Report on Organic Matter Concentration Working Group (OMCWG 2009)

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Presented at the 61st Meeting of the International Committee for Coal and Organic Petrology (ICCP)
September 19-26, 2009, Gramado, Brazil

1. Introduction

The main objective of the Organic Matter Concentration WG was to study the effect of the isolation procedure on the organic matter optical parameters. This second exercise consisted of the analysis of two samples with kerogen type II. The samples studied in this exercise were of low and medium rank and the analyses performed were:

- Vitrinite reflectance of the whole-rock sample (WR);
- Vitrinite reflectance of the kerogen concentrate sample (KC);
- Spectral fluorescence analysis of liptinite in the whole rock sample (WR);
- Spectral fluorescence analysis of liptinite in the kerogen concentrate sample (KC);

This report includes the results obtained by fourteen participants (Table 1) of the exercise proposed in the last ICCP meeting (Oviedo-Spain) in order to continue with the activities of the Organic Matter Concentration Working Group that began in 2008.

Table 1: *List of Participants in the OMCWG*

Participant	Affiliation	Country
Araujo, Carla V.	Petrobras R&D Center	Brazil
Borrego, Angeles G.	INCAR-CSIC	Spain
Cook, Alan	Keiraville Konsultants Pty. Ltd	Australia
Flores, Deolinda	University of Porto	Portugal
Hackley, Paul	U.S. Geological Survey	USA
Hower, Jim	University of Kentucky	USA
Kern, Marcio L.	Federal University of Rio de Janeiro	Brazil
Kus, Jolanta	Geozentrum Hannover	Germany
Mastalerz, Maria	Indiana University	USA
Mendonça Filho, João G.	Federal University of Rio de Janeiro	Brazil
Mendonça, Joalice O.	Federal University of Rio de Janeiro	Brazil
Menezes, Taíssa R.	Petrobras R&D Center	Brazil
Souza, Igor V. A. F.	Petrobras R&D Center	Brazil
Suarez-Ruiz, Isabel	INCAR-CSIC	Spain

The studied samples from OMCWG 2008 were composed by two outcrop carbonaceous shales (Type III Kerogen): one of them was from Spain (sample OMC1), Montsacro Mine, Asturian Central Coal Basin (Pennsylvanian) and the other one was from Nigeria (sample OMC2), Mamu Formation (Maastrichtian), Benin-Flank Basin. The samples showed that the scatter of the readings was higher in the Whole-Rock sample than in the Kerogen Concentrate sample for most participants in the low ranking samples. These results indicated that it was easier to identify the vitrinites in the Kerogen Concentrate sample than in the Whole-Rock sample for the low rank stage or that the vitrinite reflectance measurements were more reliable without the mineral matrix influence or the mineral matrix may affect the polishing quality (Mendonça Filho et al., 2008).

In this exercise, following the criteria and parameters and in the statistical evaluation system (www.iccop.org), in general excellent results were obtained and the selected samples allowed an accurate study on the effect of the isolation procedure on the organic matter optical parameters.

Now, for the OMCWG 2009, the studied samples were composed by two outcrop carbonaceous marine shales: one of them was from Spain (sample OMC3), Rodiles Formation (medium rank, Type II-kerogen), Asturian Mesozoic Cover and the other one was from Portugal (sample OMC4), Vale das Fontes Formation (low rank, Type II-I kerogen), Lusitanian Basin. The age of two studied samples is Pliensbaquian (Lower Jurassic).

The set of studied samples comprises 4 samples numbered as follows:

Sample OMC3 (Rodiles Formation - Asturian Mesozoic Cover - Spain): OMC3A = whole rock and **OMC3B** = kerogen concentrate

- Total Organic Carbon (TOC) about 3.5 wt%
- The Hydrogen Index (HI) is 188 mg HC/g TOC and the Oxygen Index (OI) is 9 mg CO_2/g TOC. These results from Rodiles Formation are plotted close to origin of the diagram, indicating that they may be in the oil window. (Figure 1).
- The value from Tmax (445°C) pointing out that this sample was thermally mature (medium rank).
- The hydrocarbon source potential is depleted, but the value is good (S2 = 6.65 mg HC/ g Rock) pointing out to an original good quality of organic matter for hydrocarbon generation.

Sample OMC4 (Vale das Fontes Formation - Lusitanian Basin - Portugal): OMC4A = whole rock and **OMC4B** = kerogen concentrate

- Total Organic Carbon (TOC) about 16 wt%;
- The HI is 667 mg HC/g TOC and the OI is 9 mg CO_2/g TOC, characterizing type II-I kerogen (Figure 1);
- Tmax = 415°C pointing out that this sample was thermally immature (low rank);
- The hydrocarbon source potential is excellent (S2 = 104.81 mg HC/ g Rock).

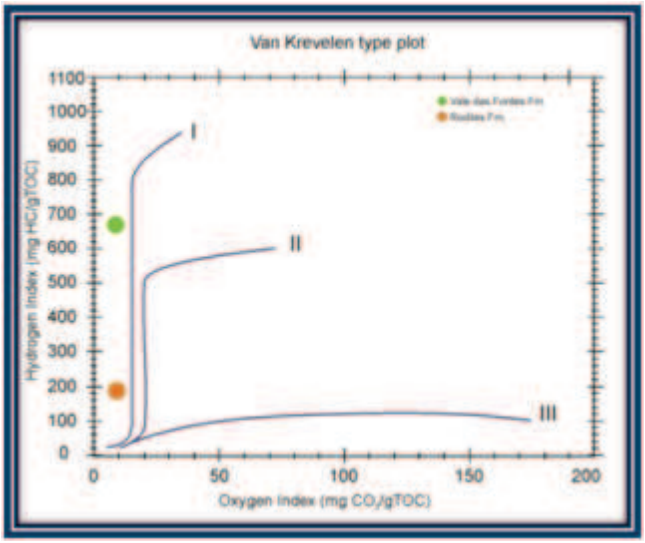


Figure 1: *Van Krevelen type plot (Espitalié et al., 1977) showing hydrogen and oxygen indices from studied samples.*

2. Sample Preparation:

2.1. Whole-Rock Preparation Procedure:

The studied samples were ground to approximately 2 mm size and embedded in resin. A single block was prepared for each sample.

2.2. Plug of Kerogen Concentrate Preparation Procedure:

The studied samples were ground to approximately 2 mm size. HCl (37%) was added to the sample during 18 hrs. After this procedure the sample was washed with distilled water until the washing water was neutral. In the next step HF (40%) was added during 24hrs, repeating the washing procedures and 37% HCl was added to the sample during 3 hrs to remove the fluorides. The sample washed with water again until neutralization. After this procedure the sample was floated using $ZnCl_2$ (= 1.9 to 2 g/cm^3) and centrifuged to separate sulphides. The washing procedures were repeated adding some HCl (10%) drops + distilled water to eliminate the heavy liquid. The isolated kerogen was sieved (20 μm) and embedded in resin (SERIFIX-STRUERS).

2.3. Sample Polishing:

The particulate blocks had their surfaces grounded down using progressively finer grades of wet silicon carbide papers; the grinds used were 800, 1200 and 4000 grit wet silicon carbide paper. A single set of samples was sent to each laboratory.

3. Statistical Evaluation Criteria and Parameters

Precision and bias for the analysts: an evaluation of the suitability of the data for an accreditation program (based on Borrego *et al.* 2006 and http://www.iccop.org) was used to interpret data.

This report is based on the rules for ICCP Accreditation Program for Vitrinite Reflectance Measurements on Dispersed Organic Matter described in Borrego *et al.* (2006). According to these authors, one of the objectives of a round robin exercise is to highlight the difficulties that must be taken into account to initiate an accreditation program for vitrinite reflectance assessment on dispersed organic matter. Before initiating this task

there was a need to know how the scatter of results around the calculated group means was.

The system applied is the same one used in the accreditation program for vitrinite reflectance in coal. The criteria used for coal might be too strict for dispersed organic matter but there is no doubt that the precision achieved for coal vitrinite reflectance should be the goal. The parameters considered in the accreditation program are:

UMSD: refers to participant's **U**nsigned **M**ultiple of the **S**tandard **D**eviation, calculated against the group mean and standard deviation data, for each sample analyzed as per the formula below:

$$UMSD = \left| \left(\frac{X_i - \overline{X}}{\sigma} \right) \right|$$

X_i = the participant vitrinite reflectance
X = the group mean vitrinite reflectance
σ = the standard deviation of the group

SMSD: refers to participant's **S**igned **M**ultiple of the **S**tandard **D**eviation, calculated against the group mean and standard deviation data, for each sample analyzed.

AUMSD and **ASMSD** are the average UMSD and SMSD values respectively for each participant. The AUMSD value is a measure of the participant's **accuracy** and the ASMSD is an indicator of the participant's **measurement bias** in the techniques being assessed.

Once all these parameters are calculated depending on the figures obtained by each participant the information received is the following:

(A) AUMSD: dispersion around group mean values, that is, a measure of accuracy.

<1.5	≥ 1.5
Pass	Fail
Your analytical technique is acceptable	You have serious problems with your analytical technique

(B) ASMSD: bias of reported results (±), that is, indicates consistency of an analyst. A negative bias (for example, -1.3061) indicates that your results, on average, are always lower than the group mean values and a positive bias (for example, +1.3061) indicates that your results, on average, are higher than the group mean values. Where the AUMSD and ASMSD values are **exactly the same** indicates that your results are always below (negative value) or above (positive value) the established group values.

<± 0.5	± 0.5-< ±1.0	± 1.0-<± 1.5	≥± 1.5
Minor bias	Medium bias	Significant bias	Extreme bias
Your results are always consistent	Some improvement is required	Examine the method being used	You have serious problems with your analytical technique

The SMSD was calculated for each vitrinite population and also the averaged AUMSD and ASMSD for each participant.

It is worth mentioning that these statistical systems are being used only as a learning tool, giving information on how the participants should proceed in the vitrinite reflectance analysis on dispersed organic matter.

4. Results and Discussion:

The participants are being identified by alphabetic letters (from A to N) in this report. Fourteen participants provided results based on standard vitrinite reflectance, and eight participants provided results based on spectral fluorescence analysis of liptinite.

Table 2 shows the distribution of vitrinite reflectance for the different samples as reported by the participants. The samples from Rodiles Fm. (OMC3A and OMC3B) and Vale das Fontes Fm. (OMC4A and OMC4B) presented an enough amount of measureable vitrinite particles. Furthermore, it was observed a large variation in the number of readings by each participant in both samples. The selected samples allowed the accurate study of the effect of the isolation procedure on the organic matter optical parameters in Type II-kerogen.

The average of vitrinite reflectance for sample OMC3 of whole-rock was 1.04% and for kerogen concentrate was 0.97%. For sample OMC4, the result was 0.45% for whole-rock and for kerogen concentrate was 0.41% (Plate 1). In general, the Standard Deviation (SD) values in both samples were high.

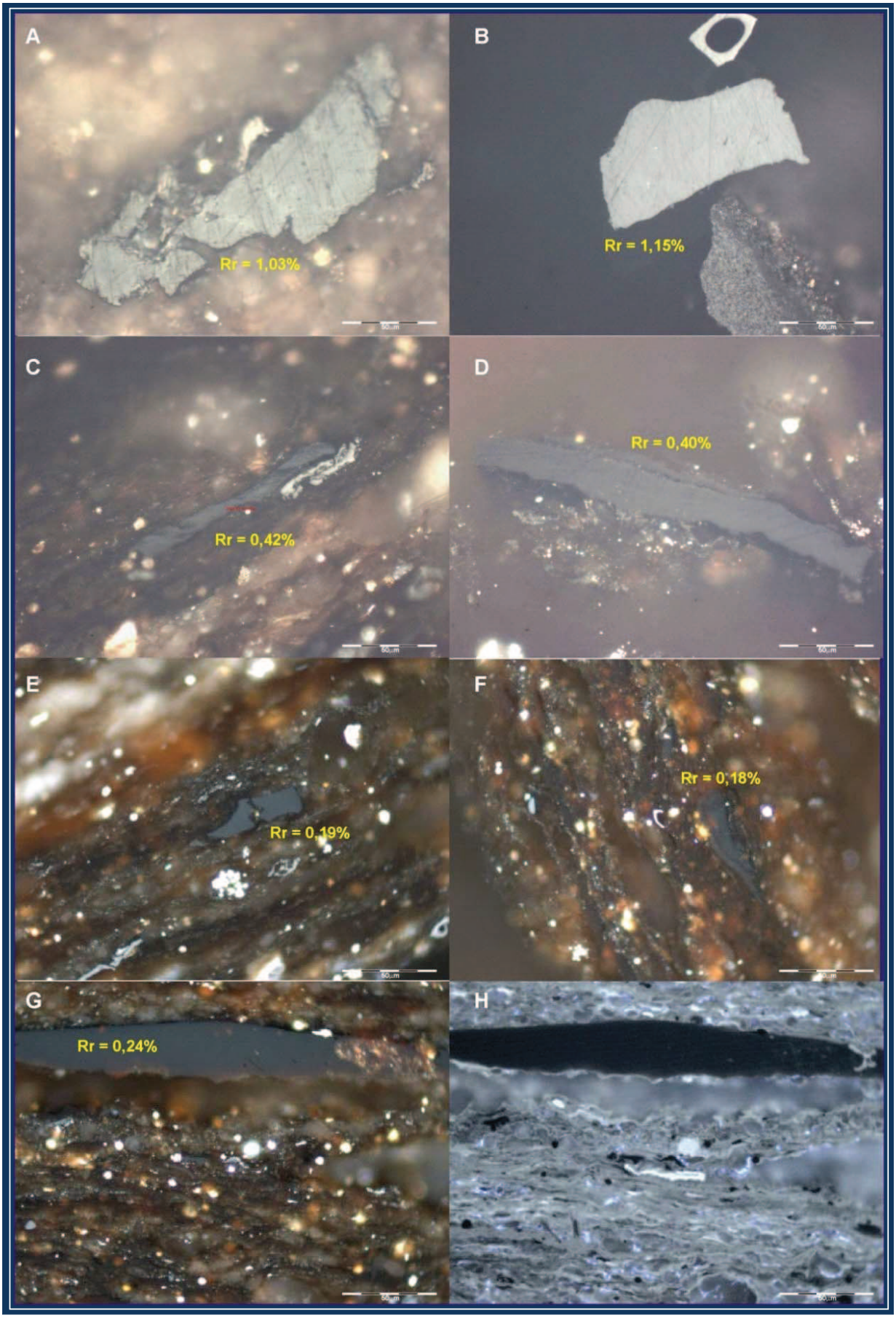


Plate 1: *Examples of vitrinites. A: Sample OMC3A; B: Sample OMC3B; C: Sample OMC4A; D: Sample OMC4B; E-H: Second vitrinite population identified by some participants (G-H: Phyllovitrinite?). All photomicrographs were taken under white incident light, oil immersion, exception photomicrograph 1H under fluorescence mode.*

Table 2: *Distribution of vitrinite reflectance as reported by the participants.*

Participant	Sample 3A			Sample 3B			Sample 4A			Sample 4B		
	Whole-Rock			Kerogen Concentrate			Whole-Rock			Kerogen Concentrate		
	Rr (%)	SD	N	Rr (%)	SD	N	Rr (%)	SD	N	Rr (%)	SD	N
A	1.02	0.10	31	0.97	0.1	48	0.65	0.09	72	0.26	0.06	25
B	0.87	0.11	14	0.79	0.14	14	0.62	0.12	35	0.57	0.11	18
C	1.12	0.15	28	1.09	0.12	26	0.56	0.07	24	0.53	0.07	17
D	1.15	0.03	12	1.14	0.02	13	0.45	0.02	21	0.45	0.03	20
E	0.89	0	1	0.34	0.06	7	0.31	0.05	6	0.28	0.00	1
F	1.13	0.12	9	1.07	0.12	26	0.24	0.07	52	0.24	0.07	18
G	1.16	0.11	25	1.15	0.19	30	0.40	0.11	16	0.39	0.08	14
H	1.10	0.05	18	1.11	0.06	18	0.45	0.05	17	0.45	0.04	21
I	1.13	0.07	31	1.08	0.11	52	0.37	0.09	29	0.36	0.11	12
J	1.16	0.08	20	1.15	0.06	13	0.46	0.03	21	0.47	0.05	16
K	1.09	0.12	44	1.07	0.16	47	0.49	0.08	64	0.46	0.09	20
L	0.96	0.17	16	0.97	0.21	19	0.42	0.13	31	0.38	0.14	29
M	0.93	0.07	50	0.97	0.11	50	0.49	0.04	50	0.52	0.07	30
N	0.89	0.04	3	0.73	0	1	0.37	0.09	32	0.31	0.12	28
Average	1.04			0.97			0.45			0.41		
SD	0.11			0.22			0.11			0.1		

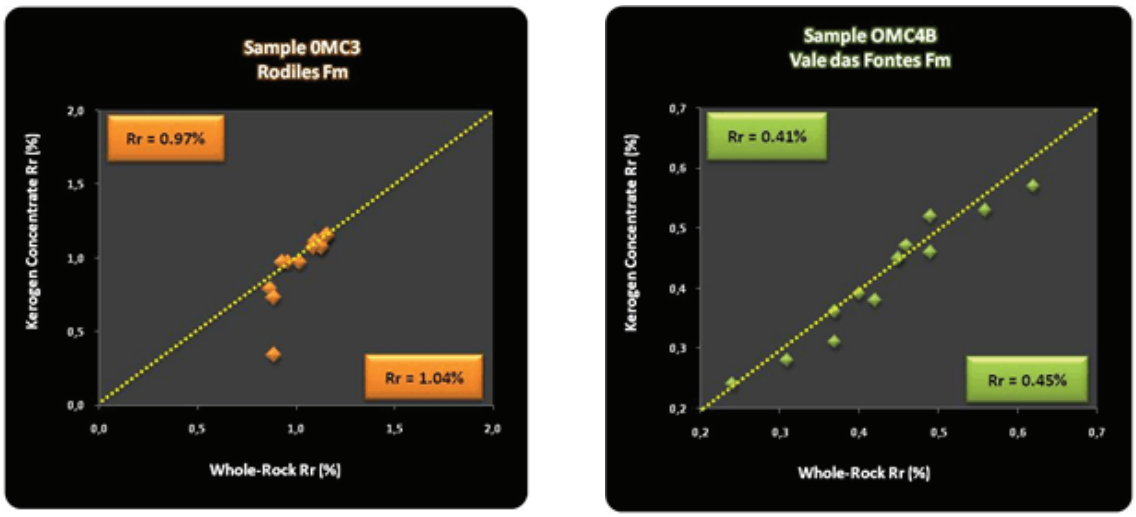


Figure 2: *Comparison of mean reflectance values between WR and KC*

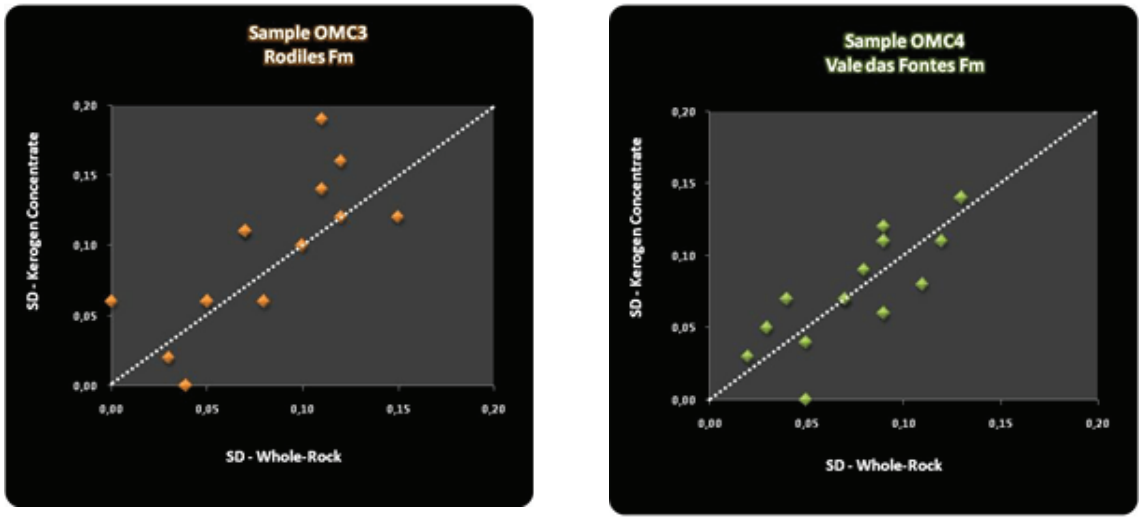


Figure 3: *Comparison of standard deviation (SD) between WR and KC - Scatter of data in the analysed samples*

The graph of kerogen vs whole rock (Figure 2) allowed comparing the results of the whole-rock and the kerogen concentrate samples. If the x and y axes have the same dimensions and the results were equivalent, all the points should be on the median or closer. This happens in the sample OMC3 for the reflectance considering the most of participants, but Participant E presented a very low value for OMC3B (kerogen concentrate). However, in sample OMC4 the reflectance tended to be slightly higher in the whole-rock, where it can be observed clearly that most of the points are below the median, showing that the results for sample OMC4A (whole-rock) were slightly higher than in the sample OMC4B (kerogen concentrate).

Figure 3 shows the **Standard Deviations** graph, which helped to see if there was more dispersion of data in the kerogen analyses than in those of whole-rock. If the SD values were always higher in one than in the other, this would indicate a bigger difficulty to identify the population.

In general, high values of SD were observed in the two analyzed samples, which indicate a larger scatter of the readings. In the case of the sample OMC3, the SD values tend to be higher in the kerogen concentrate, which could indicate a bigger difficulty to identify the vitrinite particles in kerogen concentrate than whole-rock. In the case of the sample OMC4, the results showed no definite patterns. The readings display a scatter of measurements in the whole-rock for some participants and in the kerogen concentrate for others.

Figures 4 and 5 are representing the Cumulative Frequency graph, which can be grouped into various families according to the shape of the curves: curves showing a single population of vitrinite; curves showing a bimodal distribution with different proportion of the low reflecting and high reflecting population and curves showing large scatter without modal values.

Figure 4 shows the reflectance class distributions of the participants for sample OMC3A and OMC3B (Rodiles Fm.). The shape of the curves indicates that most of the participants identified a single vitrinite population with a rather narrow distribution of reflectance classes. However, the Participants B and L included readings whose values are lower than the group mean in the samples OMC3A and OMC3B. On the other hand, the Participant G included some readings whose values are higher than the average in the sample OMC3B. The results of these participants show a large scatter of readings (high SD values) indicating some problems with the

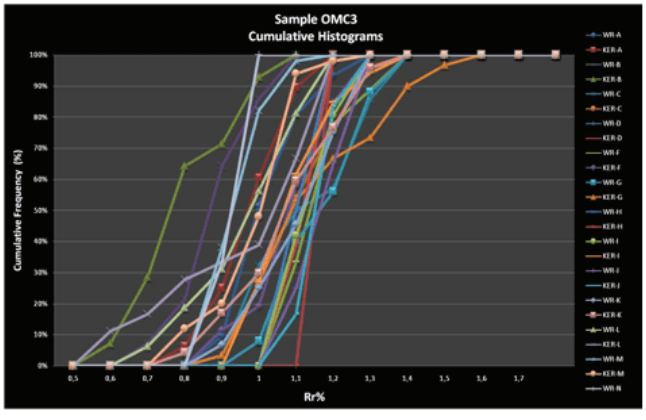


Figure 4: *Graph of the Cumulative Frequency Plot (sample OMC3A and OMC3B)*

identification of vitrinites. The readings obtained for some participants (Participant E in the WR sample and Participant N in the KC sample) were not enough to show the reflectance class distributions.

Besides this, Participant E indicated different readings for the same sample (OMC3), 0.89%Rr for whole-rock and 0.34%Rr for kerogen concentrate. As the average of reflectance considering all the data was 0.97% for sample OMC3B, this result (0.34% Ro) could indicate the inclusion of readings taken on another component (some participants reported the occurrence of zooclasts with reflectance measurements from 0.20% to 0.35% (Plate 2A). It is worth to mention that if this anomalous value of Rr% (0.34%) be excluded, the group mean would be 1.02% (SD = 0.13, Table 3). Another characteristic found in this sample (OMC3) is that some participants reported the presence of bitumen (Plate 2B). The inclusion of these particles in the readings for some participants could have influenced in the group mean and consequently in the SD value.

Table 3: *New distribution of vitrinite reflectance excluding the anomalous value.*

Partic-ipant	WR Rr (%) (OMC3A)		KC Rr (%) (OMC3B)		KC Rr (%) (OMC3B)	
	Rr (%)	SD	Rr (%)	SD	Rr (%)	SD
A	1.02	0.10	0.97	0.1	0.97	0.1
B	0.87	0.11	0.79	0.14	0.79	0.14
C	1.12	0.15	1.09	0.12	1.09	0.12
D	1.15	0.03	1.14	0.02	1.14	0.02
E	0.89	0	0.34	0.06		
F	1.13	0.12	1.07	0.12	1.07	0.12
G	1.16	0.11	1.15	0.19	1.15	0.19
H	1.10	0.05	1.11	0.06	1.11	0.06
I	1.13	0.07	1.08	0.11	1.08	0.11
J	1.16	0.08	1.15	0.06	1.15	0.06
K	1.09	0.12	1.07	0.16	1.07	0.16
L	0.96	0.17	0.97	0.21	0.97	0.21
M	0.93	0.07	0.97	0.11	0.97	0.11
N	0.89	0.04	0.73	0	0.73	0
Average	1.04		0.97		1.02	
SD	0.11		0.22		0.13	

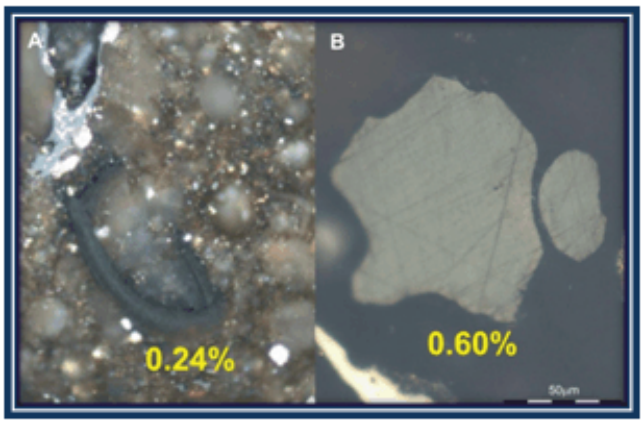


Plate 2: *A: Sample OMC3A, Zooclast; B: Sample OMC3B, Bitumen. Photomicrographs were taken under white incident light, oil immersion.*

Figure 5 shows the reflectance class distributions of the participants for sample OMC4A and OMC4B (Vale das Fontes Fm). The shape of the curves indicates that some of participants identified two vitrinite populations, one of them showing values lower than the average. However, Participant A, who spread the readings from Rr = 0.46% to Rr = 0.84% to sample OMC4A (whole-rock) and from Rr = 0.12% to Rr = 0.37% to sample OMC4B (kerogen concentrate), characterized two different averages for the same sample (OMC4). Besides Participant A, Participant B also included readings whose values are higher than the group mean in the sample OMC4 indicating the probable inclusion of readings taken on inertinites or re-worked vitrinites. In general, the participants were consistent in the vitrinite population selected. This situation has also been reported for organic-rich samples with abundance of vitrinite particles to be measured (Borrego et al., 2006).

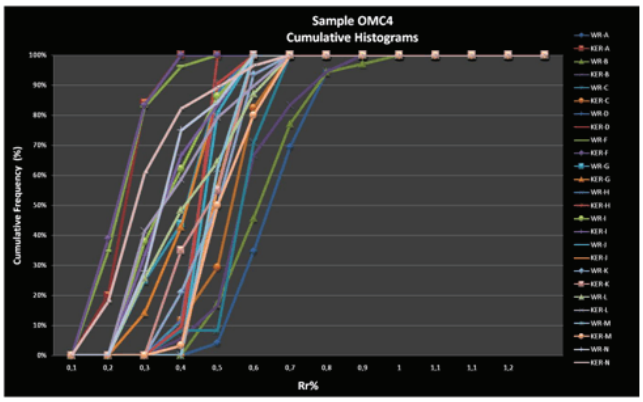
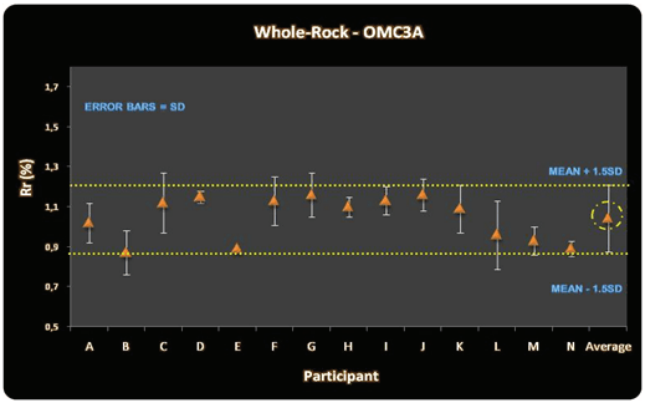


Figure 5: *Graph of the Cumulative Frequency Plot (sample OMC4A and OMC4B).*

The scatter of results is better observed in Figures 6 and 7 where it were plotted the mean

reflectance reported by of each participant with the error bars corresponding to the standard deviation (SD). The scatter of the results was more reasonable and most of the values are within, according to ICCP Accreditation Criteria, 1.15 ± 1.5xSD[1] for the low and high reflecting populations.

The average of reflectance considering all the data was 1.04% for sample OMC3A (Whole-Rock) and it was 0.97% for sample OMC3B (Kerogen Concentrate). The scatter of results in the sample OMC3B was larger than (high SD values) in the OMC3A sample (Figure 6A), that could indicate some problems with vitrinite identification and/or low quality of particles. Some participants read higher values than the group mean in OMC3A. In the case of the sample OMC3B there was a single result (Participant E) that was outlying (a statistical observation that was markedly different in value from the others of the sample) (Figure 6B).



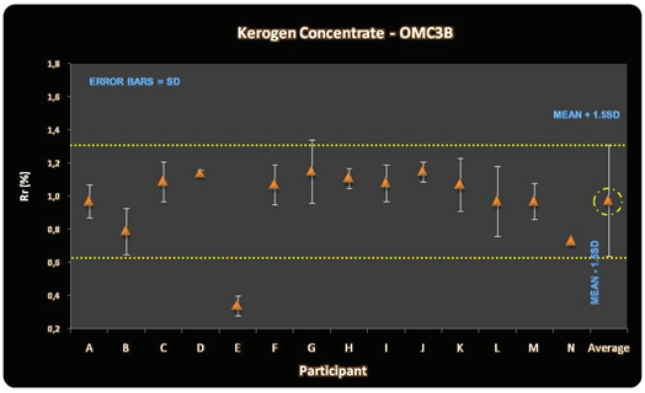
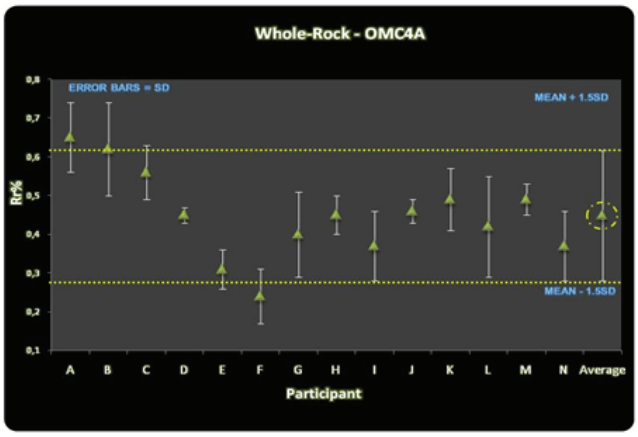


Figure 6: *Average Rr (%) values for the low and high reflecting populations in samples OMC3A (WR) and OMC3B (KC).*

The group mean considering all the data was 0.45% for the sample OMC4A (Whole-Rock) and 0.41% for the sample OMC4B (Kerogen Concentrate) (Figure 7).

Then, it can be observed a difference in the average of reflectance between sample OMC4A (Whole-Rock) and OMC4B (Kerogen Concentrate). Two participants (A and B) included readings which values are higher than the group mean in the sample OMC4A (WR, Figure 7A), and Participant F included lower value than the group mean in samples OMC4A and OMC4B. However, for sample OMC4B, just Participant B read higher values than the group mean (Figure 7B). Participant A, which included higher values than group mean in sample OMC4A, showed lower values than the group mean for sample OMC4B, indicating different average for the same sample (OMC4).



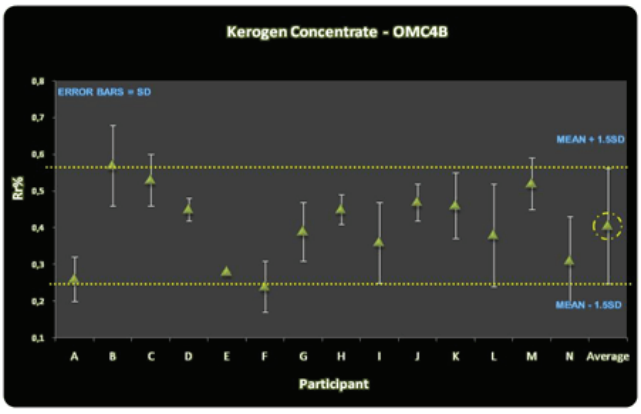


Figure 7: *Average Rr (%) values for the low and high reflecting populations in samples OMC2A (WR) and OMC2B (KC).*

In Figure 8 it can be observed that in sample OMC3 the UMSD values were higher for the whole-rock due to the large group SD decreases

[1] 1.5 x SD = represents 80% of a Gaussian distribution that gives a reasonable percentage of error

this parameter. It can be observed in this sample (OMC3) that two analysts (Participants B and E) presented good data in only one sample (one of them presented a good result to the WR but high value to the KC and the other one presented a good result to the KC but high value to the WR), but in general the results were dispersed reasonably around the median.

Sample OMC4 presented few values over the accepted 1.5SD threshold. Moreover, two analysts (Participant B and F) presented results out of the group mean in both samples (OMC4A and OMC4B), and one analyst (Partipant A) presented a good data in only one sample (OMC4B), but in general the results were dispersed more evenly around the median.

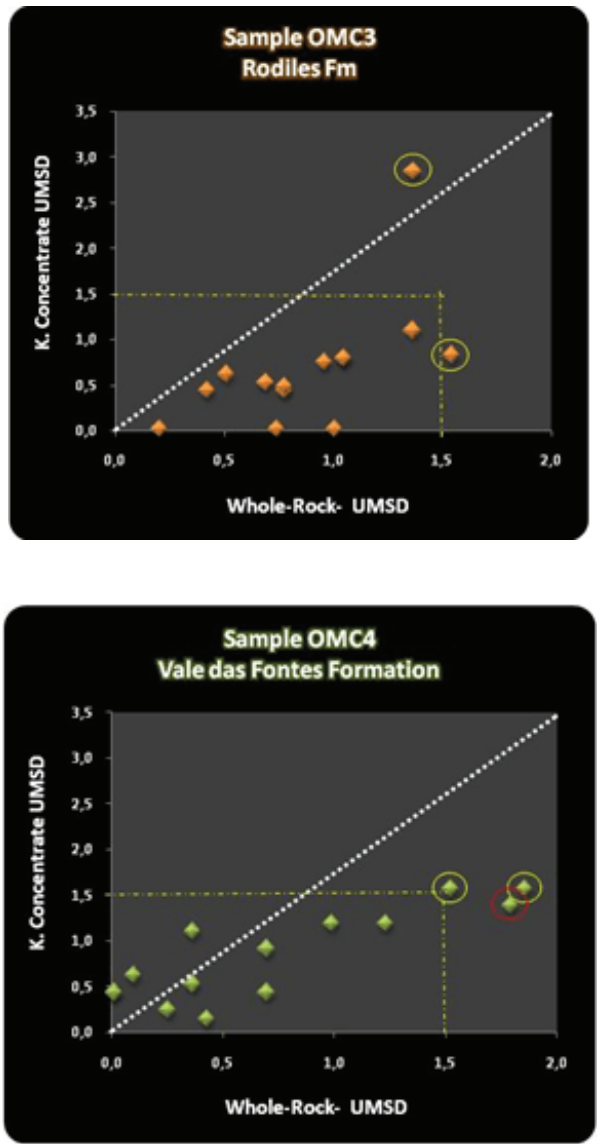


Figure 8: *UMSD (Unsigned Multiple of the Standard Deviation)*[2]

[2]calculated against the group mean and standard deviation data

Using the criteria and parameters applied for Coal Reflectance Analysis in the existing ICCP accreditation program, www.iccop.org, (Table 4), excellent results were obtained in this exercise (Table 5). Only one participant had an AUMSD value over 1.5, probably related to problems with the vitrinite identification. The majority of participants presented consistent results and their analytical techniques were acceptable.

Table 4: *Coal Reflectance Analysis Criteria (ICCP)*

Parameters	Precision and bias for the analysts	
ASMSD	< ± 0.5	Low - Your results are always consistent
	± 0.5 < ± 1.0	Medium - Some improvement is required
	± 1.0 < ± 1.5	High - Examine the method being used
	> ± 1.5	Very High - You have serious problems with your analytical technique
AUMSD	< 1.5	Your analytical technique is acceptable
	> 1.5	You have serious problems with your analytical technique

Table 5: *Accuracy of results calculated against the group mean and standard deviation data, for each sample analyzed: SMSD (Signed Multiple of the Standard Deviation), AUMSD and ASMSD*

Partic-ipant	SMSD	AUMSD	ASMSD	Remarks
A	0,19	0,85	0,05	Low
B	0,73	1,37	0,18	Low
C	3,40	0,85	0,85	Medium
D	2,15	0,54	0,54	Medium
E	-6,63	1,66	-1,66	Very High
F	-2,22	1,16	-0,55	Medium
G	1,26	0,60	0,32	Low
H	1,56	0,39	0,39	Low
I	0,13	0,60	0,03	Low
J	2,56	0,64	0,64	Medium
K	1,75	0,44	0,44	Low
L	-1,25	0,31	-0,31	Low
M	0,44	0,62	0,11	Low
N	-4,06	1,02	-1,02	High

5. Spectral fluorescence analysis:

Eight 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). Three participants gave spectral curves for liptinites of the Rodiles Fm. (OMC3). One analyst provided results for samples OMC3A and OMC3B and the other two analysts provided results only for the sample OMC3A (whole-rock). The others participants reported a lack of fluorescence in sample OMC3. Eight participants provided results for liptinites of the Vale das Fontes Formation (OMC4).

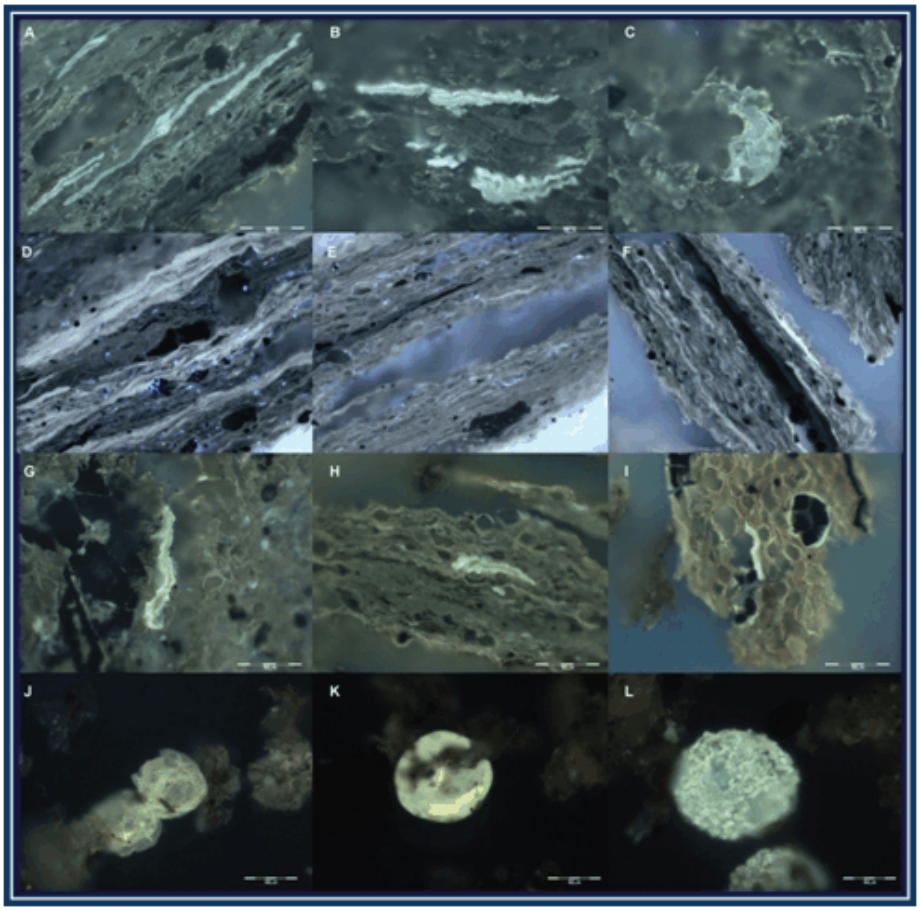
The λ_{max} results for sample OMC3 provided by three participants confirm the medium rank of Rodiles Fm. However, the Participant A provided a low λ_{max} value for the sample OMC3A indicating a low maturity. This feature could be related to the selection of objects for measurements. Table 6 summarizes the fluorescence parameters obtained by the three participants.

Table 6: *λ_{max} values obtained for Rodiles Fm. sample*

Partic-ipant	Para-meters	Organic Component	Whole-Rock OMC3A	Kerogen Concentrate OMC3B
A	λ_{max}	Liptinite	414	620
G	λ_{max}	Liptodetrinite	610	
I	λ_{max}	Liptodetrinite	610	

For the Vale das Fontes Fm. sample two participants provided curves for liptinite, five participants for alginite and one participant provided curves for bituminite, sporinite and alginite (Table 7, Plate 3, Figure 9).

Plate 3 shows examples of liptinites. The telalginites were observed and identified on strew slides as Prasinophyte algae (genus: *Leiosphaeridia* - Plate 3J and *Tasmanites* - Plate 3K) besides the presence of sporomorphs (Plate 3L).



Plates 3A to 3I: *Examples of Liptinites. A-E: Sample OMC4A; F I: Sample OMC4B; J-K: Sample OMC4 on strew slides (J* - Leiosphaeridia*; K*- Tasmanites*; L- Sporomorph). All photomicrographs were taken under fluorescence mode*

Table 7: *λ_{max} values obtained for Vale das Fontes Fm.*

Partic-ipant	Parameters	Organic Component	Whole-Rock - OMC4A	Kerogen Concentrate - OMC4B
A	λ_{max}	Liptinite	567	569
C	λ_{max}	Telalginite	538	557
D	λ_{max}	Telalginite	530	565
F	λ_{max}	Telalginite	586	588
G	λ_{max}	Alginite	520	550
I	λ_{max}	Alginite	520	550
J	λ_{max}	Telalginite	530	565
M	λ_{max}	Liptinite	530	550

The λ_{max} results for sample OMC4 provided by participants confirm the low rank of Vale das Fontes Fm. Nevertheless, some participants provided results from liptinite and alginite indicating a wide range of λ_{max} values for sample OMC4A. In general, it was observed a shift of the λ_{max} to higher values for sample OMC4B suggesting that the preparation procedures affects fluorescence properties (Table 7, Figure 9).

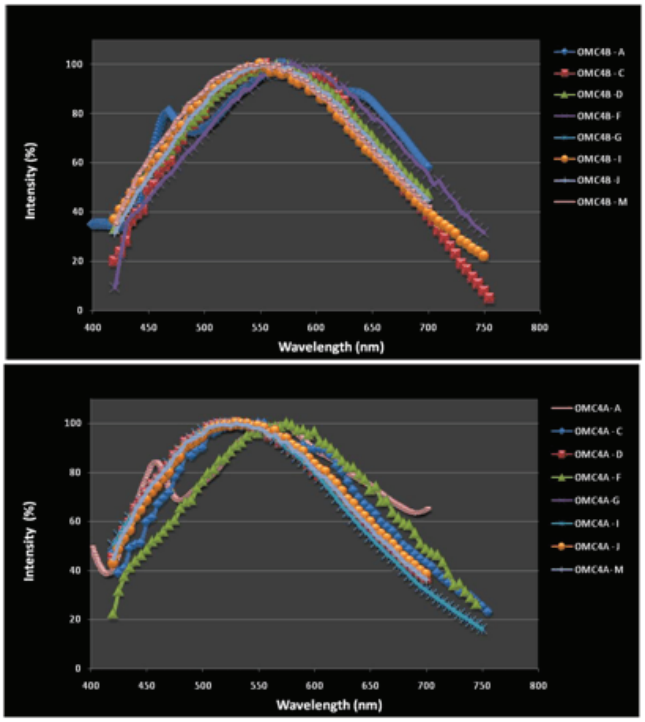


Figure 9: *Spectral curves for alginite of samples OMC4A and OMC4B*

The graph represented in Figure 10 allowed comparing the results of the λ_{max} values for sample OMC4 in whole-rock and kerogen concentrate. It can be observed in this graph that the λ_{max} values were higher in the kerogen concentrate, where it can be noted clearly that all points are above the median.

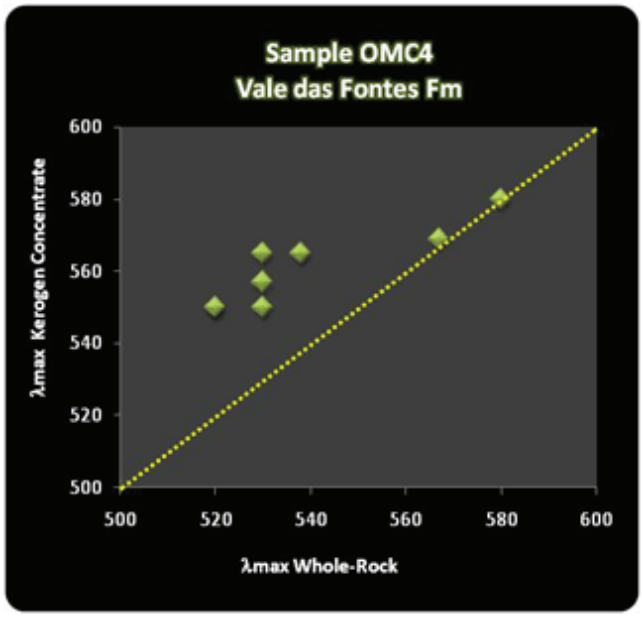


Figure 10: *Comparison of λ_{max} values between OMC4A and OMC4B*

Table 8 and Figures 11 and 12 show the λ_{max} values obtained from samples OMC4A and OMC4B and their equivalent vitrinite reflectance values. Table 9 shows the correlation between vitrinite measured (Rr%) and vitrinite equivalent (Rr%eq) for samples OMC4A (whole-rock) and OMC4B (kerogen concentrate). Figure 12 shows the comparison vitrinite equivalent reflectance values (Rr%eq) between for OMC4 in whole-rock and kerogen concentrate. Through these results it can be observed that the equivalent vitrinite reflectance for sample OMC4A presents an excellent correlation with the measured vitrinite reflectance and the values were higher in kerogen concentrate (OMC4B) than whole-rock (OMC4A). For sample OMC4B the misfit between the equivalent vitrinite reflectance and measured vitrinite reflectance should be related to the acid treatment (kerogen isolation procedure) that seems to affect the fluorescence properties.

Table 8: *Correlation between SF and Rr% parameters for sample OMC4*

λ_{max} values OMC4A	Equi-valent Rr OMC4A	Group Mean OMC4A	λ_{max} values OMC4B	Equi-valent Rr OMC4B	Group Mean OMC4A
520	0,38		550	0,53	
520	0,38		550	0,53	
530	0,43		550	0,53	
530	0,43		557	0,54	
530	0,43	0,45	565	0,57	0,41
538	0,49	SD= 0.11	565	0,57	SD= 0.11
567	0,58		569	0,59	
580	0,65		580	0,65	
Mean	0,47		Mean	0,57	
SD	0,10		SD	0,06	

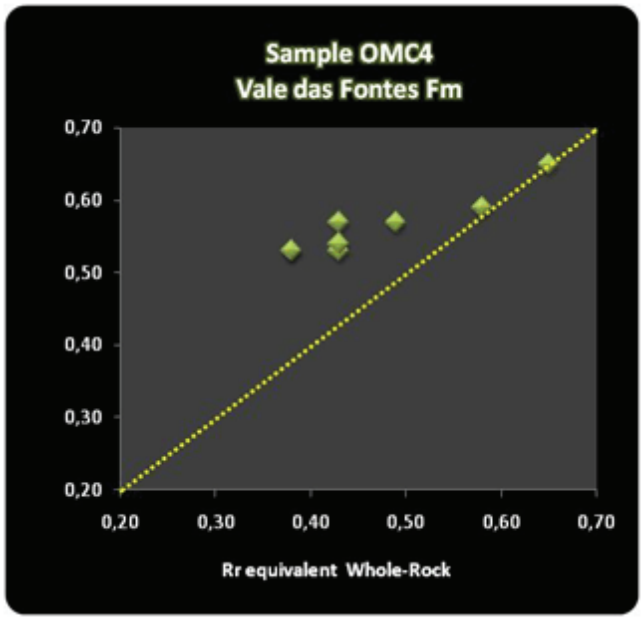


Figure 11: *Comparison of Rr_{eq} values between OMC4A and OMC4B*

Table 9: *Correlation between vitrinite measured (Rr) and equivalent (Rr_{eq}) for OMC4*

Results	OMC4A - WR	OMC4B-KC
Rr (%)	0.45	0.41
Rr_{eq} (%)	0.49	0.58

6. Conclusions:

Based on the proposed objectives and results obtained, it is concluded that the Type II kerogen yield a low amount of vitrinite than Type III kerogen (OMCWG 2008) and its identification was more difficult for medium rank sample than for low rank sample.

Samples OMC3A and OMC3B (Rodiles Fm.) and OMC4A and OMC4B (Vale das Fontes Fm.) showed an enough amount of measureable vitrinite particles. Furthermore, it was observed a large variation in the number of readings by each participant in both samples.

The statistical evaluation system applied in this exercise is the same one used in the accreditation program for vitrinite reflectance in coal. However, these statistical systems are being used only as a learning tool, giving information on how the participants should proceed in the vitrinite reflectance analysis on dispersed organic matter.

The average of reflectance considering all the data was 1.04% for sample OMC3A (whole-rock) and 0.97% for sample OMC3B (kerogen concentrate) and the group mean considering all the data was 0.45% for sample OMC4A (Whole-Rock) and 0.41% for sample OMC4B (Kerogen Concentrate). These results suggest no influence of the kerogen isolation procedures (acid treatment) on vitrinite reflectance.

In general, the Standard Deviation (SD) values in both samples were high and they could indicate some problems with vitrinite identification and/or low quality of particles. In the case of sample OMC3, the participants identified a single vitrinite population. Regarding sample OMC4 the results indicate some participants identified two vitrinite populations, one of them showing values lower than the group mean. Besides this, some participants included readings of vitrinite reflectance which values are lower or higher than the average, indicating the probable inclusion of readings taken on inertinites or re-worked vitrinites and liptinites in the data set.

The scatter of the readings was large in the two analyzed samples. In the case of sample OMC3, the SD values tend to be higher in the kerogen concentrate, which could indicate a higher difficulty to identify the vitrinite particles in kerogen concentrate than whole-rock. On the other hand, in sample OMC4 the results showed no definite patterns. The readings display a scatter of

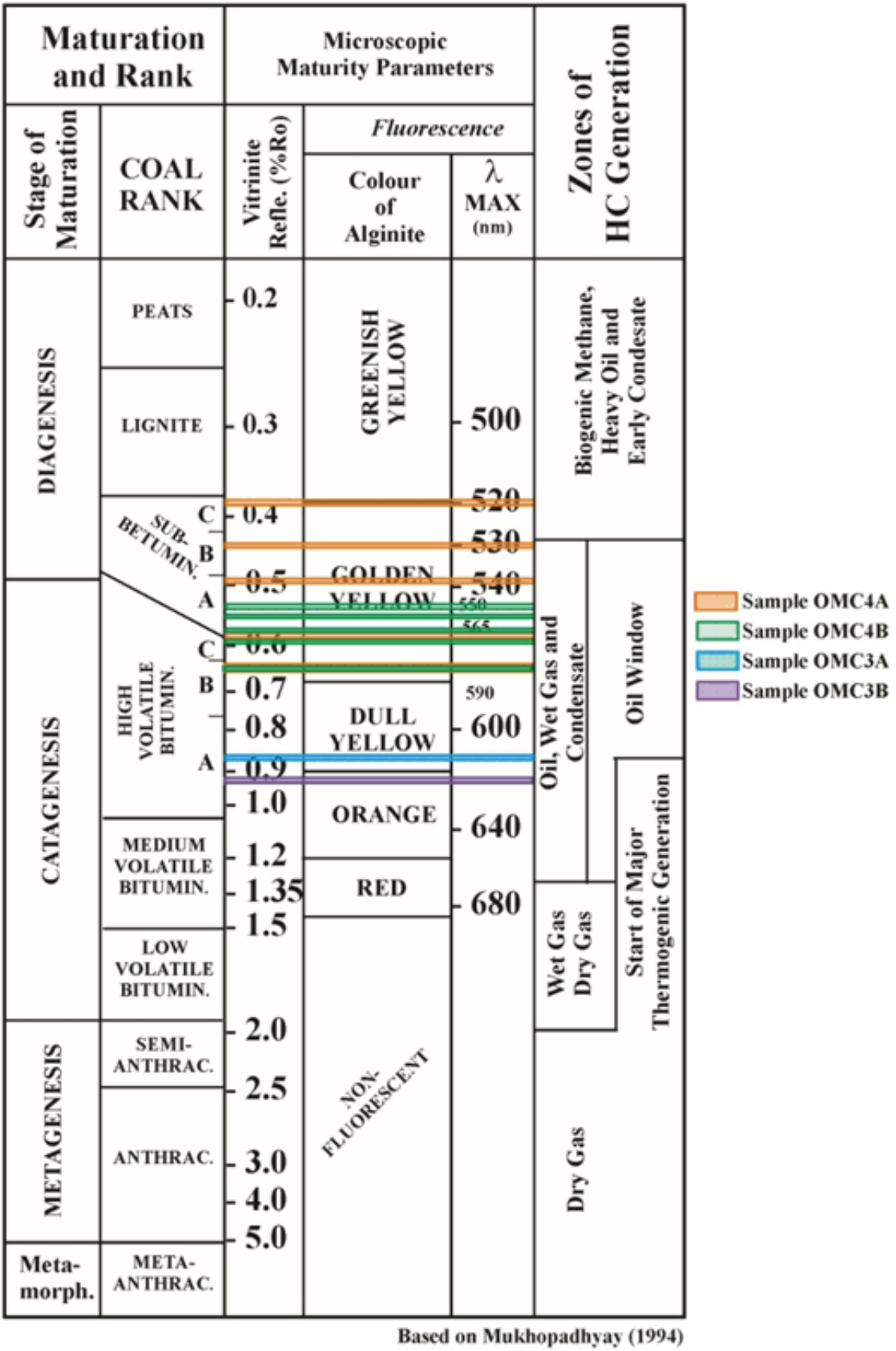


Figure 12: *Correlation of microscopic parameters from Rodiles Fm. and Vale das Fontes carbonaceous shale (based on Mukhopadhyay, 1994)*

measurements in the whole-rock for some participants and in the kerogen concentrate for others.

The spectral fluorescence results showed that λ_{max} values for sample OMC3 and OMC4 confirm a medium rank for sample from Rodiles Fm. and a low rank for sample Vale das Fontes Fm., respectively.

It was observed that the equivalent vitrinite reflectance (Rr_{eq}) for sample OMC4A (WR) presents an excellent correlation with the measured vitrinite reflectance (Rr). However, it was observed a misfit between the equivalent vitrinite reflectance (Rr_{eq}) and measured vitrinite reflectance (Rr) for sample OMC4B (KC).

Considering the spectral fluorescence results, it was observed that the lmax presents a shift to higher wavelengths in sample OMC4B (KC) in comparison to sample OMC4A (WR), thus revealing an influence of preparation methods (acid treatment) on fluorescence properties.

In summary, following the criteria and parameters described in the statistical evaluation system (www.iccop.org), in general excellent results were obtained and the selected samples allowed an accurate study on the effect of the isolation procedure on the organic matter optical parameters in Type II-kerogen.

7. References:

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

Borrego, A.G.; Araujo C.V.; Balke A.; Cardott B; Cook, A.C.; 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.; Rhanasinghe; P.; Suárez-Ruiz, I.; 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. *International Journal of Coal Geology*, **68**, p.151 - 170.

http://www.iccop.org

Mendonça Filho, J. G.; Araujo, C. V.; Borrego, A. G.; Cook, A.; Flores, D.; Hackley, P.; Hower, J.; Kern, M. L.; Kommeren, K.; Mendonça, J. O.; Menezes, T. R.; Newman, J.; Ranasinghe, P.; Souza, I. V. A. F.; Suarez-Ruiz, I.; Ujiié, Y. (2008) Report on Organic Matter Concentration Working Group (OMCWG 2008). *ICCP News*, **45**, p. 43-51.

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

8. Acknowledgments:

★ The sample from Vale das Fontes Formation was provided by Dr. Luis Victor Duarte (University of Coimbra).

★ The sample from Rodiles Formation was provided by Dr. José Carlos Martínez Garcia-Ramos (Scientific Director of the Jurassic Museum of Asturias - MUJA).

★ The effort of Alexandre J. Sant'Anna (CENPES/PETROBRAS) and Antonio D. de Oliveira (Palynofacies and Organic Facies Laboratory / IGEO / UFRJ) for sample preparation is gratefully acknowledged.

★ To Petrobras Research Development Center (CENPES) for providing the organic geochemistry analysis.

★ Special thanks to Angeles G. Borrego for her help with the statistical treatment and encouragement of the creation of the OMCWG.

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