



Petrographic thermal indices of a Devonian shale maturation series, Appalachian Basin, USA. ICCP Thermal Indices Working Group interlaboratory exercise

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Abstract

This paper presents results of an interlaboratory exercise on organic matter optical maturity parameters using a natural maturation series comprised of three Devonian shale samples from the Appalachian Basin, USA. This work was conducted by the Thermal Indices Working Group of the International Committee for Coal and Organic Petrology (ICCP) Commission II (Geological Applications of Organic Petrology). This study aims to compare: 1. maturation predicted by different types of petrographic thermal index measurements (vitrinite reflectance and spectral fluorescence of telalginite); 2. reproducibility of the results for these thermal indices obtained by different laboratories; and 3. improvements in the spectral fluorescence measurement obtained using modern detection systems in comparison with the results from historical round robin exercises (Araujo et al., 1998).

Mean random vitrinite reflectance measurements presented the highest level of reproducibility (mean standard deviation 0.05%) for low maturity and reproducibility diminished with increasing maturation (mean standard deviation 0.12%).

Corrected fluorescence spectra, provided by 14 participants, showed a fair to good correlation. Standard deviation of the mean values for spectral parameters was lowest for low maturity sample but was also fairly low for higher maturity samples.

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1 A significant amelioration in the reproducibility of corrected spectral fluorescence curves was obtained
2 in the current exercise compared to a previous investigation of Toarcian organic matter spectra in a
3 maturation series from the Paris Basin. This improvement is demonstrated by lower values of
4 standard deviation and is interpreted to reflect better performance of newer photo-optical measuring
5 systems.
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7 Fluorescence parameters measured here are in good agreement with vitrinite reflectance for the least
8 mature sample but indicate higher maturity than shown by vitrinite reflectance for the two more mature
9 samples. This red shift in $\lambda_{\max}$ beyond 0.65% vitrinite reflectance also was observed in studies of
10 Devonian shale in other basins, suggesting that the relational scheme for these two petrographic
11 thermal maturity parameters needs to be re-evaluated.
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16 A good linear correlation between $\lambda_{\max}$ and $T_{\max}$ for this maturation series was observed and $\lambda_{\max}$
17 600 nm corresponds to $T_{\max}$ of 440°C. Nevertheless if a larger set of Devonian samples is included the
18 correlation is polynomial with a gap in $\lambda_{\max}$ range of 540-570nm. Up to 440°C $T_{\max}$, the $\lambda_{\max}$, mostly
19 reaches up to 500nm; beyond a $T_{\max}$ of 440°C, $\lambda_{\max}$ is in the range of 580-600nm. This relationship
20 places the “red shift” when the onset of the oil window is reached at $T_{\max}$ of 440 °C. Moreover, the
21 correlation between HI and $\lambda_{\max}$ ($r^2 = 0.70$) shows a striking inflection and decrease in HI above a $\lambda_{\max}$
22 of 600nm, coincident with the approximate onset of hydrocarbon generation window for these rocks.
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29 **Keywords:** Devonian source rocks, fluorescence parameters, maturation, vitrinite reflectance,
30 interlaboratory studies, spectral fluorescence
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33 **1. Introduction**

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35 Fluorescence microscopy has become an important tool in the evaluation of maturity and hydrocarbon
36 source potential of dispersed organic matter (DOM), since the principles of spectral fluorescence
37 methods were established in pioneering studies by Jacob (1965), van Gijzel (1967, 1975, 1981),
38 Ottenjann et al. (1975), Ting and Lo (1975), Alpern (1976), Teichmüller and Ottenjann (1977),
39 Ottenjann (1980), and Teichmüller (1982). Quantitative methods such as spectral fluorescence
40 microscopy and derivative parameters [Red/Green Quotient (Q) and $\lambda_{\max}$] are useful to determine
41 thermal maturity in DOM, particularly where vitrinite is rare, absent or ambiguous (Wolf and Corrêa da
42 Silva, 1974; Thompson-Rizer and Woods, 1987; Stasiuk, 1994; Pradier et al., 1988, 1991). The major
43 problem spectral fluorescence measurement has faced is the lack of standardization in analytical
44 procedures. Some efforts within International Committee for Coal and Organic Petrology (ICCP) have
45 used the measurement of plexiglass of different colors for which encouraging results were obtained
46 although short of a standardized approach to standardization. Calculation correction function to
47 remove differences in microscope optics was derived by measuring the fluorescence spectra of an
48 iodine-quartz lamp (Baranger et al., 1991). Other difficulties in obtaining reproducible results relate to
49 low signal to noise ratios (Thompson-Rizer et al., 1988). To address these issues, the Thermal Indices
50 Working Group (WG) within the ICCP, Commission II (Geological Applications of Organic Petrology)
51 included evaluation of spectral fluorescence as a maturation parameter in sample exchange studies.
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1 Previous exercises of the Thermal Indices WG in 1996 and 1997 were conducted with the objective to
2 improve interlaboratory reproducibility of spectral fluorescence parameters (Araujo et al., 1998). In this
3 approach, a calibrated common lamp source (Baranger et al., 1991) was used by participating
4 laboratories to obtain a relative correction function for measured fluorescence parameters. Araujo et
5 al. (1998) found that spectral fluorescence measurements of Paris Basin Toarcian shale samples
6 showed decreasing interlaboratory reproducibility for more mature samples due to lower signal to
7 noise ratios for the lower fluorescence intensities present at higher maturity samples.
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10 To further compare and improve relational schemes among organic thermal maturity parameters, the
11 Thermal Indices WG has also evaluated other maturity parameters such as vitrinite reflectance,
12 vitrinite-inertinite reflectance and fluorescence (VIRF), fluorescence alteration of multiple macerals
13 (FAMM), and parameters derived from organic geochemistry analyses (Araujo et al., 2003; Araujo,
14 2006). Araujo et al. (2003) studied the Alpha torbanite (R_o in the range of 0.29 to 0.31%) and
15 associated Alpha coal (R_o in the range of 0.36 to 0.45%) from New South Wales, Australia. Results
16 indicated that spectral fluorescence parameters did not indicate thermal maturity suppression,
17 whereas VIRF and FAMM methods indicated a reflectance suppression of about 0.15-0.20% for the
18 Alpha torbanite. Random vitrinite reflectance of the associated Alpha coal was about 0.1% higher than
19 for the Alpha torbanite, pointing towards suppression of vitrinite reflectance in the torbanite. However,
20 according to FAMM results, vitrinite reflectance of Alpha torbanite and associated Alpha coal were
21 both suppressed. Maturity parameters derived from organic geochemistry studies including
22 isomerization ratios of hopanes and steranes indicated that the Alpha torbanite sample was immature.
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31 In subsequent round robin exercises, Araujo (2006) investigated correlations among maturation
32 parameters for Asturias carbonaceous shale and Posidonia shale samples (see also Borrego et al.,
33 2006). In addition to fluorescence studies, analyses of VIRF and parameters derived from organic
34 geochemistry were obtained. Comparison of these maturity parameters revealed a narrower scattering
35 for the Asturias carbonaceous shale than for the Posidonia shale sample. Good agreement of
36 chemical maturity parameters, including T_{max} from Rock-Eval pyrolysis, indicated higher maturity for
37 the Posidonia sample than the 0.37% R_o value obtained by Borrego et al. (2006), suggesting that
38 reflectance suppression may be present in this sample. However, a good correlation was observed
39 between the group mean R_o of 0.37% (Borrego et al., 2006) and spectral fluorescence parameters
40 (Araujo, 2006), suggesting that spectral fluorescence parameters do not reveal potential vitrinite
41 suppression at this maturity level. This same relationship previously was observed by the Thermal
42 Indices WG for the Alpha torbanite sample (Araujo et al., 2003).
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50 A major problem has proven to be finding an appropriate maturity series with clearly distinguishable
51 components on which participants could determine petrographic thermal index measurements. The
52 most recent round robin exercise completed by the Thermal Indices WG focused on a natural
53 maturation series comprising three samples from the Devonian Huron Shale of the Appalachian Basin,
54 USA. Samples were collected from two correlated transects oriented perpendicular to regional thermal
55 maturity isolines (Hackley et al., 2013; Ryder et al., 2013) and consisted of core chips and cuttings
56 from three wells in Ohio and West Virginia.
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1 The quantity of material available was sufficient to prepare four sets of samples, distributed across
2 four continents, with the aim to draw as much participation in the round robin as possible. Sample sets
3 were distributed to the following participants with the intention that they would remain available in
4 perpetuity for other researchers:
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- 6 1) North America - Paul Hackley (*U.S. Geological Survey*)
- 7
- 8 2) South America - Carla Viviane Araujo (*Petrobras-Cenpes GEOQ/PDGeo*)
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- 10 3) Europe - Angeles Gomez Borrego (*Instituto Nacional del Carbón, (INCAR-CSIC)*)
- 11
- 12 4) Oceania - Jane Newman (*Newman Energy Research Ltd*)
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14 Participants received the maturation series set, consisting of three polished blocks without any
15 information on previously-derived maturation data of the samples and were asked to provide
16 petrographic results for: 1. mean random vitrinite reflectance; and 2. spectral fluorescence
17 measurements of telalginite. Participants were requested to provide a mean value representing about
18 ten individual measurements of spectral fluorescence of *Tasmanites* (thick-walled telalginite). All
19 participants were required to correct their reported mean spectral curve in accordance with a
20 correction function obtained from the calibrated Baranger lamp source (Araujo et al., 1998).
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22 The objectives of this exercise were to: 1. compare maturation results obtained by different types of
23 petrographic thermal indices (vitrinite reflectance and spectral fluorescence of telalginite); 2. compare
24 results obtained by different laboratories for these thermal indices; and 3. compare results of
25 interlaboratory spectral fluorescence measurements obtained using modern detection systems to
26 results from historical round robin exercises (Araujo et al., 1998).
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28 **2. Geological context**

29 Samples were collected from the Upper Devonian Huron Member of the Ohio Shale from three wells
30 in the Appalachian Basin of Ohio and West Virginia, USA (Figure 1). These black, organic-rich marine
31 shales were deposited in a broad intercontinental sea developed during foreland basin subsidence
32 west of the Acadian orogen (Ettensohn, 1998). Thermal maturity of the Devonian section increases
33 from immature in the northwest to overmature in the southeast in the Appalachian Basin (Repetski et
34 al., 2008), due to the effects of the late Paleozoic Alleghenian orogeny. The Devonian shales crop out
35 in central Ohio, dipping and thickening southeastward in the subsurface towards the Alleghenian
36 hinterland (Rimmer, 2004).
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38 **3. Sampling and analytical procedures**

39 Samples used in this study were taken from cuttings and core chips collected from the repositories of
40 the Ohio and West Virginia state geological surveys (Hackley et al., 2013; Ryder et al., 2013).
41 Samples were identified as C3, C5, and D5, in order of increasing thermal maturity. Sample location,
42 lithologic information, and supporting geochemical information are available from Hackley et al. (2013)
43 and Ryder et al. (2013) and compiled in Tables 1 and 2.
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45 A portion of each core chip was selected to make a composite representative sample; homogenized
46 cuttings samples were considered representative. Polished blocks were prepared by embedding the
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1 samples in a resin medium to present a circular examination surface with a diameter of about 2cm.
2 Blocks were polished using progressively finer grades of wet grinding papers and polishing alumina
3 stages in an automatic polisher. Random vitrinite reflectance analyses were provided by participants
4 following the recommendations of ISO 7404-5 (2009), although measuring fewer particles. Participants
5 were required to use microscope settings for random reflectance measurements (without polarizer and
6 analyzer) and measure only organic fragments presenting homogeneous surfaces clear of scratches
7 and pores. In addition to mean random vitrinite reflectance values, standard deviation and number of
8 measurements collected also were required to be reported.
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12 Spectral fluorescence measurements were obtained from *Tasmanites*. Each measurement represents
13 a mean spectral curve of about 10 single measurements corrected with a correction function from the
14 calibrated lamp source (Baranger et al., 1991). The correction function is specific for each microscope
15 system and dependent on the entire photo-optical path (*i.e.*, lamp, lenses and objectives, emission
16 and barrier filters, vertical illuminator), as well as the sensitivity of the photomultiplier or alternative
17 detection systems. There is no standardized consensus method for measuring the fluorescence
18 spectra of organic matter.
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23 Results from VIRF measurements were provided by J. Newman. The VIRF method is outlined in
24 Newman (1997a, b) and Newman et al., (2000). In this method, reflectance and fluorescence intensity
25 are measured for individual vitrinite and inertinite particles and plotted as an x-y chart
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31 **4. Results**

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33 Seventeen participants (in eight laboratories) provided results for mean random vitrinite reflectance,
34 and fourteen participants (in five laboratories) provided spectral fluorescence measurements.
35 Participants are identified as 1 to 18.
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37 **4.1 Petrography**

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39 The fine-grained shale samples are dominated by clay minerals, followed by quartz and sulfides, with
40 some feldspar and carbonate. Organic matter includes dominant amorphous material (bituminite)
41 intimately mixed with the mineral matrix, with lesser amounts of terrestrial macerals including vitrinite
42 and inertinite, consistent with previous studies (Robl et al., 1992). Some solid bitumen with void-filling
43 structures against euhedral mineral faces is present. Marine telalginite (*Tasmanites* and
44 *Leiosphaeridia* ?) are abundant (Figure 3). Zooclasts (conodonts and graptolites) are present locally.
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50 **4.2. Mean random vitrinite reflectance**

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52 Mean random reflectance measurements reported by the round robin participants are compiled in
53 Table 3. Except for sample D5, all participants provided results for vitrinite reflectance. For sample D5,
54 participant 1 did not recognize primary vitrinite and measured bitumen reflectance instead (Table 3).
55 The equivalent vitrinite reflectance based on reported bitumen reflectance has not been included in
56 the calculation of group mean and group standard deviation
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Results from sample C3 show a high level of agreement among participants, with the lowest group standard deviation (0.05%; Table 3 and Figure 3). The level of agreement among participants diminished for samples C5 and D5 with higher group standard deviation values (0.12% for both samples; Table 3 and Figure 3). For participant 1, the value reported in Table 3 and Figure 3 is calculated based on the reported bitumen reflectance. Participant 17 reported results for both vitrinite and bitumen reflectance for samples C3 and D5 (Table 3).

Results changed for all three samples if participants within the same laboratory are grouped and represented by a single mean value (Table 4). Nevertheless, the most significant change is observed for sample C5 with a decrease in group mean from 0.64% to 0.58%. However, with this approach a higher density of values coincides with the group mean vitrinite reflectance.

In general, based on group mean vitrinite reflectance, the least mature sample is C3, the intermediate maturity sample is C5 and the sample with highest maturity is D5, regardless of the fluctuations amongst participants for each sample. These results correspond to the documented regional thermal maturity pattern wherein thermal maturity increases from northwest to southeast (Repetski et al., 2008; Ruppert et al., 2010; East et al., 2012) and are consistent with the geochemical thermal indices determined for these same samples (Table 2; Ryder et al., 2013).

4.3. Spectral Fluorescence Measurements

A significant improvement in the reproducibility of corrected spectral fluorescence curves was observed between results of the current exercise and similar prior studies (Araujo et al., 1998). However, in current exercise, no efforts were made to compare uncorrected spectral curves.

A clear maturation evolution was observed based on the qualitative change in fluorescence color and intensity of telalginite (Figure 2). This affected not only color and intensity but also the development of cracks in the outer margin of telalginite in sample C5, as well as the development of brightly fluorescing spots near the telalginite margins. Telalginite from sample D5 presented the least intense fluorescence and a halo was often observed between the telalginite body and groundmass, suggesting that telalginite shrank during condensation reactions (Kus et al., 2012) due to increasing maturation (Figure 2).

The level of agreement among mean spectral curves decreases with increasing maturation (Figure 4; Table 5). This dispersion may be related to fluorescence heterogeneities of objects selected for measurement or to lower fluorescence intensities at higher thermal maturity and lower signal to noise ratios. A comparison of the $\lambda_{\max}$ values, Red/Green quotient ($Q_{650/500}$) and $Q_{\max/500}$ ($I_{\max}/I_{500}$) is presented in Figure 5 and Table 5. In general, samples C3 and C5 show a higher level of agreement than sample D5, as indicated by increasing standard deviation.

In addition to the thick, double-walled *Tasmanites* telalginite, sample C3 also contains abundant thin-walled telalginite (*Leiosphaeridia*?). Figure 2 presents photomicrographs of telalginite in this sample. Since thin-walled telalginite was abundant in C3, one participant measured both types of telalginite. Mean fluorescence spectra for both types of telalginite are shown in Figure 4 and indicate essentially

identical fluorescence character, similar to results obtained by Stasiuk (1994) and Obermajer et al. (1997).

4.4. VIRF Analysis

VIRF analyses were carried out for the three samples by one participant. Figure 6 shows VIRF curves for Samples C3, C5 and D5. These curves are fluorescence vs reflectance relationships defined by data points for inertinite, perhydrous vitrinite and normal (orthohydrous) vitrinite, which are identified based on VIRF criteria (Newman et al., 2000). R_o (normal) averages are provided in this figure and in Table 6. Normal vitrinite in sample D5 is clustered towards the low reflectance end of the normal compositional range, giving R_o (normal) a low bias. However, the VIRF curve for this sample plots to the right of the curve for sample C5 (Figure 6), indicating that sample D5 has higher maturity. An inferred R_o (normal) for sample D5 has been approximately determined based on comparison with VIRF reference charts (Table 6). Population H reflectance values shown in Table 6 refer to a constituent which resembles vitrinite morphologically but is inferred to have distinct chemistry and substantially lower reflectance than true vitrinite. Population H is a common constituent in Devonian shales whereas true vitrinite is rare (Newman et al., 2013). The original VIRF charts for samples C3, C5 and D5 all feature significant Population H assemblages.

5. Discussion

The identification of primary vitrinite or first-cycle vitrinite (Barker, 1996; ASTM 2013) for reflectance measurement is not equally satisfactory for samples C3, C5 and D5, based on the group standard deviation values. Sample C3 presented the best correlation among analysts, with lower individual standard deviation values and the lowest group standard deviation value of 0.05%. This result may be a consequence of this sample having more abundant and more readily identified vitrinite.

Samples C5 and D5 presented higher complexity in identification of primary vitrinite suitable for measurement. For these samples, individual standard deviation values were higher, as well as group standard deviation values. The group standard deviation values for C5 and D5 were 0.12%, for both samples (Table 3).

Qualitative changes in fluorescence color and intensity definitely indicate an evolution in the maturation level of this sample series. Visual correlation among corrected spectral curves is good, indicating increasing maturity from sample C3 to D5, consistent with reported reflectance values. The best visual correlation among corrected spectral curves was observed for sample C3 (Figure 4), with poorer agreement for samples C5 and D5. Nevertheless, comparing results obtained in this exercise with the results from Araujo et al. (1998), shows that a clear improvement in the signal to noise ratio of the higher maturity sample was observed for the majority of participants (Figure 7). Sample 4 of Araujo et al. (1998) and sample D5 of this study are approximately equivalent in thermal maturity. Comparison between values for λ_{max} and $Q_{650/500}$ shows a substantial reduction of standard deviation for sample D5 compared to Sample 4 from Araujo et al. (1998), besides the fact that only five of nine participants were able to present results for Sample 4 in the earlier study (Tables 5 and 7). This result

is interpreted to reflect an improvement in the sensitivity of signal detection devices, development of digital detection capabilities, and other technical advances such as software protocols for signal multiplication. Reproducibility in spectral parameters for samples 1 and 2 of Araujo et al. (1998) are comparable to those obtained for Sample C3 (Tables 5 and 7).

A good correlation was observed between vitrinite reflectance and λ_{max} for the least mature sample (C3) in the relational scheme for different thermal maturity parameters after Mukhopadhyay (1994) (Figure 8). For samples C5 and D5, the group mean λ_{max} was significantly shifted to red wavelengths, suggesting a higher maturation stage than the respective group mean vitrinite reflectance in Mukhopadhyay's (1994) relational scheme. Relatively little is known about the change of fluorescence properties of the various alginites in source rocks. *Tasmanites* type algae fluoresce with green to bright yellow colors in the immature stage ($\lambda_{\text{max}} < 550\text{nm}$) and its fluorescence loss is reached at a maturation stage corresponding to 0.9-1.0% R_o vitrinite (Taylor et al., 1998). Stasiuk (1994) studied fluorescence properties of prasinophyte alginite (*Tasmanites* and *Leiosphaeridia*) from a Devonian section, noting minimal change in λ_{max} (shift from 450-500nm) while vitrinite reflectance increased from 0.35 to 0.65%. Beyond vitrinite reflectance values of 0.65%, a striking red shift in λ_{max} (from 560 to 600nm) was observed. According to Stasiuk (1994), this rapid red shift in fluorescence spectra corresponds to a hydrocarbon generation peak for Devonian source rocks containing Type II alginite-bituminite kerogen. The similarity of our results to Stasiuk's (1994) study suggests that the Mukhopadhyay (1994) relational scheme for vitrinite reflectance and λ_{max} is flawed at higher thermal maturities for prasinophytes, perhaps due to differences in fluorescence changes with increasing maturation for distinct alginite macerals.

VIRF results indicate higher maturity for all three samples in comparison to mean random vitrinite reflectance (Figure 8). The λ_{max} derived from fluorescence spectral curves indicate lower maturity than VIRF for samples C3 and C5 and higher maturity for sample D5. VIRF analysis inferred relatively little unaltered vitrinite to be present for C3. For C5, only two subjects were inferred to have normal vitrinite composition and for D5 normal vitrinite population was biased towards the low reflectance end of normal range, and the true R_o (normal) was inferred to be approximately 1.05% (Table 6 and Figure 6).

Spectral fluorescence parameter λ_{max} is strongly correlated with T_{max} ($r^2 : 0.98$; T_{max} data from Ryder et al., 2013; summarized in Table 2). The λ_{max} values of 600nm correspond to T_{max} slightly higher than 440°C and the approximate onset of the oil window (Ryder et al., 2013). Correlation of λ_{max} and T_{max} of samples C3, C5 and D5 and Devonian samples studied by Stasiuk (1994) is polynomial with a gap in λ_{max} range of 540-570nm. Up to 440°C of T_{max} the λ_{max} , mostly, reaches up to 500nm (except for 1 sample); beyond a T_{max} of 440°C, λ_{max} is in the range of 580-600nm (except for one sample). This relationship indicates the "red shift" related to the onset of the oil window corresponding to a T_{max} at 440 °C (Figure 9). Hydrogen index plotted vs. λ_{max} shows a minor decrease in HI for λ_{max} in the range 540-600nm followed by a substantial decrease in HI at $\lambda_{\text{max}} > 600\text{nm}$ (Figure 10). These data are in

accordance to the regional studies of Ryder et al. (2013) that observed the 600nm red shift in $\lambda_{\max}$ coincident with the onset of the oil window.

7. Conclusions

The results of an interlaboratory exercise to test the consistency of optical parameters based on fluorescence and reflectance using a natural maturation series of three Devonian shale samples from the Appalachian Basin, USA have been analyzed and discussed within the auspices of the Thermal Indices Working Group of Commission II of the ICCP.

Regarding vitrinite reflectance, almost all participants determined that thermal maturity increases in the order C3<C5<D5. This result corresponds to the documented regional thermal maturity pattern wherein thermal maturity increases from northwest to southeast and is consistent with the geochemical thermal indices determined for these same samples. Mean random reflectance measurements of the lowest maturity sample presented the highest level of agreement among participants. The greatest uncertainty regarding reflectance was obtained for the intermediate maturity sample in which few participant's values were consistent with the group mean.

Corrected fluorescence spectra, provided by 14 participants, presented fair to good reproducibility based on a comparison of standard deviation. Reproducibility is better for the two samples with lower maturity (C3 and C5) according to low standard deviation values for $\lambda_{\max}$, $Q_{650/500}$ and $Q_{\max/500}$ ($I_{\max}/I_{500}$) but is also acceptable for the most mature sample.

A significant improvement in the reproducibility of corrected spectral fluorescence curves was obtained in the current exercise over a previous study of a maturation series from the Toarcian of the Paris Basin (Araujo et al., 1998). Comparison between values for $\lambda_{\max}$ and $Q_{650/500}$ shows a reduction in standard deviation for the most mature sample of both studies, interpreted to be related to improvements in the photo-optical measuring systems. This could be an initial step in finding a standardized procedure for spectral fluorescence measurements. Although this improvement in the reproducibility of corrected spectral fluorescence curves was observed, no attempt to check the performance and correlation of uncorrected spectral curves provided by newer photo-optical measuring systems were carried out. Future developments should include this evaluation.

Fluorescence parameters are in good agreement with vitrinite reflectance for the least mature sample but indicate higher maturity than vitrinite reflectance for the two more mature samples. This red shift in $\lambda_{\max}$ beyond 0.65% vitrinite reflectance also was observed in extant studies of Devonian shale in other basins, suggesting that the relational scheme for these two petrographic thermal maturity parameters needs to be re-evaluated.

The results from the current exercise can be used to improve future interlaboratory comparison of organic matter spectral fluorescence parameters and further can be applied to development of a standardized methodology for spectral fluorescence measurement. In addition, the results can be used to improve relational schemes among organic thermal maturity parameters for hydrocarbon exploration. Finally, this exercise is necessary to extend the use of organic matter spectral fluorescence to a generic thermal maturity calibration, rather than a basin-specific parameter.

Acknowledgements

Alexandre Jonas Sant'Anna and Rafael da Silva Mello from Petrobras R&D Center prepared the polished blocks used in this study. Reviews by Nicholas Geboy from USGS and x improved the manuscript or Anonymous reviewers improved the manuscript . Bob Ryder (U.S. Geological Survey, retired) contributed the samples used for this study.

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Figure Captions

Figure 1. Location map of USA showing northern Appalachian Basin and Devonian shale outcrop, locations of samples used in this study, and Devonian gas accumulations. Modified from Ryder et al. (2013).

Figure 2. Qualitative telalginite maturation series showing progressive changes in fluorescence color and intensity due to increasing maturation. *Telalginite also shows cracking, high fluorescence intensity 'spots' and shrinkage at higher maturity. Examples of telalginite in samples C3, C5 and D5. Red bar = 100 μ m.*

Figure 3. Mean random vitrinite reflectance and standard deviation for samples C3, C5 and D5. Black square shows the group mean. Participant 1 provided bitumen reflectance of 0.66% for sample D5, which computes to $BR_{o1}=0.81\%$ (Jacob, 1989) and $BR_{o2}=0.98\%$ (Landis and Castaño, 1994).

Figure 4. Characteristic corrected spectral fluorescence curves of *Tasmanites* obtained by the participants of this exercise for samples C3, C5 and D5 and comparison between fluorescence spectra of two different telalginite types: thick, double-walled *Tasmanites* and thin-walled *Leiosphaeridia* (?) in sample C3.

Figure 5. Comparisons of λ_{max} values derived from the corrected spectral fluorescence curves of each participant for samples C3, C5 and D5 (left column); of red/green quotient ($Q_{I_{650}/I_{500}}$) values derived from the corrected spectral fluorescence curves of each participant for samples C3, C5 and D5 (medium column) and of I_{max}/I_{500} values derived from the corrected spectral fluorescence curves of each participant for samples C3, C5 and D5 (right column). *Obs: I_{max} is always 100% since the values are normalized to 100% for comparison.*

Figure 6. VIRF charts for samples C3, C5 and D5.

Figure 7. Qualitative telalginite maturation series from the Toarcian of Paris Basin (Araujo *et al.*, 1998). Photomicrographs of *Tasmanites* in fluorescence mode and corrected spectral fluorescence curves representing increasing level of maturation (from A to D).

Figure 8. Comparison among group mean vitrinite reflectance, VIRF, and group mean λ_{max} for samples C3 (black square), C5 (white square) and D5 (gray square) (modified from Mukhopadhyay, 1994).

Figure 9. T_{max} versus λ_{max} for samples C3, C5 and D5 and samples from Upper Devonian Bakken and Middle Devonian Winnipegosis Formations (Stasiuk, 1994). *The arrow points out a general shift in λ_{max} from 540 to 570nm*

Figure 10. Hydrogen Index (HI) versus λ_{max} for samples C3, C5 and D5.

Table 1. Location and lithologic information.

API: American Petroleum Institute well number; Lati:latitude; Long:longitude; Fm:formation; ft:feet

Sample	API	Lati	Long	Fm	Member	State	Depth (ft)
C ₃	34-073-20497	39,4446	-82,2996	Ohio Shale	Huron	OH	1,995-2,070
C ₅	47-035-01371	38,8734	-81,8482	Ohio Shale	Huron	WV	3,564
D ₅	47-043-01656	38,0967	-82,2408	Ohio Shale	Huron	WV	3,542

Table 2. Organic geochemical data.

Sample	Depth (ft)	Sample Type	TOC (wt%)	S ₁ (*)	S ₂ (*)	S ₃ (**)	HI (#)	OI (##)	T _{max} °C	PI (!)
C ₃	1,995-2,070	cuttings	5.22	2.51	25.91	0.49	496	9	434	0.09
C ₅	3,564	core	4.99	2.91	24.38	1.42	488	28	441	0.11
D ₅	3,542	core	6.36	4.2	22.24	0.4	350	6	448	0.16

(*: mg of hydrocarbon/g of rock; **:mg of CO₂/g of rock; #:mg of hydrocarbon/g of TOC; ##: mg of CO₂/g of TOC; !:S₁/S₁+S₂)

Table 3. Mean random vitrinite reflectance, standard deviation and number of measurements. Bitumen reflectance and equivalent vitrinite reflectance for samples C3 and D5.

Participant	C3			C5			D5		
	R _o %, Rr%	SD%	N	R _o %, Rr%	SD%	N	R _o %, Rr%	SD%	N
1	0.45	0.06	14	0.54	0.08	21			
2	0.52	0.07		0.43	0.04		0.47	0.07	
3	0.51	0.06	25	0.55	0.03	25	0.67	0.07	30
4	0.48	0.07	23	0.52	0.08	24	0.78	0.08	10
5	0.50	0.06	22	0.64	0.05	22	0.71	0.06	21
6	0.44	0.06	20	0.69	0.04	12	0.76	0.06	19
7	0.46	0.02	19	0.75	0.06	37	0.81	0.08	18
8	0.46	0.02	19	0.74	0.03	35	0.84	0.05	17
9	0.46	0.02	20	0.76	0.06	37	0.83	0.08	17
10	0.46	0.02	19	0.73	0.06	35	0.82	0.08	18
11	0.45	0.02	17	0.78	0.03	32	0.83	0.06	16
12	0.45	0.02	18	0.77	0.03	32	0.80	0.08	18
13	0.45	0.02	16	0.75	0.06	35	0.83	0.08	16
14	0.41	0.07	30	0.42	0.08	44	0.49	0.05	48
15	0.45	0.10	32	0.55	0.07	16	0.64	0.11	18
16	0.59	0.06	37	0.63	0.06	23	0.72	0.07	35
17	0.59	0.05	24	0.65	0.05	22	0.87	0.16	23
Group	0.48	0.05		0.64	0.12		0.74	0.12	
1: bitumen							0.66	0.81 R _{o1}	0.98 R _{o2}
17: bitumen	0.28	0.57 R _{o1}	0.63 R _{o2}				0.45	0.68 R _{o1}	0.79 R _{o2}

R_{o1}: Equivalent vitrinite reflectance based on the equation [(0.618*BRo)+ 0.40] from Jacob (1989).
R_{o2}: Equivalent vitrinite reflectance based on the equation ([%BRo + 0.41]/1.09) from Landis and Castaño (1994).
1 and 17 bitumen: are bitumen reflectance.

Table 4. Mean random vitrinite reflectance, standard deviation and number of measurements grouped by laboratories for the three samples. Bitumen reflectance and equivalent vitrinite reflectance for samples C3 and D5.

	C3			C5			D5		
<i>Participant</i>	<i>R_o%, Rr%</i>	<i>SD%</i>	<i>N</i>	<i>R_o%, Rr%</i>	<i>SD%</i>	<i>N</i>	<i>R_o%, Rr%</i>	<i>SD%</i>	<i>N</i>
1	0.45	0.06	14	0.54	0.08	21			
2	0.52	0.07	-	0.43	0.04	-	0.47	0.07	-
3	0.51	0.06	25	0.55	0.03	25	0.67	0.07	30
16	0.59	0.06	37	0.63	0.06	23	0.72	0.07	35
17	0.59	0.05	24	0.65	0.05	22	0.87	0.16	23
Lab A	0.46*	0.01**	-	0.75*	0.02**	-	0.82*	0.01**	-
Lab B	0.47*	0.03**	-	0.62*	0.09**	-	0.75*	0.03**	-
Lab C	0.43*	0.03**	-	0.49*	0.09**	-	0.57*	0.11**	-
Group	0.50	0.06	-	0.58	0.10	-	0.70	0.14	-
1: bitumen							0.66	0.81 <i>R_o 1</i>	0.98 <i>R_o 2</i>
17: bitumen 0.28 0.57 <i>R_o 1</i> 0.63 <i>R_o 2</i>							0.45	0.68 <i>R_o 1</i>	0.79 <i>R_o 2</i>

* (Group mean vitrinite reflectance of Lab X); ** (Group standard deviation of Lab X)

Table 5. Fluorescence parameters for samples C3, C5 and D5.

Participant	1	4	5	6	7	8	9	10	11	12	13	14	15	18	GM	SD
Samples																
C3																
<i>Mean λ_{max} (nm)</i>	535	530	515	515	535	535	535	510	535	550	550	555	555	540	535	14.47
<i>Mean $Q_{650/500}$</i>	0.78	0.54	0.47	0.51	0.55	0.74	0.53	0.52	0.54	0.6	0.58	0.68	0.68	0.64	0.60	0.09
<i>Mean Q_{max}/I_{500}</i>	1.09	1.04	1.02	1.04	1.07	1.06	1.06	1.05	1.06	1.1	1.08	1.14	1.14	1.17	1.08	0.04
C5																
<i>Mean λ_{max} (nm)</i>	612	575	590	590	590	575	575	590	590	595	590	610	610	655	596	20.88
<i>Mean $Q_{650/500}$</i>	1.59	1.11	1.14	1.17	1.39	1.25	1.25	1.3	1.29	1.35	1.3	1.89	1.86	1.85	1.41	0.27
<i>Mean Q_{max}/I_{500}</i>	1.75	1.32	1.35	1.37	1.53	1.44	1.46	1.49	1.47	1.53	1.48	2.01	1.98	2.02	1.59	0.25
D5																
<i>Mean λ_{max} (nm)</i>	661	670	665	670	620	610	670	620	620	610	670	690	690	680	653	30.12
<i>Mean $Q_{650/500}$</i>	2.39	1.59	1.56	1.64	1.55	1.74	1.62	1.47	1.5	1.42	1.52	2.52	2.02	2.06	1.76	0.35
<i>Mean Q_{max}/I_{500}</i>	2.25	1.61	1.57	1.67	1.57	1.52	1.64	1.49	1.52	1.45	1.53	2.68	2.23	2.97	1.84	0.49

Obs: λ_{max} is always 100% since maximum intensity is normalized to 100%

Table 6. VIRF data for the sample set.

Ro (normal) values are calculated from actual measurements on indigenous vitrinite subjects of normal chemistry when these are present in the sample.

Sample	Ro (normal) %			Ro (population H) %		
	Av & n	s.d	range	Av & n	s.d.	range
C3	0.63 (n=3)	0.049	0.56-0.65	0.58 (n=20) ¹	0.106	0.37-0.72
C5	0.96 (n=2)	0.163	0.84-1.07	0.48 (n=23)	0.109	0.35-0.74
D5	0.95 (n=5) ²	0.064	0.87-1.04	0.55 (n=21)	0.150	0.31-0.86
D5	Ro (inferred) ~1.05%					

¹ may include some altered normal vitrinite

² biased towards the low reflectance end of the normal vitrinite compositional range

Table 7. Mean values, standard deviation and number of participants that provided results for the Paris Basin maturation Series (Araujo et al., 1998).

Paris Basin maturation series			
Sample 1			
	Mean	Standard Deviation	Number of participants
λ_{max}	534	13.47	9
$Q_{650/500}$	0.56	0.12	9
$Q_{max}/500$	1.09	0.06	9
Sample 2			
	Mean	Standard Deviation	Number of participants
λ_{max}	555	16.71	7
$Q_{650/500}$	0.77	0.14	7
$Q_{max}/500$	1.18	0.08	7
Sample 3			
	Mean	Standard Deviation	Number of participants
λ_{max}	594	28.73	9
$Q_{650/500}$	1.2	0.23	9
$Q_{max}/500$	1.36	0.16	9
Sample 3			
	Mean	Standard Deviation	Number of participants
λ_{max}	661	48.38	6
$Q_{650/500}$	1.68	0.60	5
$Q_{max}/500$	1.55	0.06	5

Figure 1
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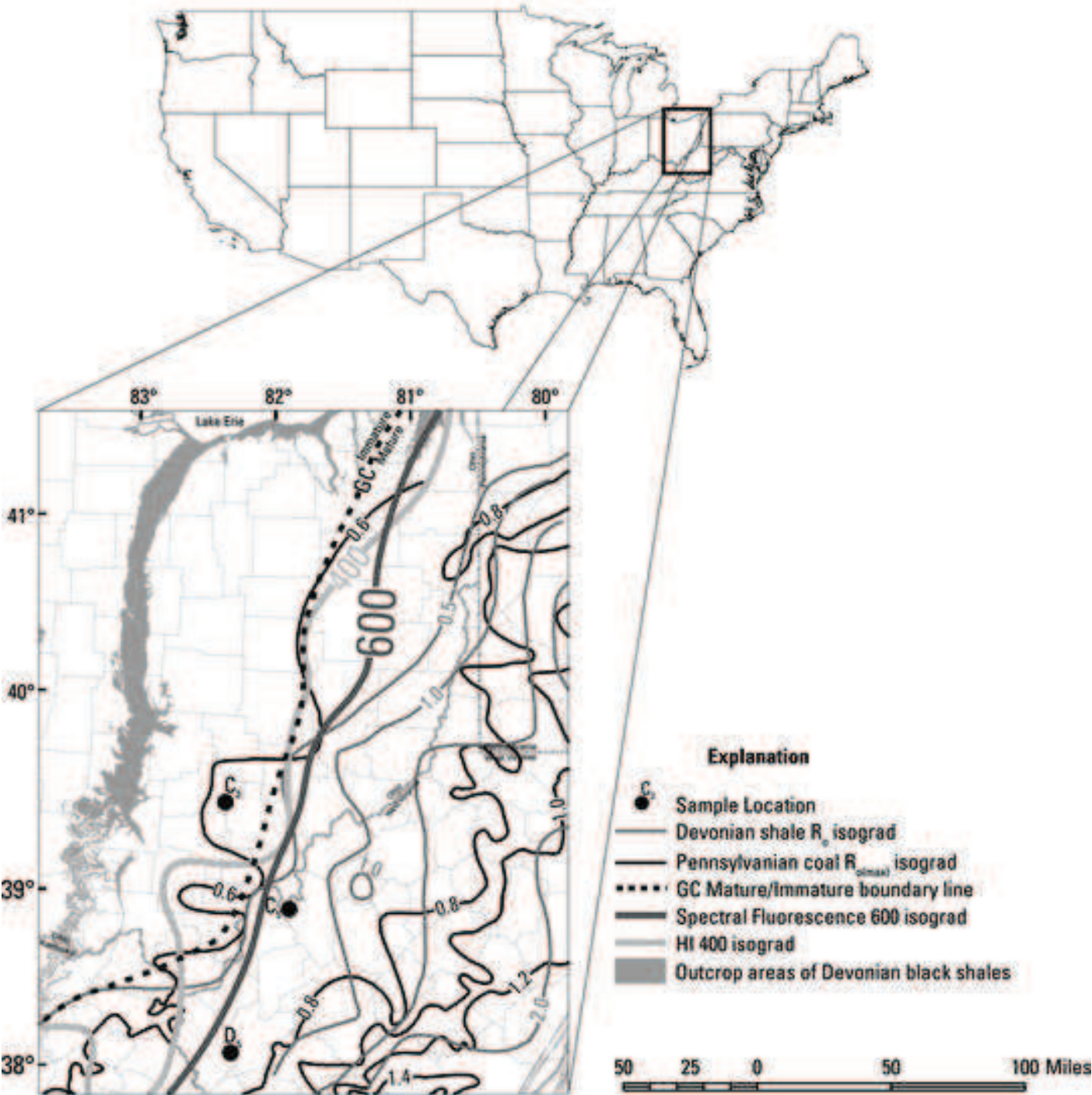


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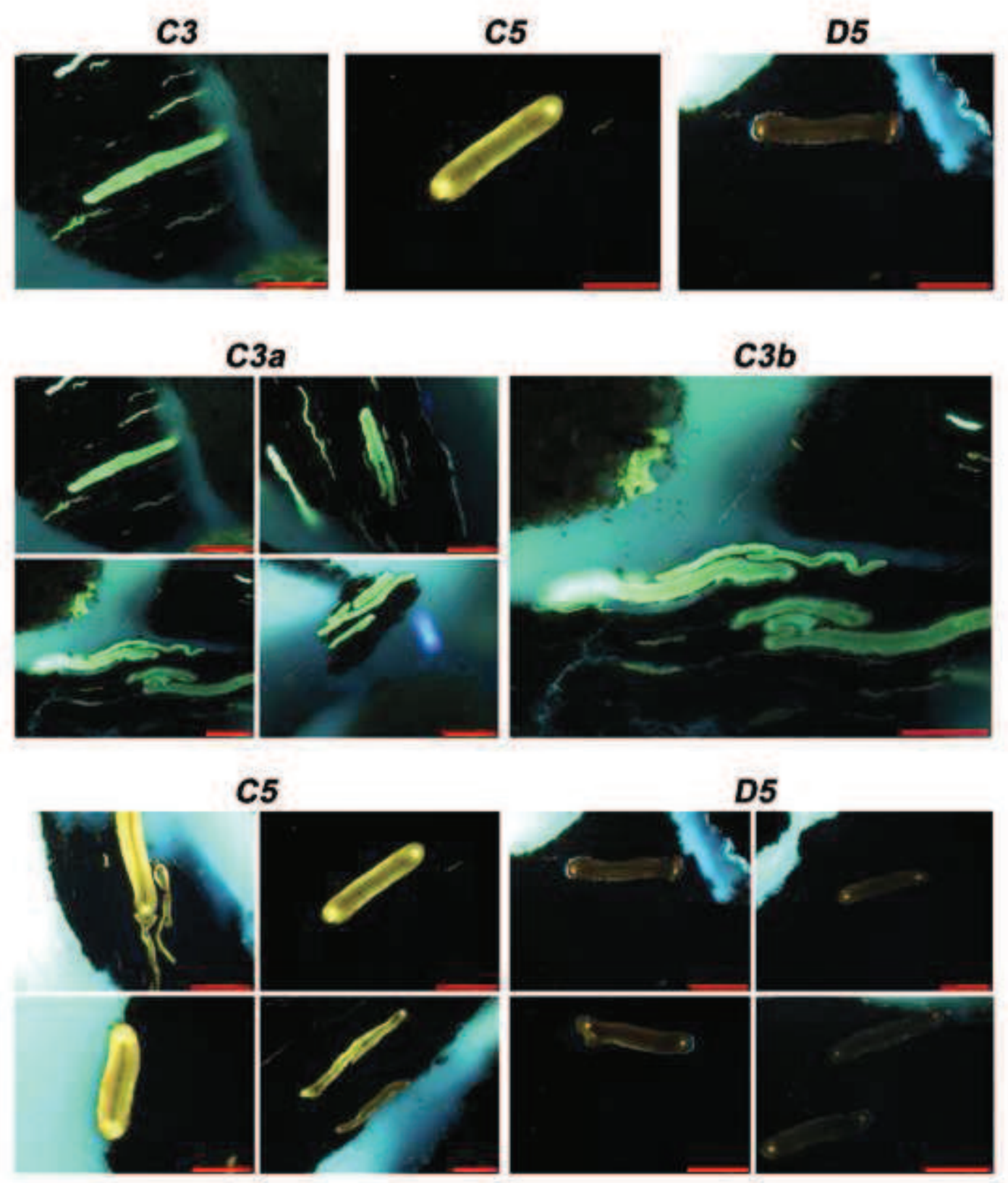


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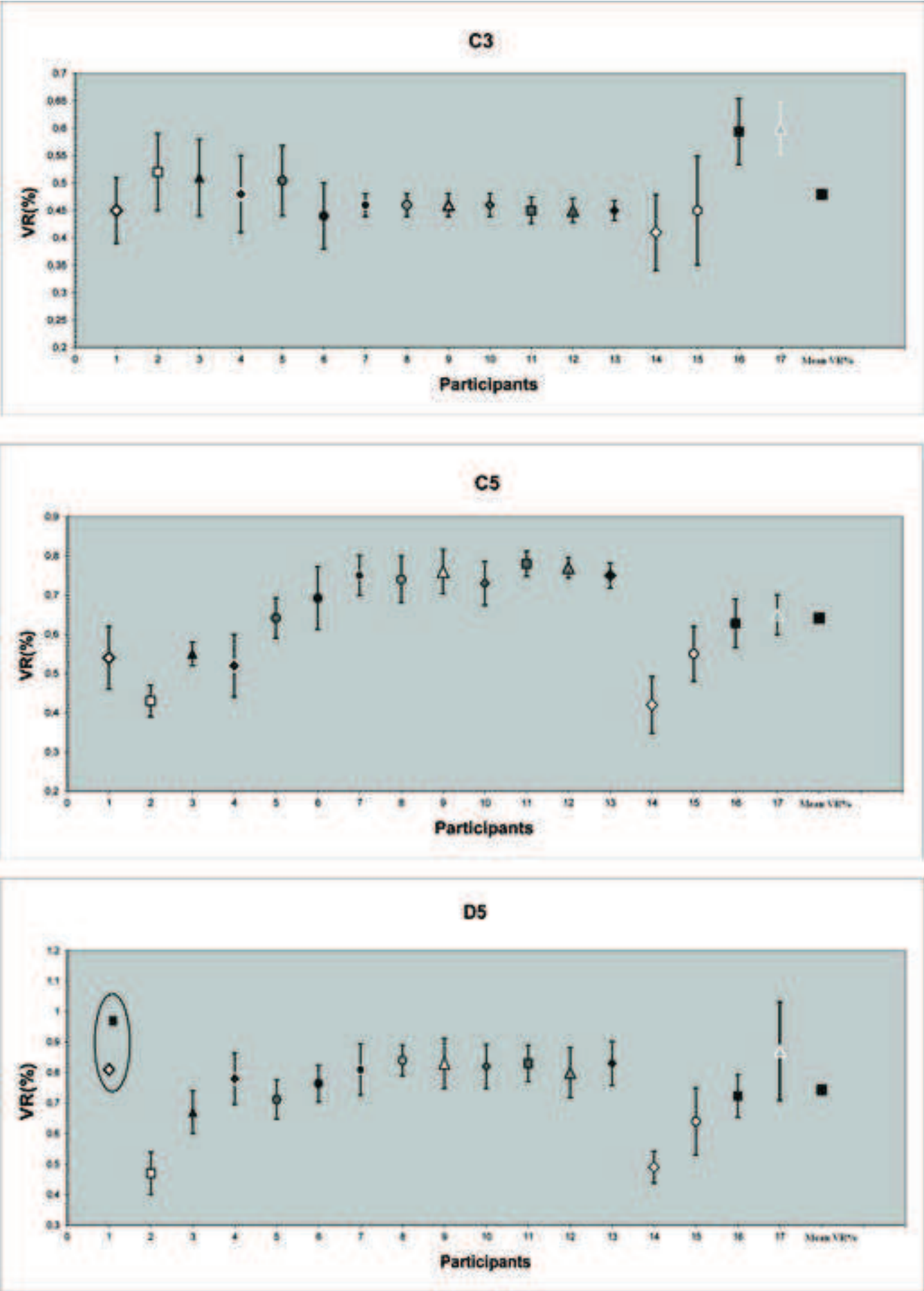


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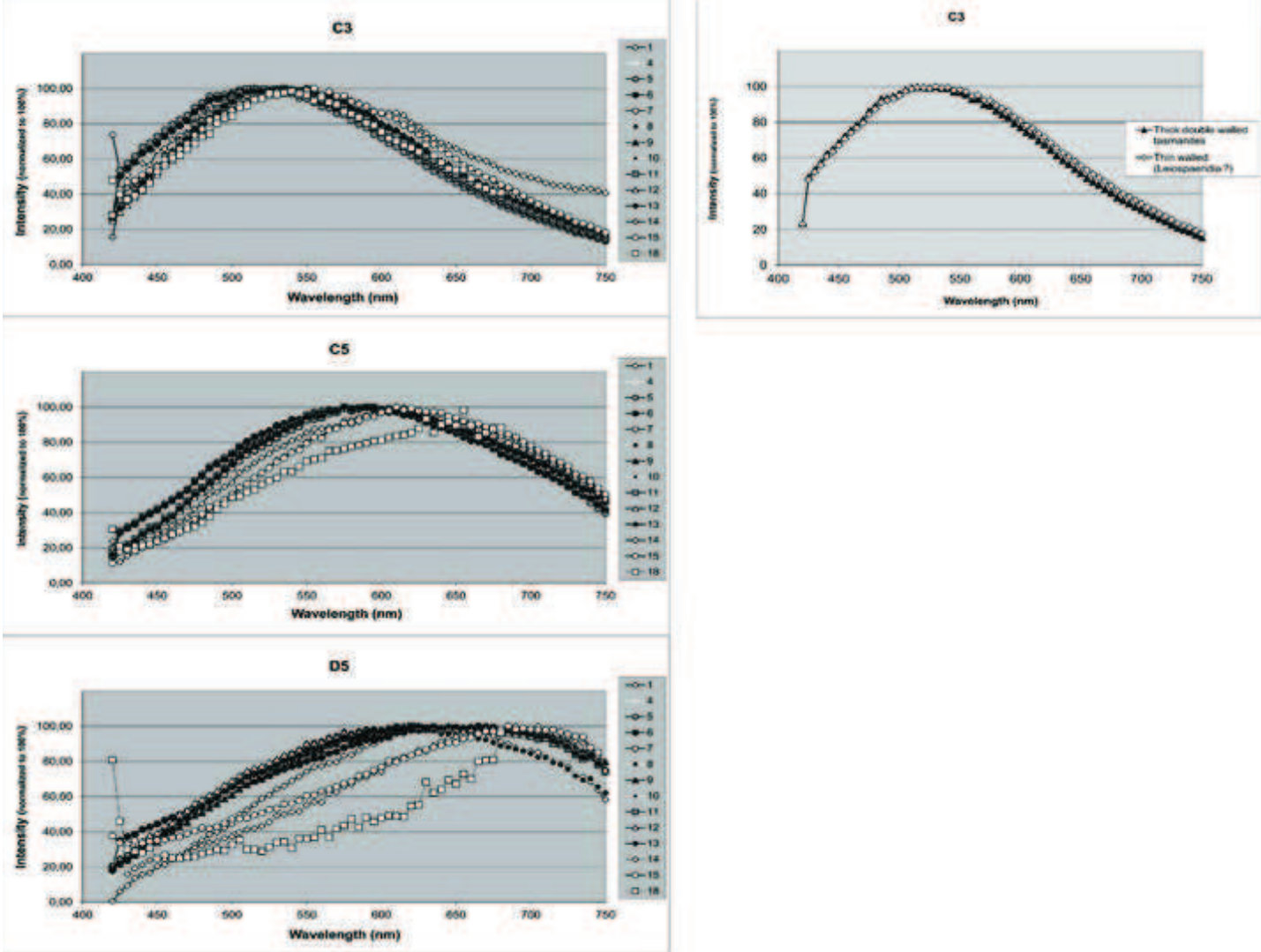


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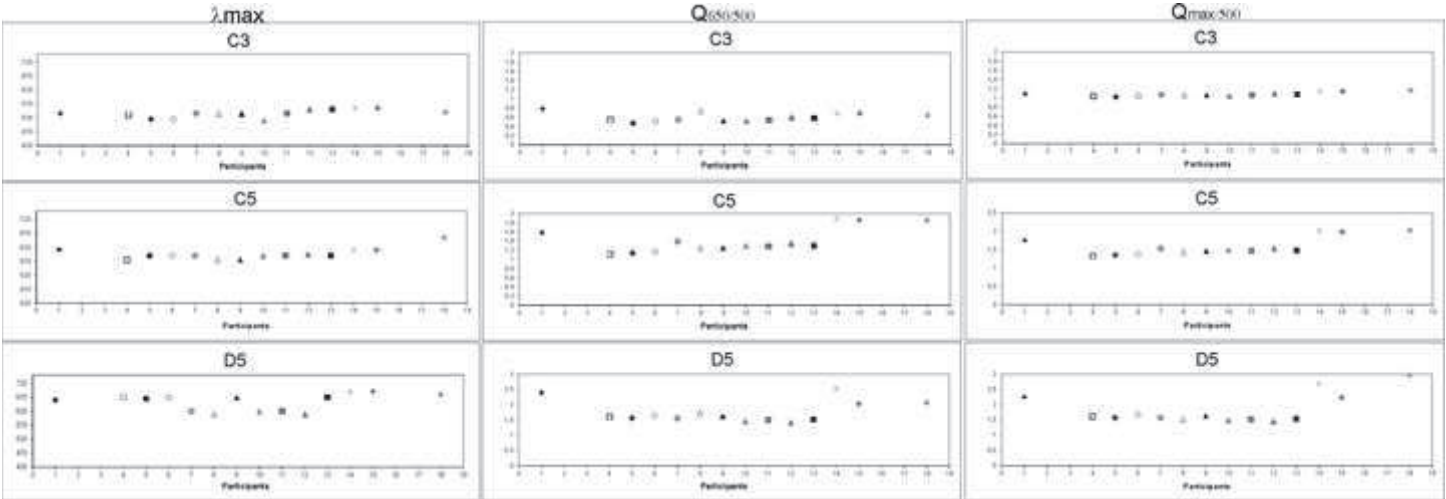


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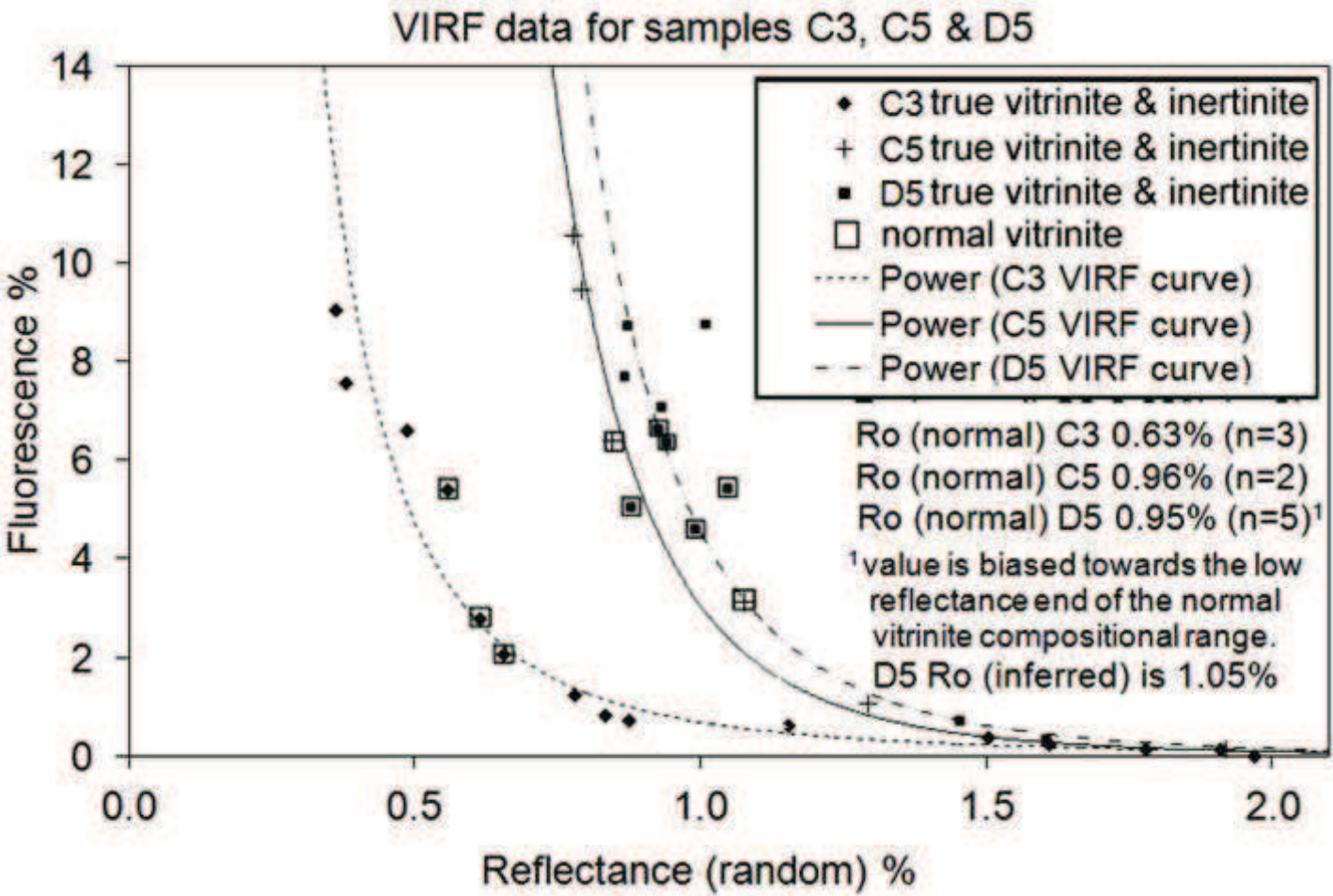


Figure 7

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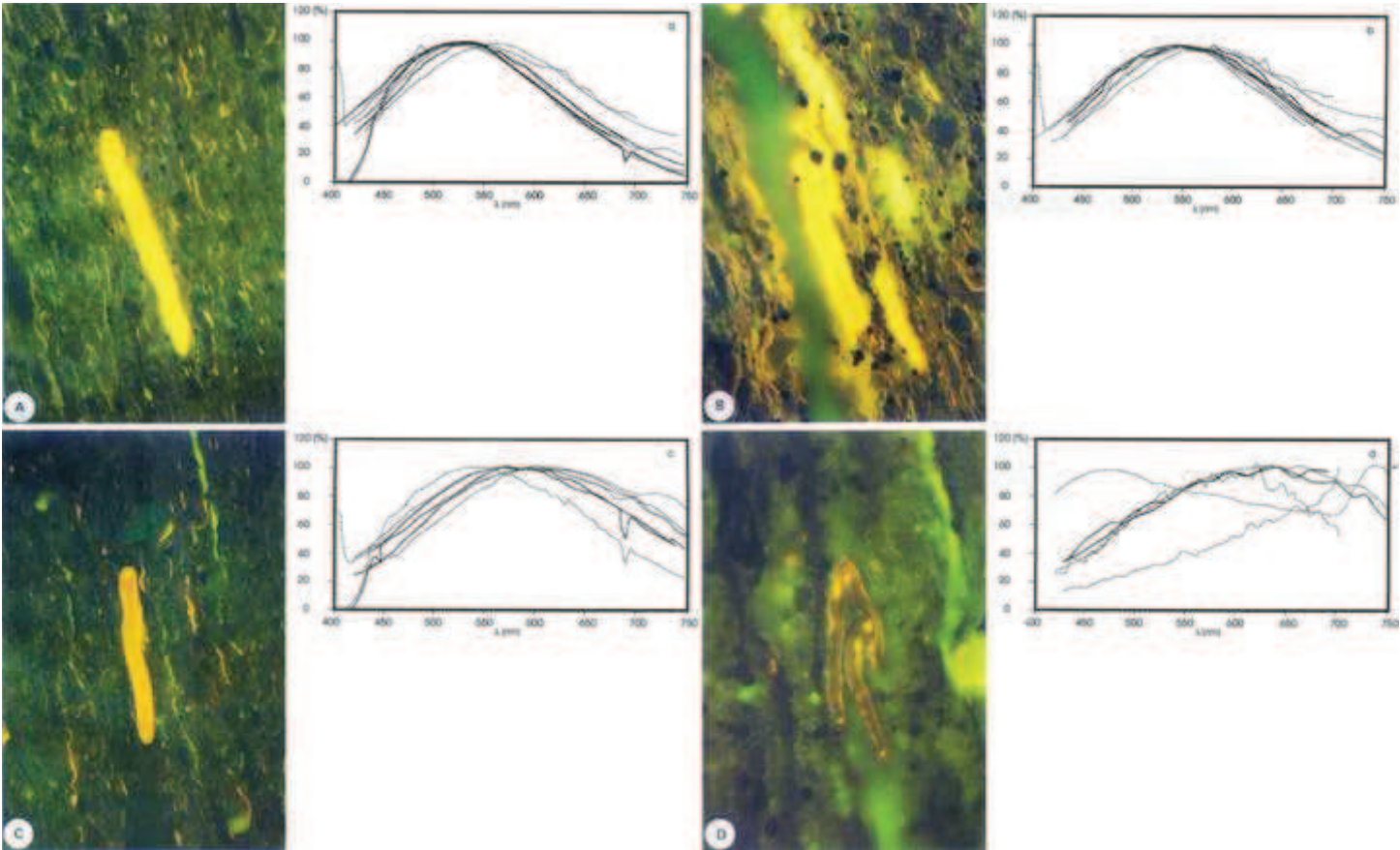


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Maturation and Rank		MICROSCOPIC MATURITY PARAMETERS					
Stages of Maturation	COAL RANK	Vitrinite Refl. (%Ro)	VIRF	FLUORESCENCE			
				Colour of Alginite	λ MAX (NM)		
DIAGENESIS	PEAT	0.2		GREENISH YELLOW	500		
	LIGNITE	0.3					
		SUB-BITUMIN.	0.4		GOLDEN YELLOW	540	
CATAGENESIS		0.5	■				
	HIGH VOLATILE BITUMIN.	0.6	□	■			
		0.7	■				
		0.8			DULL YELLOW	600	□
		0.9					
		1.0		■	ORANGE	640	
	MEDIUM VOLATILE BITUMIN.	1.2				■	
		1.35			RED	680	
	1.5						
METAGENESIS	SEMI-ANTHRAC	2.0		NON-FLUORESCENT			
		2.5					
	ANTHRAC	3.0					
		4.0					
		5.0					
Meta-morph.	META-ANTHRAC						

Figure 9
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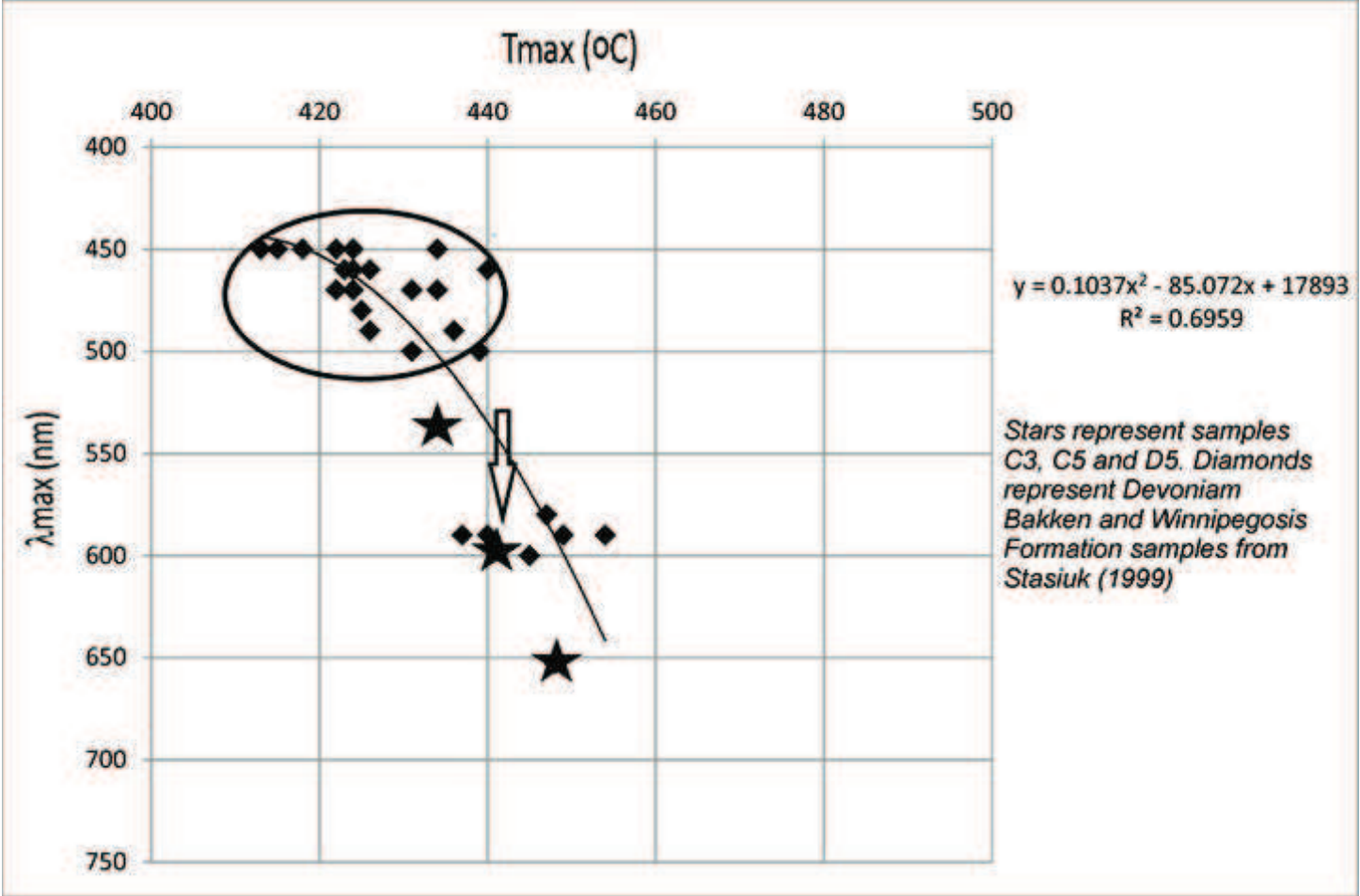


Figure 10
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