinite reflectance may be suppressed in the torbanite sample (Table 2).

***Table 2** - Correlation between equivalent vitrinite reflectance based on spectral fluorescence parameters, VRF and FAMM and vitrinite random reflectance of Alpha Torbanite*

Alpha Torbanite			
Lab	Parameter	VR and VR % equivalent	Rr % measured
1	(λmax) 475	~0.27	0.29
2	(λmax) 508	~0.32	0.29
3	(λmax) 485	~0.29	
4	(VRF^{TM})	0.45	
5	(FAMM)	0.53	0.31

<u>2002 Exercise:</u>

The last exercise (2002 Round Robin Exercise) of this WG (Table 3) was the geochemical characterization of sample 1 (Alpha shale) and the comparison of random reflectances between the oil shale and the associated coal.

***Table 3** - Participants of Thermal Indices WG 2002 exercise*

Participants	Random Reflectance (Alpha Coal)	Organic Geochemistry
W. Kalkreuth Instituto de Geociencias Universidade Federal do Rio Grande do Sul	X	
C.V. Araujo/ V.C. Condé (GC/biomarkers - S.M. Barbanti /A.C. Macedo) Petrobras Research and Development Center	X	X
L. Stasiuk Canadian Geological Survey		X
W. Pickel (GC/biomarkers - H. Volk) CSIRO Petroleum	X	X

2. RESULTS AND DISCUSSION OF THE 2002 ROUND ROBIN EXERCISE

2.1 Geochemical characterization of Alpha Torbanite

2.1.1 Bulk Geochemistry

Bulk geochemical analysis comprised TOC determination and Rock-Eval pyrolysis. Alpha Torbanite is characterized by a high TOC content (62.5-70.4 wt.%). Free hydrocarbon content (S_1) and the source rock potential (S_2) is high. High

Hydrogen Indices (HI) and low Oxygen Indices (OI) are typical of type I kerogen. T_{max} values are relatively high (445 - 450ºC) and are known to vary only little with thermal maturity for type I organic matter (Espitalié, 1985; Table 4).

***Table 4** - TOC and Rock-Eval pyrolysis data of Alpha Torbanite* (*S3CO, **OICO)

Lab	TOC	Pyrolysis Rock Eval					
		S1	S2	S3	Tmax	HI	OI
1	62.6	5	555	11	450	886	18
3 (mean)	70.4	1.9	603.7	5.9*	445	858	18**

2.1.2 Gas Chromatography and Mass Spectrometry

- <u>*n*-Alkane and isoprenoids</u>

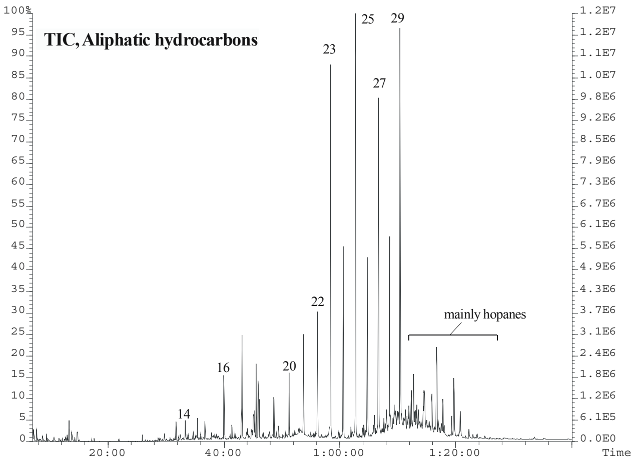
The comparison between results provided by laboratories 1 and 5 are very good in the range of n-C_{18} to n-C_{33}. Differences are mainly due to the loss of light hydrocarbons by laboratory 1 (Figure 4, Table 5).

***Table 5** - Ratios from the distribution of n-alkanes and isoprenoids*

Parameter	ratio*	
	Lab 1	Lab 5
Pr/Ph	0.86	2.6
Pr/n-C_{17}	1.63	5.76
Ph/n-C_{18}	0.88	1.01
CPI_{22-32}	2.31	2.69
CPI_{24-32}	2.32	2.69
CPI_{26-32}	2.38	2.74
CPI_{26-30}	2.37	2.80
CPI 2_{26-28}	1.61	1.98
CPI 2_{28-30}	3.46	4.12
CPI 2_{20-22}	0.99	1.03
n-C_{31}/n-C_{19}	1.10	1.28

*calculations were based on peak areas (see appendix)

The distribution of *n*-alkanes and isoprenoids conveys the impression of an immature extract dominated by terrestrial organic matter indicating that, at this rank, the organic extract reflects preferentially the terrestrially derived organic matter. The most remarkable feature is the strong odd over even predominance in the range of n-C_{23} to n-C_{29}. According to Peters and Moldowan (1993) the odd predominance in the range of n-C_{23} to n-C_{31} is a characteristic of non-marine algal input. The Alpha shale is Permian, and for some reason Permian rocks containing land plant material often have also high n-C_{23} and n-C_{25} (George *et al*., 1994; Casareo *et al*., 1996), whereas e.g. Upper Carboniferous rocks containing abundant land plant material show their odd-predominance mainly in n-C_{27}, n-C_{29} and n-C_{31}.



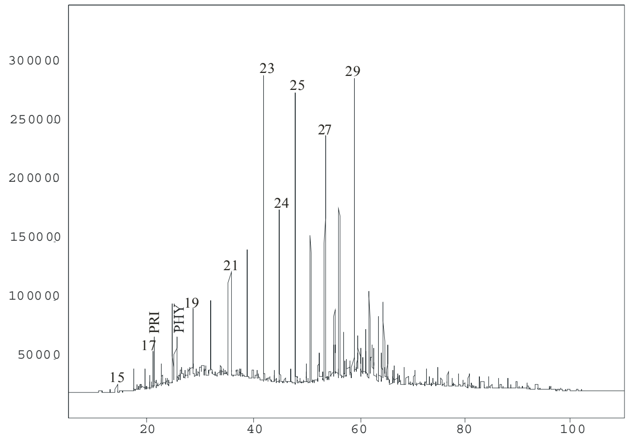
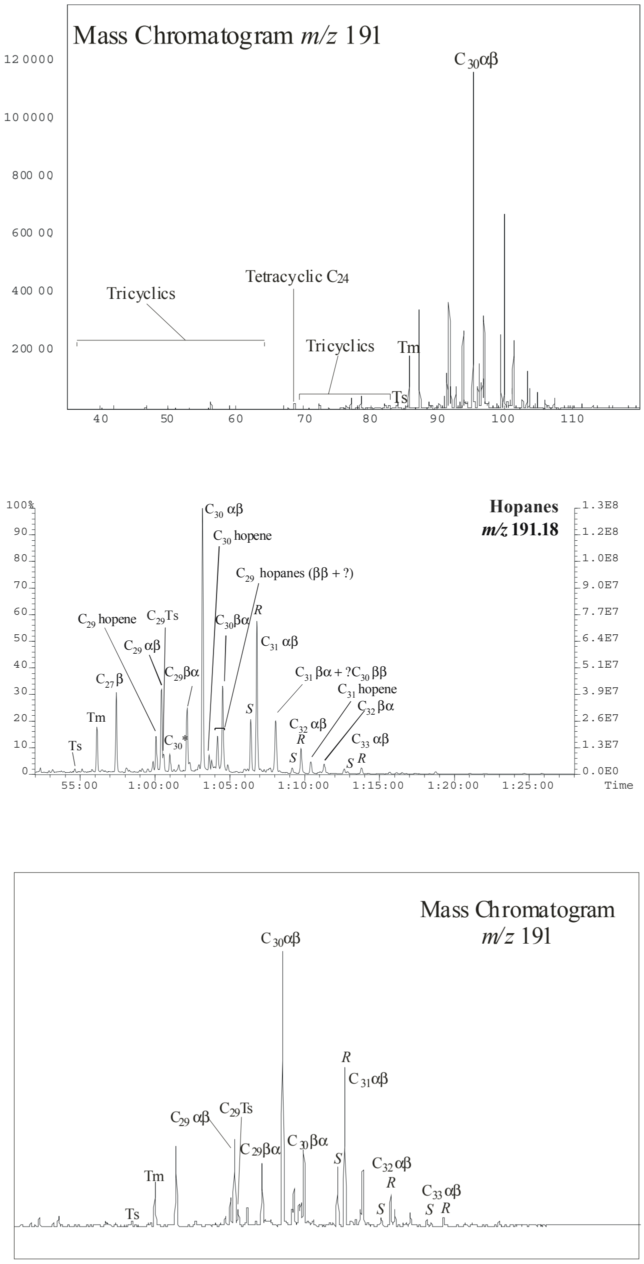


***Figure 4a (above) and b (below)** - Aliphatic hydrocarbon distribution (**a**: for Lab.5,TIC - total ion chromatogram; **b**: for Lab.1 derived from GC).*

The high Pr/Ph ratio (2.6-Lab.5; Table 5), suggests deposition of terrestrial organic matter under oxic conditions (Didyk *et al*., 1978) and high Pr/n-C_{17} ratios are characteristic of immature samples (Table 5).

- <u>Terpane distribution</u>

The correlation between results of the terpane distribution provided by laboratories 1 and 5 is very good (Table 6). The sample is characterized by the presence of tricyclic and tetracyclic terpanes in low relative abundances (Figure 5a) reflecting the input of terrestrially derived organic matter (Abdullah *et al*., 1988).



Figures 5a (top), b(middle), c(bottom) *- Terpane distribution as derived from m/z 191 mass chromatogram (**a:** Lab 1 showing tricyclic and tetracyclic terpanes, **b:** Lab 5, **c:** Lab 1)*

The maturity signal of hopanes conveys a very immature signature, typical for sediment extracts that have not yet entered the oil window. The presence of hopenes is noteworthy (Figure 5b). The very low Ts/Tm ratio (0.09/0.10; Table 6) indicates very low maturity. However, it is known that this ratio is also influenced by source, and tends to be low in coaly sediments. At a vitrinite reflectance equivalent (VRE) of ca. 0.7% the isomerization ratio of βα hopanes (moretane) to αβ hopane is about 0.05 (Peters and Moldowan, 1993). The Alpha Torbanite extract shows moretane/hopane ratios of 0.58 to 0.84 for C_{29} and C_{30} compounds, and is thus well below this maturity level (Table 6). 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 Alpha Torbanite extract shows *S*/(*S*+*R*) ratios ranging from 0.19 to 0.27 for C_{31} to C_{33} homohopanes (Table 6) and is thus far from this equilibrium. The abundance of diahopanes is low in the sample, also indicating an immature rock extract.

Table 6 *- Maturity-related terpane parameters*

Parameter	Lab 1		Lab 5	
	ratio	derived from	ratio	derived fom
Ts/Tm	0.10	S191	0.09	M
Ts/(Ts+Tm)	0.09	S191	0.08	M
Tm/C_{27}β	0.54	S191	0.58	M
C_{29}*/C_{29} αβ hopane	_	S191	0.08	M
C_{30}*/C_{30} αβ hopane	_	S191	0.07	M
C_{29} αβ/(αβ+βα)	0.58	S191	0.58	M
C_{30} αβ/(αβ+βα)	0.78	S191	0.84	M
C_{31} αβ 22*S*/(22*S*+22*R*)	0.27	S191	0.26	M
C_{32} αβ 22*S*/(22*S*+22*R*)	0.20	S191	0.19	M
C_{33} αβ 22*S*/(22*S*+22*R*)	0.25	S191	0.23	M
C_{34} αβ 22*S*/(22*S*+22*R*)	0.34	S191	_	_
Homohopanes/C_{30} αβ hopane	0.98	S191	1.06	S191
C_{27} hopanes/C_{30} αβ hopane	0.18	S191	0.18	S191
C_{31} αβ hopanes/C_{30} αβ hopane	0.80	S191	0.81	S191

S191 (Selective Ion Monitoring *m/z* 191)

M (Metastable Reaction Monitoring GC-MS)

- Sterane distribution

There is a very good correlation between results on sterane distribution provided by laboratories 1 and 5. Differences in some results are related to different analytical methods (Lab.1 GC-MS, Lab.5 GC-MS, GC-MS-MS; Table 7).

The commonly occurring series of C_{27} to C_{29} ααα and αββ steranes and βα and αβ diasteranes were detected. There is a strong dominance by C_{29} steranes (Figure 6a, b and Table 7). This dominance is consistent with a strong terrestrial input to the organic matter of the Alpha torbanite.

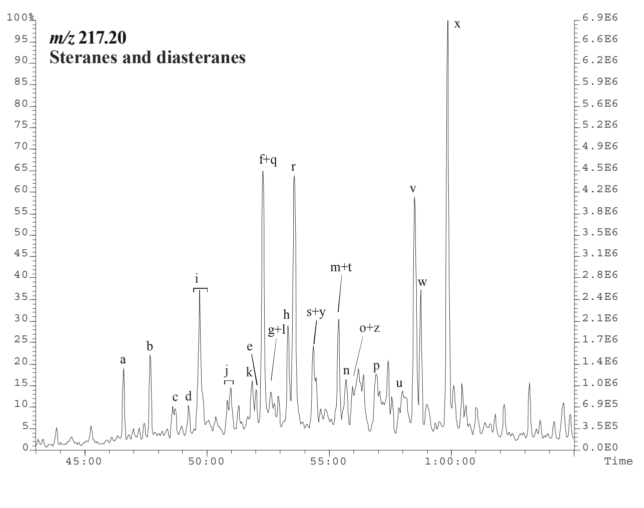
Biologically more abundant *R* isomers on C-20 position isomerise into the thermally more stable *S* configuration with thermal maturation, and αα isomers are isomerized to thermally more stable ββ isomers (Mackenzie *et al*., 1982a; Mackenzie *et al*., 1982b and Mackenzie, A.S. and Mckenzie, D., 1983). In the analysed sample both these parameters are well beyond their empirical endpoints, ie. ca. 0.54 for the ratio *S*/(*S*+*R*), equivalent to ca. 0.9% VRE, and 0.7 for the ratio C_{29}ββ/(ββ+αα), equivalent to ca. 1% VRE (Peters and Moldowan, 1993).

***Table** 7 - Maturity-related sterane parameters*

Parameter	Lab 1		Lab 5	
	ratio	derived from	ratio	derived fom
C_{27} αββ steranes 20*S*+*R* (% of total C_{27} to C_{29} αββ 20*R* steranes in 218 SIM)	20.4	S218	23.4	S218
C_{28} αββ steranes 20*S*+*R* (% of total C_{27} to C_{29} αββ 20*R* steranes in 218 SIM)	15.1	S218	14.9	S218
C_{29} αββ steranes 20*S*+*R* (% of total C_{27} to C_{29} αββ 20*R* steranes in 218 SIM)	64.6	S218	61.7	S218
C_{27} steranes (% of total C_{27} to C_{29} regular steranes)	14.0	S217	19.4	M
C_{28} steranes (% of total C_{27} to C_{29} regular steranes)	14.2	S217	16.5	M
C_{29} steranes (% of total C_{27} to C_{29} regular steranes)	71.8	S217	63.4	M
C_{27} βα diasteranes/(ααα+αββ steranes)	1.01	S217	0.87	M
C_{28} βα diasteranes/(ααα+αββ steranes)	_		0.78	M
C_{29} βα diasteranes/(ααα+αββ steranes)	_		0.84	M
C_{27}+C_{28}+C_{29} βα diasteranes/(ααα+αββ steranes)	_		0.84	M
C_{27} ααα 20*S*/(20*S*+20*R*)	0.26	S217	0.30	M
C_{28} ααα 20*S*/(20*S*+20*R*)	0.15	S217	0.21	M
C_{29} ααα 20*S*/(20*S*+20*R*)	0.12	S217	0.08	M
C_{29} ααα 20*S*/20*R*	0.13	S217	0.09	M
Vitrinite reflectance equivalent from C_{29} ααα 20*S*/20*R* (Sofer *et al*., 1993)	0.42	S217	0.39	M
C_{27} αββ/(αββ+ααα)	0.21	S217	0.26	M
C_{28} αββ/(αββ+ααα)	0.56	S217	0.48	M
C_{29} αββ/(αββ+ααα)	0.47	S217	0.45	M
C_{27} βα diasterane 20*S*/(20*S*+20*R*)	0.57	S217	0.56	M
C_{28} βα diasterane 20*S*/(20*S*+20*R*)	_		0.54	M
C_{29} βα diasterane 20*S*/(20*S*+20*R*)	_		0.53	M

S218 (Selective Ion Monitoring *m/z* 218)

M (Metastable Reaction Monitoring GC-MS)



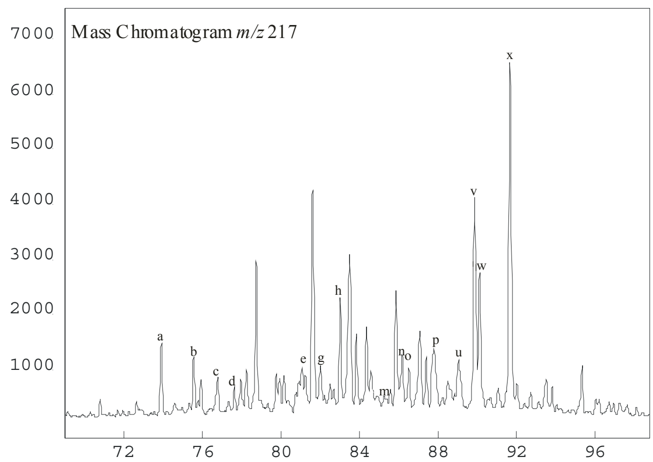


***Figure 6a (left),b (above)** - Sterane distribution as derived from m/z 217 mass chromatogram (**a:** Lab 5, **b:** Lab 1- for peaks identification see appendix)*

Laboratories 1 and 5 provided an estimation of VRE from the C_{29} *S*/*R* ratio based on a relationship published in Sofer *et al*. (1993) pointing out a maturity ranging from 0.39 to 0.42% VRE, indicating that the rock extract is immature and presenting a good correlation with the measured VRF data.

The ββ/(ββ+αα) ratios for the C_{27}, C_{28} and C_{29} steranes are consistent with a low thermal maturity for the studied sample.

2.2 Alpha Coal Random Reflectance

The determination of random vitrinite reflectance of the Alpha Torbanite and the associated coal was proposed to investigate the suppression effect on vitrinite reflectance in the oil shale. Results on R_{random} of the associated coal were provided by three laboratories (Table 8).

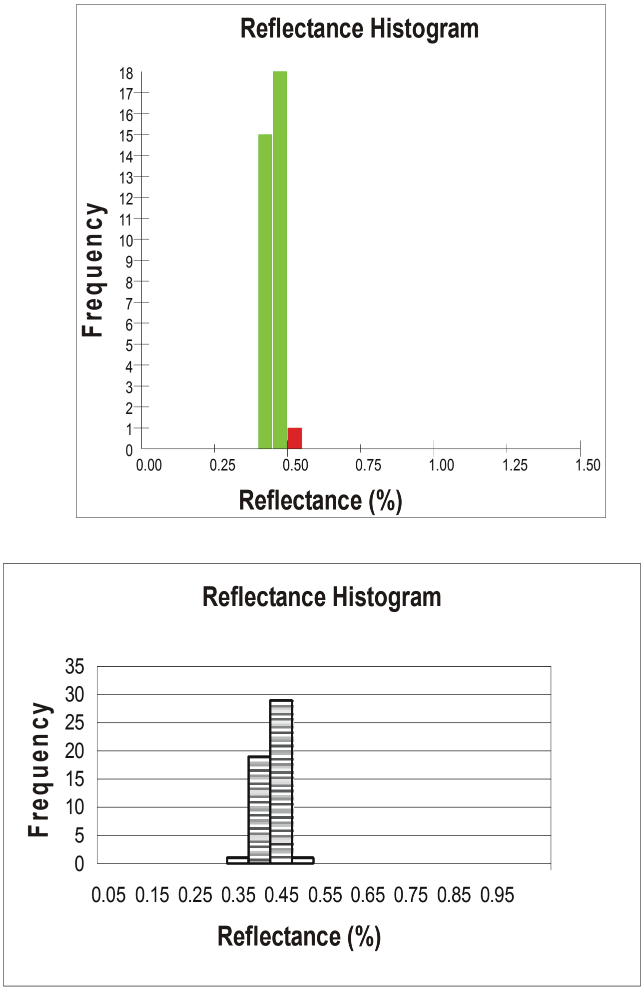


Figure 7 - *Reflectograms of the Alpha Coal*

The vitrinite reflectance of the coal (~0.41%) associated with the Alpha Torbanite is about 0.1% higher than the one determined for the oil shale (~0.30%) indicating a significant suppression of vitrinite reflectance in the torbanite (Figure 7, Table 8). FAMM equivalent VR data of the Alpha Coal suggests that the vitrinite reflectance of the coal is also suppressed (Table 8).

Table 8 *- Vitrinte random reflectance and Equivalent VR (FAMM) of Alpha Coal*

Laboratory	Alpha Coal			
	R_{random} %	Standard Deviation	Total N.	EqVR (FAMM)
1	0.45	0.03	34	
2	0.36	0.035	50	
3				
4				
5	0.41	0.03	50	0.68

Table 9 summarizes the maturity parameters obtained for the alpha torbanite and the associated coal. The equivalent vitrinite reflectance (VR) based on fluorescence parameters is in the same order as the measured R_{random} (%) and does not indicate suppression.

Table 9 *- Summary of maturity parameters of Alpha Torbanite and associated coal*

Maturity Parameters	Alpha Torbanite	Alpha Coal	Remarks
Rrandom%	0.29-0.31	0.36-0.45	
VRE based on fluor.parameters	0.27-0.32		
VRF %	0.45		
VRE (FAMM)	0.53	0.68	
Rock-Eval T_{max}	445°C 450°C		Not accurate for maturity evaluation of Type I Kerogen
Homopanes C_{31}-C_{33} *S*/(*S*+*R*)	0.19-0.27		VRE<<<0.6%Ro
ββ hopanes	detected		VRE< 0.4%
VRE (C_{29} ααα*S*/*R*)	0.39- 0.42		

On the other hand, vitrinite reflectance suppression is clearly indicated by VRF and FAMM equivalent VR. Rock-Eval T_{max} in the range of 445-450ºC is not accurate for maturity evaluation in this particular sample due to facies effects. Maturity parameters derived from hopanes and steranes point out that the sample is immature and VRE (C_{29} ααα *S*/*R*) based on Sofer's relationship present a good correlation with VRF.

3. CONCLUSIONS

The results show:

- Measured vitrinite reflectance in the Alpha Torbanite sample ranges from 0.29-0.31 %.
- Measured vitrinite reflectance of the associated coal is about 0.1% higher than the vitrinite reflectance measured in the Alpha Torbanite.
- Spectral fluorescence parameters do not indicate a suppression, whereas both results from the VRF and FAMM methods indicate a suppression of about 0.15-0.2% for the vitrinite reflectance of the oil shale. It is likely that spectral fluorescence parameters are not able to "detect" suppression in low maturity samples.
- Generally good agreement of results on bulk geochemistry (TOC, Rock Eval), and GC / GC-MS provided by three laboratories for Alpha Torbanite.
- Rock-Eval T_{max} in the range of 445-450ºC is not accurate for maturity evaluation of Type I kerogen.
- Maturity parameters derived from hopanes and steranes point out that the sample is immature and VRE (C_{29} ααα *S*/*R*) based on Sofer's relationship present a good correlation with VRF.
- Random vitrinite reflectance obtained for Alpha Coal is about 0.1% higher than random vitrinite reflectance of Alpha Torbanite indicating a suppression of the oil shale VR in that order. However, according to FAMM results, the vitrinite reflectance in the coal is also suppressed.

The consistency between most of data provided by the laboratories involved in this round robin exercise is very good. Additional work is needed to investigate the deviations of maturity parameters in marine type II (marine facies) and type III (coaly) kerogens.

Acknowledgements

The authors wish to thank Adrian Hutton for providing samples for this exercise, and Ángeles Gómez Borrego for her critical comments and help in improving this report.

REFERENCES

Abdullah, W.H., Gjelberg, J., Jones, J.M., Murchinson, D.G. and Telnaes, N. (1988) Early carboniferous coal deposition environment in Spitzbergen. *Advances in Organic Geochemistry*, **2**, 953-964.

Araujo, C., Vieth-Redemann, A., Pradier, B., Kalkreuth, W., Gomez Borrego, Á., Gurba, L., Hagemann, H., Hufnagel, W., Koch, M., Kuili, J., Laggoun-Defarge, F., Lo, H., Newmann, J., Spanic, D., Suárez-Ruiz, I. and Thompson-Rizer, C. (1998) ICCP Interlaboratory Exercise on the Application of Microspectral Fluorescence Measurements as Maturity Parameters. *Revista Latino Americana de Geoquimica Organica*, **4**, 41-50.

Araujo, C.V., Kalkreuth, W., Stasiuk, L. Pickel, W., Newman, J. and Condé, V.C. (2002) Interlaboratory Studies on Thermal Indices of Torbanite Samples from Australia. *8th. Latin American Congress on Organic Geochemistry*, Cartagena, Colombia. CD-ROM, pp. 31-34.

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.

Casareo, F. E., George, S. C., Batts, B. D. and Conaghan, P. J. (1996) The effects of varying tissue preservation on the aliphatic hydrocarbons within a high-volatile bituminous coal. *Org. Geochem*., **24**, 785-800.

Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G. (1978) Organic geochemical indicators of palaeoenvironmental conditions of organic sedimentation. *Nature*, **272**.

Espitalié, J. (1985) Use of T_{max} as a maturation index for different types of organic matter. *In:* Thermal modelling in sedimentary basins, (J. Burrus, ed.), pp. 475-496. Edit. Technip., Paris.

George, S. C., Smith, J. W. and Jardine, D. R. (1994) Vitrinite reflectance suppression in coal due to a marine transgression: case study of the organic geochemistry of the Greta Seam, Sydney Basin. *Australian Petroleum Exploration Association Journal*, **34(1)**, 241-255.

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

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

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

Newman, J (1997a) VRF™; Combined vitrinite reflectance and fluorescence. *Coal Research Conference*, Wellington, New Zealand.

Newman, J (1997b) New approaches to detection and correction of suppressed vitrinite reflectance. *APPEA Journal*, 524-535.

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.

Pickel, W., Wilkins R.W.T., Buckingham, C.P., Faiz, M., Kurusingal, J., Russell, N. and Sherwood, N. (2001) Laser Microscopy - FAMM. *In*: L. Gurba (2001, ed.) Review of New Methodologies and Techniques in Organic Petrology. *ICCP White Paper Series*, 2-10.

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.

Wilkins, R.W.T., Wilmshurst, J.R., Hladky, G., Ellacott, M.V. and Buckingham, C.P. (1995) Should fluorescence