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Effect of concentration of dispersed organic matter on optical maturity parameters. Interlaboratory results of the organic matter concentration working group of the ICCP

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Abstract:
The main objective of this work was to study the effect of the kerogen isolation procedures on maturity parameters of organic matter using optical microscopes.
This work represents the results of the Organic Matter Concentration Working Group (OMCWG) of the International Committee for Coal and Organic Petrology (ICCP) during the years 2008 and 2009. Four samples have been analysed covering a range of maturity (low and moderate) and terrestrial and marine geological settings. The analyses comprise random vitrinite reflectance measured on both kerogen concentrate and whole rock mounts and fluorescence spectra taken on alginite. Eighteen participants from twelve laboratories from all over the world performed the analyses. Samples of continental settings contained enough vitrinite for participants to record around 50 measurements whereas fewer readings were taken on samples from marine setting. The scatter of results was also larger in the samples of marine origin. Similar vitrinite reflectance values were in general recorded in the whole rock and in the kerogen concentrate. The small deviations of the trend cannot be attributed to the acid treatment involved in kerogen isolation but to reasons related to components identification or to the difficulty to achieve a good polish of samples with high mineral matter content. In samples difficult to polish, vitrinite reflectance was measured on whole

rock tended to be lower. The presence or absence of rock fabric affected the selection of the vitrinite population for measurement and this also had an influence in the average value reported and in the scatter of the results. Slightly lower standard deviations were reported for the analyses run on kerogen concentrates. Considering the spectral fluorescence results, it was observed that the λmax presents a shift to higher wavelengths in the kerogen concentrate sample in comparison to the whole-rock sample, thus revealing an influence of preparation methods (acid treatment) on fluorescence properties.

Key-words: Dispersed Organic Matter; Isolation of Organic Matter; Vitrinite Reflectance; Spectral Fluorescence; Kerogen Concentrate

1. Introduction:

The comparability of the results obtained from rocks with dispersed organic components and their respective kerogen concentrates has worried oil-exploration researchers for many years. It is not always possible to get rock cores from which a pellet for microscopy can be prepared and quite often the samples are prepared from well-cuttings samples that may contain cavings and/or drilling mud additives. The typically reported advantages and disadvantages of kerogen concentrates *versus* whole-rock pellets can be summarized as follows:

- A whole-rock sample retains original texture, helping in the identification of indigenous vitrinite and reducing the possibilities of confusion with recycled vitrinite particles or solid bitumen.
- The inspection of the whole-rock surface to find dispersed vitrinite particles is time consuming, particularly for organic-lean samples. On the other hand, this might be compensated by a shorter preparation time for the whole-rock pellet.
- Possible effects of bright or dark mineral matrices in the analytical results cannot be totally ruled out. The difficulties in polishing some mineral matrices may affect the quality of the polishing of the associated organic matter. But this refers to both whole rock and kerogen concentrates that usually have abundant pyrite.
- The aggressive acid treatment with HCl and HF used for kerogen isolation may have some effect on the optical properties of the organic matter. Most of the records describing methods for kerogen concentration state that the acid treatment does not essentially affect (Durand and Nicaise, 1980) or significantly alter the organic matter of the rock (Senftle et al., 1993). The

understanding is imprecise for establishing whether the results obtained from kerogen concentrates and whole rocks are comparable.

The international Committee for Coal and Organic Petrology (ICCP) has devoted efforts over the last twenty years to quantifying the extent to which isolation procedures may affect the optical properties of organic matter and the results of petrographic analysis. The isolation of organic matter (IOM) working group convened first by André van der Meulen and afterwards by John Castaño was created to investigate these differences. Two low-maturity samples, the Carboniferous lacustrine Pictou Shale and the Turonian marine Second White Specks shale, both from Canada, were analyzed by the Isolation Organic Matter Working Group - IOMWG (Castaño 1995, 1996). In the case of maceral analysis, the number of participants was low and they did not use a homogeneous nomenclature, which complicated the analyses of the results. Regarding vitrinite reflectance, despite the large scatter of the values (Fig. 1), lower values were reported for measurements taken on kerogen concentrates than for whole-rock samples and the differences were sample dependant (Borrego, 2007). A different result was obtained by Barker (1996), who reported vitrinite reflectance few tenths of a percent lower for the whole-rock sample than for the kerogen concentrate, although, in this case, acid treatment was avoided for kerogen concentration.

At the 2007 ICCP Meeting, the antecedents of the effect of the isolation procedure on optical parameters were reviewed and the objectives and strategy of the Working Group were redefined. The strategy of the new OMCWG was to focus on maturity parameters such as vitrinite reflectance and fluorescence measurements and use samples of different maturity and depositional environment. Four samples, two of terrestrial (Mendonça Filho et al., 2008) and two of marine origin (Mendonça Filho et al., 2010a), and their corresponding kerogen concentrates, have been analyzed and the results are presented here.

2. Experimental Section

2.1 Selection of samples

Samples were selected to cover both terrestrial and marine settings and differences in maturity. Sample OMC1, an organic-rich shale of moderate maturity (Table 1, Fig. 2), was sampled at the mine face at the top of the coal bed of the Montsacro underground mine (Asturian Central Coal Basin, Northern Spain). Sample OMC2 from the Manu Formation (Maastrichtian) from the Benin-Flank Basin (Nigeria) is an immature shale outcrop sample dominated by terrestrial organic matter with moderate organic content (Table 1, Fig. 2). Sample OMC3 is an outcrop sample of the marine Rodiles Formation (Pliensbachian) consisting of alternating marls and limestones, which is part of the Asturian Mesozoic Cover in Northern Spain. The sample has a moderate maturity and the lowest organic matter content of the sample suite (Table 1, Fig. 2). Sample OMC4, an outcrop marine shale sample of the Vale das Fontes Formation in the Lusitanian Basin (Pliensbachian), is a low-maturity organic-rich sample with a relatively high Hydrogen Index (Table 1, Fig. 2). All outcrop samples are freshly collected.

2.2 Sample Preparation

Two preparation systems were adopted for each sample as shown in Figure 3. The whole-rock sample (labeled A throughout the text) was prepared by grinding to approximately 2mm size and embedding it in resin (epoxy). A single block was prepared for each sample.

The same ground sample was used for kerogen concentrate preparation. For kerogen isolation a sequential treatment with cold or warm hydrochloric and hydrofluoric acids to dissolve the rock matrix, followed by separation of remaining or newly formed minerals is typically used (Whelan and Thompson-Rizer, 1993). Most of the concentration procedures differ in the length of the treatment, the bath temperature if different to room temperature, the washing steps and the elimination or not of sulfides (Durand and Nicaise, 1980). A single and common procedure was used in the present work to avoid extra variability derived from differences in the isolation procedures using in different laboratories. The isolation procedure is

relatively non-aggressive procedure working at room temperature which minimizes the possibilities for alteration of the organic matter and has been successfully used for many years at LAFO (laboratory for organic facies and palynofacies in the Federal University of Rio de Janeiro, Brazil). A detailed description of the isolation procedure is found elsewhere (Mendonça Filho et al., 2010b) and is briefly summarised below. Samples were treated successively to remove carbonates (HCl 37% for 18 hours), silicates (HF 40% for 24 hours), and neoformed fluorides (HCl 37% for 3 hours). Between steps, samples were washed with distilled water until washing water was neutral (pH=7). After this procedure $ZnCl_2$ (ρ = 1.9 to 2 g/cm^3) was added, stirred and then centrifuged in order to separate sulphides. The floated material was washed following the same procedure and some HCl (10%) drops + distilled water were added to eliminate the heavy liquid. The isolated kerogen was sieved (20 μm) and embedded in resin (epoxy).

Two polished pellets of each sample corresponding to the whole rock (A) and kerogen concentrate (B), were distributed to the participants, who were invited to re-polish the samples if preferred**.**

2.3 Proposed Analytical Procedure

The participants were asked to measure random vitrinite reflectance on the whole rock and kerogen concentrate of each sample following the same procedure used for the Dispersed Organic Matter Vitrinite Reflectance Accreditation Program (DOMVR) of the ICCP (http://www.iccop.org/index.php?id=25). The procedure essentially follows the standard for vitrinite reflectance analysis in coal (ISO 7404-5; 1994**),** although a lower number of readings was required (50). Participants provided individual readings for each sample in addition to the relevant statistics. Participants were also asked to measure fluorescence spectra of liptinite in the samples in which liptinite was fluorescing with enough intensity. Spectra were corrected, applying the procedure described in Baranger et al. (1990) using the spectral function of a halogen lamp. This correction procedure is also used in the Thermal Indices WG of the ICCP (see www.iccop.org). Spectra from different

liptinite macerals were measured. The provided spectra were the result of averaging ten individual spectra.

For OMC1A, OMC1B, OMC2A, and OMC2B samples, sixteen individual results are identified by alphabetic letters (from A to P). Fifteen results based on standard vitrinite reflectance and one result based on VIRF (Vitrinite and Inertinite Reflectance and Fluorescence) were received and treated.

2.4. Statistical analysis

A simple statistical evaluation based on the group mean (GM) and group standard deviation (GSD), calculated using all the values for each sample reported by participants, was used to evaluate the results. The signed multiple of the standard deviation (SMSD = $(X_i$-GM) / GSD, where X_i is the average vitrinite reflectance calculated by the participants) or its absolute value (UMSD) was used to determine bias and precision, respectively because they are an estimation of the distance to the mean of any given value. Typically, UMSD values of 1.5 or below are considered acceptable. In a Normal Gaussian distribution, 86.6% of the results are within ±1.5 SD. These parameters were established by the ICCP (www.iccop.org) for their Accreditation Programs and afterwards used to evaluate ring analysis by Borrego et al. (2006).

3. Results and Discussion:

3.1. Vitrinite reflectance of the samples analysed

Participants are labeled from A to P in Table 2. The lettering has no relation with the order of authors on this paper. Sixteen participants performed the exercise on samples from continental setting (OMC1 and OMC2) and fourteen participants on samples from marine setting (OMC3 and OMC4). Overall the results have a high reliability based on the high number of participants.

Sample OMC1 had abundant vitrinite particles, the major organic component of the sample (Fig. 4). Vitrinite was easy to identify in the whole rock and the kerogen concentrate and most participants recorded at least 50 measurements as recommended in the instructions (Table 2). The SD of the

analyses performed was 0.07 in average for whole rock and 0.05 for kerogen concentrate indicating a moderate dispersion of reflectance measurements. Participant F reported very high standard deviation in the analysis of whole rock (0.19%), which can be attributed to the measurements of lower and higher reflecting particles than the indigenous vitrinite of the sample. The SD of this participant was reduced to common values (0.06%) in the kerogen concentrate analysis. The GM was 1.15% and the scatter around this value was moderate except for participant E who reported very high vitrinite reflectance values in both the whole rock and the kerogen concentrate (1.52% and 1.41% respectively). This participant reported moderate SD and therefore the high values can be attributed to calibration difficulties.

Sample OMC2 had abundant vitrinite particles, although, in this case, liptinite and inertinite macerals were also frequent, making identification of vitrinite more difficult (Figure 4). Most participants provided the requested 50 readings or numbers close to it and only participant P reported less than ten readings (8) in the whole rock sample. The SD reported by participants was always below 0.09% (Table 2) with average values around 0.04%. The GMs were close to each other in both samples and the value was slightly higher in the kerogen concentrate (0.40% vs. 0.37% in the whole rock).

A different situation regarding the abundance of vitrinite particles was faced when analyzing the marine samples. Sample OMC3 showed significant differences between the numbers of reported measurements. Only half of the participants reported 20 or more readings and two participants reported less than 10 readings indicating difficulties in finding or identifying vitrinite particles (Table 2). In the subsequent discussion of the results at the 2009 ICCP meeting in Gramado (ICCP News 46), the appearance of vitrinite in this sample was discussed and the presence of solid bitumen with similar appearance to vitrinite was mentioned. Thus, the bitumen could be confused with the vitrinite. Figure 5 illustrates the appearance of some of the organic components in the OMC3 sample with indication of their reflectance and the probable assignment based on the reported results. This sample contained zooclasts with lower reflectance, than the vitrinite, inertinite with

higher reflectance and bitumen with reflectance close to that of the vitrinite, apparently adding to the difficulty in selecting vitrinite. The SDs reported by participants were generally higher than those of samples OMC1A and OMC1B, which are samples of similar maturity but with different types of organic matter. GMs around 1.04% and around 0.97% were obtained for the whole rock and kerogen concentrate, respectively. The GSD of sample OMC3A was in the range of those obtained for the continental samples of similar maturity (Table 2). The high GSD of sample OMC3B (0.223%) can be attributed to the low value reported by participant I (0.34%) for the vitrinite reflectance in the kerogen concentrate. This value probably corresponds to the measurements of zooclast reflectance. This component was easier to find in the kerogen concentrate than in the whole rock sample. This may have led to the miss-selection of the vitrinite population.

Sample OMC4 had a high organic content with an abundance of liptinite macerals showing intense fluorescence. They include bituminite with reflectance around 0.09 % and orange fluorescence. The majority of participants were able to find over 20 measurable vitrinite particles in the sample and only participant I reported less than 10 readings. On average, more particles were measured in the whole rock than in the kerogen concentrate. Most of the participants were consistent in the selection of a population regardless of the type of sample preparation. For both samples the reported values were systematically higher or lower than the mean (Table 2). Participant Q, on the contrary, selected a population of higher reflectance in the whole rock (Rr = 0.65%) than in the kerogen concentrate (Rr = 0.26%). The participants with the highest mean reflectance may have included inertinite readings because their SDs were also high. The corresponding values in the kerogen concentrate were always lower, indicating that inertinite was easier to exclude in this sort of preparation.

Two populations of vitrinite were identified in sample OMC4 and the analyses centered around Rr=0.23% and Rr=0.42% (Fig. 6). The scatter reported by participants, with reflectance values ranging between 0.24% and over 0.55% for both the whole rock and the kerogen concentrate reflects the preference for one or another population (Table 2). Also about half of the participants reported SD of

0.09% or above, which for such low reflectance values (GM around 0.45%) indicate a significant scatter in the readings. Similar scatter as a result of differences in criteria for selecting the vitrinite population has been reported for other organic-rich samples (Borrego et al., 2006).

3.2. Whole rock vs. kerogen concentrates results

The pair of results of each participant corresponding to whole rock reflectance and kerogen concentrate reflectance is plotted in Figure 7 for the four samples analysed. This plot allows identification of any positive or negative deviation of results as a function of the type of sample preparation analysed. If the results randomly scatter around the angle bisector, which corresponds to equal vitrinite reflectance values in whole rock and kerogen concentrate, no effect of isolation on reflectance can be deduced. On the contrary values over or below the angle bisector indicate systematically higher or lower vitrinite reflectance values in either whole rock or the kerogen concentrate.

As seen in Figure 7 the values are close to the angle bisector in the higher maturity samples (Fig. 7a and c), indicating very similar vitrinite reflectance values in both types of sample preparation. A value in the OMC1 sample plots close to the angle bisector but at a higher reflectance (Participant E; Table 2) suggesting the inclusion of an inertinite population in both the whole rock and the kerogen concentrate samples. A single value plots far away from the angle bisector in sample OMC3 (Fig. 7c), indicating the measurement of a different population in the kerogen concentrate and the whole rock. Among the values plotting very close to the line, the majority tended to be over the line indicating slightly higher reflectance vitrinite in the kerogen concentrate.

For the low-rank samples (Fig. 7b and d), larger differences between values recorded in the kerogen concentrate and whole rock were observed. The reflectance numbers reported in the sample with terrestrial organic matter (OMC2) were higher for the kerogen concentrate than for the whole rock. This is thought to be a result of an improvement in polishing quality of the kerogen concentrate, once the mineral matter was removed (Mendonça Filho et al., 2008). A similar result was

reported by Barker (1996), although, in this study, the effect of polishing was considered negligible and the difference was attributed to an easier selection of indigenous vitrinite in the whole rock. Slightly higher reflectance values in the whole rock than in the kerogen concentrate were recorded in the low rank marine derived sample (OMC4). The values of participant Q indicated the measurement of a different suite of particles in the kerogen concentrate and the whole rock preparation. The plot in Figure 7 allows a detailed discussion of the reflectance values obtained by the participants in the whole rock vs the kerogen concentrate for the four samples analysed stressing the differences of the values. A similar plot in the maturity range peat-anthracite (0.2-2.0% vitrinite reflectance) showed that the values obtained by the different participants for the samples analysed (Fig. 8) grouped generally close together supporting the consistency of the reflectance values provided by different analysts.

A similar type of plot for the SD allowed a comparison of the scatter of measurements in the different samples. The continental samples (Fig. 9a and b) generally showed low dispersion around the angle bisector and a concentration of the points below 0.10% standard deviation. In the marine samples (Fig. 9c and d), the range of standard deviation is larger, as is the scatter around the angle bisector. When the standard deviations of kerogen concentrate and whole rock measurements for each sample were compared, no general trends for SD to be higher or lower in one type of preparation were found. Only in the continental low rank sample, slightly SD were recorded for the whole rock preparation compared to the kerogen concentrate (Fig. 9b).

The bias expressed as a multiple of the standard deviation (SMSD) is shown in Table 3, together with the summation of the values (ΣSMSD) and the average values of the unsigned multiple (AUMSD) for both the samples and the analysts. Despite both ΣSMSD and AUMSD being sensitive to the number of values involved, they are still useful to find out significant deviations. Values in Table 3 indicate AUMSD in the range 0.7 to 1.1. The lowest value corresponded to a sample with a large GSD (0.22% in sample OMC3B), which made the test easier and the deviations higher for the sample with the lowest GSD (0.02% in sample

OMC2B). The summation of the deviations was typically below one (Table 3), indicating that the values reported scattered reasonably below and over the mean value.

Regarding the analysts, good values for precision (AUMSD) were obtained with most of the values being below the threshold 1.5. The summation of the signed multiple (ΣSMSD) indicated some preference in the selection of vitrinite population. Analysts I, J, and M showed preference for the lowest-reflecting vitrinite population with some relevant differences. Analyst J selected the lowest-reflecting population in immature samples whereas the mean reflectance was close to the average in mature samples. A lower-reflecting population was selected by analyst I in marine samples and analyst M in continental samples. Calibration difficulties may be the cause for the results of participant E. The measurement of some recycled vitrinite or inertinite of higher reflectance than primary vitrinite might be responsible for the results of participant P and B.

3.3. Spectral fluorescence results

Participants were asked to perform spectral fluorescence measurements on liptinite components if they exhibited enough intensity to be recorded. The number of responses was enough to perform a statistical treatment of results only in the case of alginite from the low-rank marine sample (OMC4). Spectra on other components or other samples were only recorded by one or two participants (Mendonça Filho et al., 2010a). Figure 10 shows examples of liptinite in these samples. The fluorescing organic matter was dominated by yellow to orange lamalginite (Figures 10a-10i). Telalginite identified as *Leiosphaeridia* (Figures 10a and 10j) *and Tasmanites* (Fig. 10c and k) and sporinite (Fig. 10b, g, h and i) were identified between the lamellae. Vitrinite (Fig. 10d and f), inertinite (Fig. 10b and g), and pyrite (Fig. 10i) were identified among the non-fluorescing components.

Figure 11 shows the fluorescence spectra of alginite provided by participants for the whole rock and kerogen concentrate of sample OMC4. The parameter used to compare the spectra was λ_{max}, the wavelength of the spectral maxima. The λ_{max} values were in the range 520-586 nm for whole rock and 550-

588 for the kerogen concentrate (Table 4) indicating a red shift in the kerogen concentrate compared to the whole rock, thus revealing an influence of preparation methods (acid treatment) on fluorescence properties. An equivalent reflectance value can be calculated from λ_{max} (Mukhopadhyay, 1994). The results of the calculated reflectance were in the range of the experimental values recorded by participants (Table 2 and 4) and were systematically lower for the whole rock than for the kerogen concentrate. The measured GMs were lower than the calculated mean reflectance derived from λ_{max}. This is normally interpreted as indicating vitrinite reflectance suppression, a phenomenon commonly reported in liptinite-rich rocks (Hutton and Cook, 1980; Kalkreuth, 1982; Price and Baker, 1985).

4. Conclusion

The main conclusions from an interlaboratory exercise performed by the International Committee for Coal and Organic Petrology (ICCP) to study the effect of isolating organic matter on optical parameters used for maturity assessment are as follows:

- As expected, it was easier to find appropriate vitrinite particles for reflectance measurements in rocks with terrestrially-derived organic matter than in marine samples. In addition, the primary vitrinite population was easier to identify in the continental samples, as indicated by the generally lower standard deviation of the reflectance readings.
- Comparing the vitrinite reflectance results obtained by participants for the pairs of whole rock/kerogen concentrate, in general similar values were reported for the four samples studied covering different origin of organic matter and maturity. This indicates no effect of the isolation procedure on the vitrinite reflectance regardless the maturity and organic matter type. The differences recorded must be attributed to a different reason. In the case of the lower reflectance values recorded for the whole rock compared to kerogen concentrate in the low-maturity continental rock, the differences can be attributed to the poorer polishing of the whole rock sample. Slightly lower

vitrinite reflectance values were recorded for the kerogen concentrate of the low-maturity marine sample. The difference could not be attributed to a decrease of reflectance during acid treatment, but, rather, to an easier discrimination of recycled vitrinite or inertinite when they are concentrated in the preparation.

- The acid treatment appeared to have an effect on the fluorescence spectra of alginite which were generally shifted to higher wavelengths in the kerogen concentrate as observed for the low-rank marine sample.

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References

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

Barker, C.H., 1996. A Comparison of vitrinite reflectance measurements made on whole-rock and dispersed organic matter concentrate mounts. Organic Geochemistry 24, 251-256.

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, 151 - 170.

Borrego, A.G., 2007. Re-appraisal of previous activities in Commission II. Minutes of the Meeting. ICCP News 42, 20-21. (www.iccop.org/fileadmin/documents/pdf/ICCP42.pdf)

Castaño, J.R., 1995. Isolation Organic Matter Working Group.Final Report 1995. ICCPNews 10, p. 6, 1994. (www.iccop.org/fileadmin/documents/pdf/ICCP10.pdf)

Castaño, J.R., 1996. Isolation Organic Matter Working Group.Final Report 1996. ICCP News 12, p. 6, 1995. (www.iccop.org/fileadmin/documents/pdf/ICCP12.pdf)

Durand, B., Nicaise, G., 1980. Procedures for kerogen isolation. In: Durand B. (Ed.), Kerogen. Insoluble organic matter from sedimentary rocks. Editions Technip,Paris, pp. 35-53.

Espitalié, J., Laporte, J. L., Madec, M., Marquis, Leplat, P., Paulet, J.,Boutefeu, A., 1977. Methode Rapide de Caracterisation des Roches Meres de leur Potentiell Petrolier e de leur Degre d'Evolution. Revue de Institut Francais du Petrole 32, 23-42.

Hutton, A.C. and Cook, A.C., 1980. Influence of alginite on the reflectance of vitrinite from Joadja, NSW and some other coals and oil shales containing alginite. Fuel 59, 711-714.

ISO 7404-5, 1994. Methods for the Petrographic Analysis of Bituminous Coal and Anthracite: Part 5. Method of Determining Microscopically the Reflectance of Vitrinite. International Organization for Standardization, Geneva. 11 pp.

Kalkreuth, W.D., 1982. Rank and petrographic composition of selected Jurassic-Lower Cretaceous coals of British Columbia, Canada. Can. Pet.Geol. Bull. 30, 112-139.

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, 43-51. (www.iccop.org/fileadmin/documents/pdf/ICCP45.pdf)

Mendonça Filho, J. G., Araujo, C. V., Borrego, A. G., Cook, A., Flores, D., Hackley, P., Hower, J., Kern, M. L., Mendonça, J. O., Menezes, T. R., Souza, I.V.A.F., Suarez-Ruiz, I., 2010a. Report on Organic Matter Concentration Working Group (OMCWG 2009). ICCP News 49, 15-28.

Mendonça Filho, J. G., Araujo, C. V., Borrego, A. G., Cook, A., Flores, D., Hackley, P., Hower, J., Kern, M. L., Mendonça, J. O., Menezes, T. R., Souza, I.V.A.F., Suarez-Ruiz, I., 2010a. Report on Organic Matter Concentration Working Group (OMCWG 2009). ICCP News 49, 15-28.

Mendonça Filho, J. G., Menezes, T. R., Mendonça, J. O.Oliveira, A. D. , Carvalho, M. A.; Sant'Anna, A. J.; Souza, J. T., 2010b. Palinofácies. In: Ismar de Souza Carvalho (Ed.), Paleontologia. Interciência, Rio de Janeiro, pp. 379-413.

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. Washington, American Chemical Society Symposium Series 570, p. 1-24.

Price L.C., Baker C.E. 1985. The suppression of vitrinite reflectance in amorphous-rich kerogen. A major unrecognized problem. Journal of Petroleum Geology 8, 59-84.

Senftle J.T, Landis C.R., McLaughlin R.L., 1993. Organic Petrographic approach to kerogen characterization. In: Engel M.H., Macko, S.A. (Eds.), Organic Geochemistry. Plenum Press, New York, pp. 355-374.

Whelan J.K., Thompson-Rizer C.L., 1993. Chemical methods for assessing kerogen and protokerogen types and maturity. In: Engel M.H., Macko, S.A. (Eds.), Organic Geochemistry. Plenum Press, New York, pp. 289-353.

Captions for the Figures

Figure 1. Vitrinite reflectance in whole rock versus kerogen concentrate based on the results of the Isolation of organic matter working group of the ICCP in 1995 for the Pictou Shale (IOM 95; a) and in 1996 for the Second White Specks (IOM 96, b) sample (Borrego, 2007 based on Castaño 1995, 1996).

Figure 2. Van Krevelen type plot (Espitalié et al., 1977) showing hydrogen and oxygen indices from studied samples.

Figure 3. Scheme of the sample preparation procedure.

Figure 4. Example of different vitrinite particles in the studied samples.

Figure 5. Example of different organic components found in sample OMC3 which could have been measured as vitrinite by some participants: a) zooclast in reflected white light; a1) same field in fluorescence, b) solid bitumen in reflected white light; b1) same field in fluorescence; c) solid bitumen in reflected white light; c1) same field in fluorescence d and g) examples of inertinite as a fragment and forming part of a tissue; f and g) examples of vitrinite.

Figure 6. Examples of a low reflecting vitrinite population (a-b) and a higher reflecting vitrinite population (c-d) in sample OMC4

Figure 7. Plot of reflectance values reported in the whole rock samples versus the kerogen concentrates. a) OMC1-medium rank terrestrial organic matter, b) OMC2-low rank terrestrial organic matter; c) OMC3-medium rank marine organic matter; d) OMC4-low rank marine organic matter

Figure 8. Plot of reflectance values reported in the whole rock samples versus the kerogen concentrates in a similar reflectance interval (0.2-2.0%). a) OMC1-medium rank terrestrial organic matter, b) OMC2-low rank terrestrial organic matter; c) OMC3-medium rank marine organic matter; d) OMC4-low rank marine organic matter

Figure 9. Plot of standard deviation reported by participants in the whole rock samples versus the kerogen concentrates. a) OMC1-medium rank terrestrial organic matter, b) OMC2-low rank terrestrial organic matter; c) OMC3-medium rank marine organic matter; d) OMC4-low rank marine organic matter

Figure 10. Examples of Liptinites in OMC4; a-e examples from whole rock preparation; f-i, example from kerogen concentrate and j-l examples from strew mounts (J – *Leiosphaeridia*; k- *Tasmanites*; l- Sporomorph). All photomicrographs were taken under fluorescence mode.

Figure 11. Spectral curves for alginite of samples OMC4A and OMC4B.

Table(s)

Table 1 - Distribution of vitrinite reflectance as reported by the participants

Results	Sample OMC1A			Sample OMC1B			Sample OMC2A			Sample OMC2B		
	Whole-Rock			*Kerogen Concentrate*			*Whole-Rock*			*Kerogen Concentrate*		
	Rr (%)	SD	N	Rr (%)	SD	N	Rr (%)	SD	N	Rr (%)	SD	N
A	1.15	0.05	50	1.14	0.04	50	0.40	0.08	50	0.41	0.02	50
B	1.06	0.09	50	1.07	0.08	50	0.39	0.05	37	0.42	0.03	50
C	1.03	0.03	72	1.03	0.02	63	0.41	0.01	50	0.41	0.01	51
D	1.17	0.04	61	1.16	0.05	52	0.35	0.03	51	0.37	0.03	50
E	1.52	0.08	50	1.41	0.08	50	0.38	0.04	22	0.38	0.04	50
F	1.01	0.19	50	1.09	0.06	50	0.34	0.09	50	0.40	0.09	50
G	1.25	0.07	50	1.22	0.05	50	0.37	0.06	50	0.38	0.06	50
H	1.22	0.05	51	1.17	0.06	43	0.35	0.05	46	0.37	0.04	40
I	1.14	0.07	50	1.24	0.09	50	0.38	0.06	8	0.43	0.05	20
J	1.14	0.08	50	1.12	0.06	50	0.30	0.04	50	0.37	0.03	50
K	1.02	0.06	50	1.02	0.05	50	0.40	0.02	50	0.41	0.02	50
L	1.04	0.03	50	1.04	0.03	50	0.42	0.03	49	0.44	0.04	49
M	1.01	0.09	50	1.09	0.05	50	0.34	0.08	50	0.39	0.05	50
N	1.12	0.10	100	1.10	0.06	100	0.34	0.04	100	0.37	0.04	100
O	1.25	0.06	50	1.24	0.06	50	0.38	0.05	50	0.39	0.05	25
P	1.27	0.05	22	1.22	0.04	22	0.39	0.05	16	0.44	0.05	16
Average	**1.15**			**1.15**			**0.37**			**0.40**		
SD	**0.13**			**0.10**			**0.03**			**0.02**		

Table 2 - 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 3 - Accuracy of results calculated against the mean group and standard deviation data, for each sample analyzed: SMSD, AUMSD and ASMSD

Results	SMSD	AUMSD	ASMSD	BIAS
A	0.93	0.26	0.23	Low
B	-0.02	0.70	-0.01	Low
C	-0.2	0.97	-0.05	Low
D	-1.44	0.52	-0.36	Low
E	4.88	1.57	1.22	High
F	-2.49	0.72	-0.62	Medium
G	0.81	0.57	0.20	Low
H	-1.23	0.71	-0.31	Low
I	2.05	0.56	0.51	Medium
J	-3.71	0.93	-0.93	Medium
K	-0.88	0.93	-0.22	Low
L	1.20	1.24	0.30	Low
M	-2.65	0.66	-0.66	Medium
N	-2.87	0.72	-0.72	Medium
O	1.38	0.58	0.35	Low
P	3.99	1.00	1.00	Medium

Table 4: Distribution of vitrinite reflectance as reported by the participants.

Results	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**			**0.10**		

Table 5: New distribution of vitrinite reflectance excluding the anomalous value.

Results	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**	

Table 6: **Accuracy of results calculated against the group mean and standard deviation data: SMSD (Signed Multiple of the Standard Deviation), AUMSD and ASMSD.**

Results	SMSD	AUMSD	ASMSD	Remarks
A	0.19	0.85	0.05	Low
B	0.73	1.37	0.18	Low
C	3.4	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	0.6	0.32	Low
H	1.56	0.39	0.39	Low
I	0.13	0.6	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

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

Results	Parameters	Organic Component	WR OMC4A	KC 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

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

λ_{max} values OMC4A	Equivalent Rr OMC4A	Group Mean OMC4A	λ_{max} values OMC4B	Equivalent Rr OMC4B	Group Mean OMC4A
520	0.38	0.45 SD = 0.11	550	0.53	0.41 SD = 0.11
520	0.38		550	0.53	
530	0.43		550	0.53	
530	0.43		557	0.54	
530	0.43		565	0.57	
538	0.49		565	0.57	
567	0.58		569	0.59	
580	0.65		580	0.65	
Mean	**0.47**		**Mean**	**0.57**	
SD	**0.10**		**SD**	**0.06**	

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

Figure(s)

Figure 1

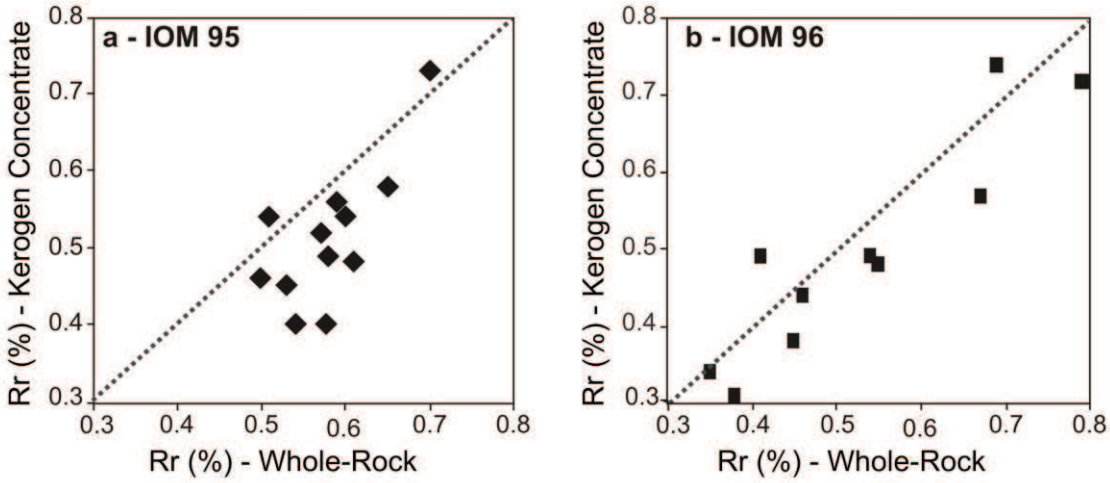
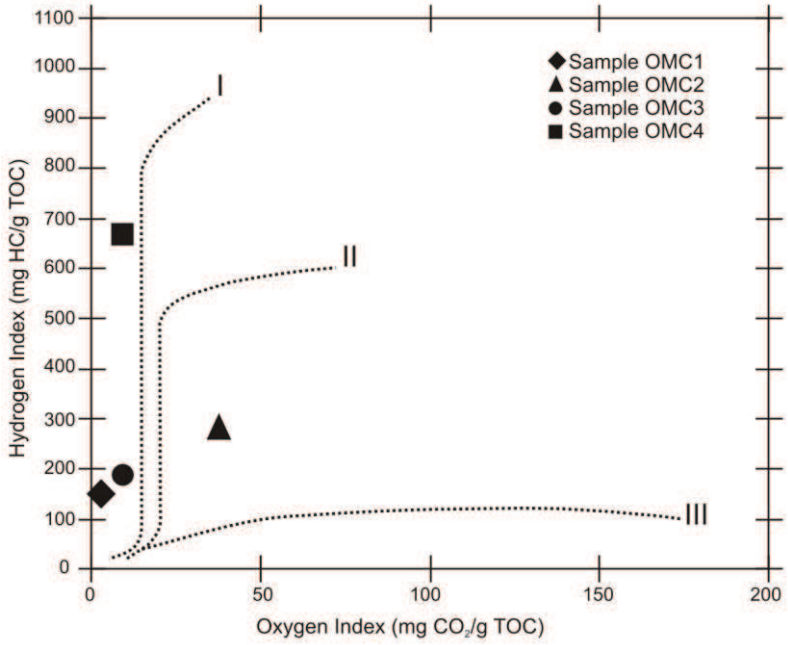


Figure 2


Sample OMC1
Sample OMC2
Sample OMC3
Sample OMC4
I
II
III
Hydrogen Index (mg HC/g TOC)
Oxygen Index (mg CO2/g TOC)
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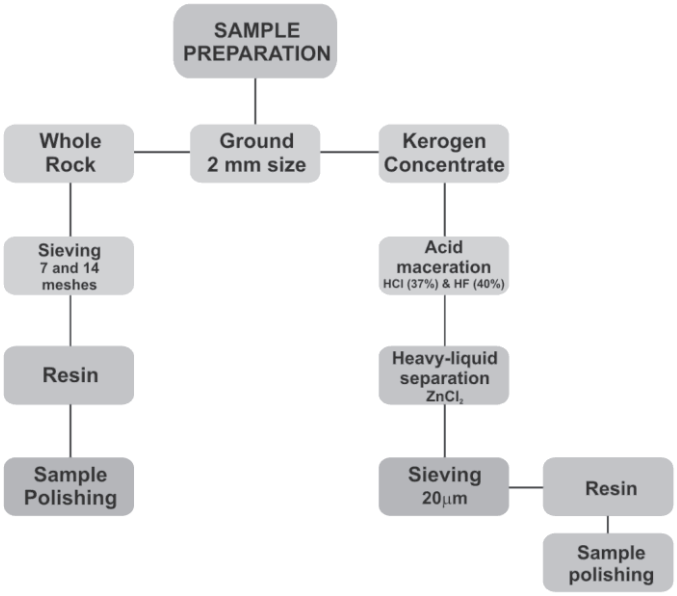
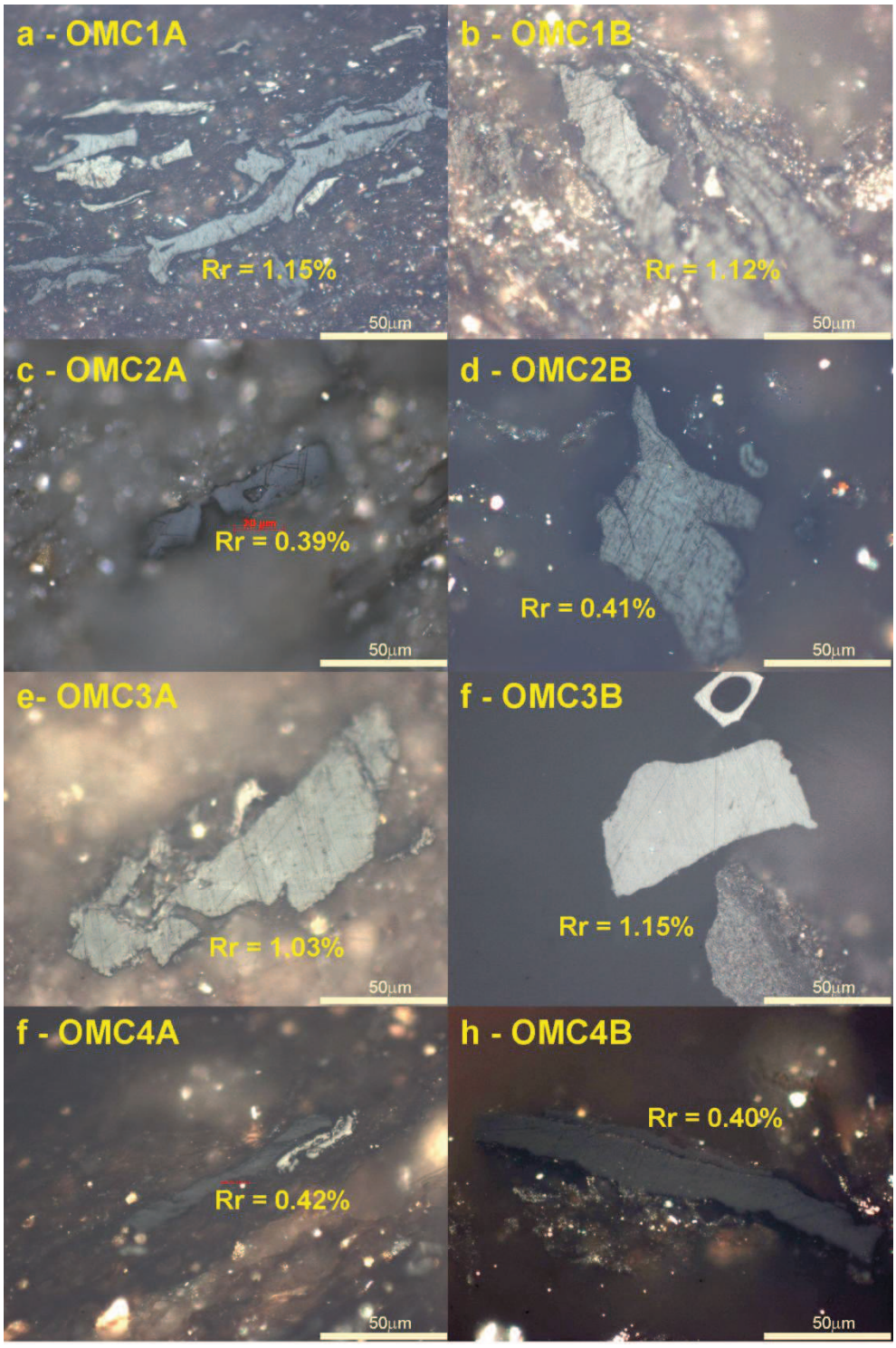
1000
900
800
700
600
500
400
300
200
100
0
0
50
100
150
200

Figure 3


SAMPLE PREPARATION
Whole Rock
Ground 2 mm size
Kerogen Concentrate
Sieving 7 and 14 meshes
Acid maceration HCl (37%) & HF (40%)
Resin
Heavy-liquid separation ZnCl2
Sample Polishing
Sieving 20μm
Resin
Sample polishing

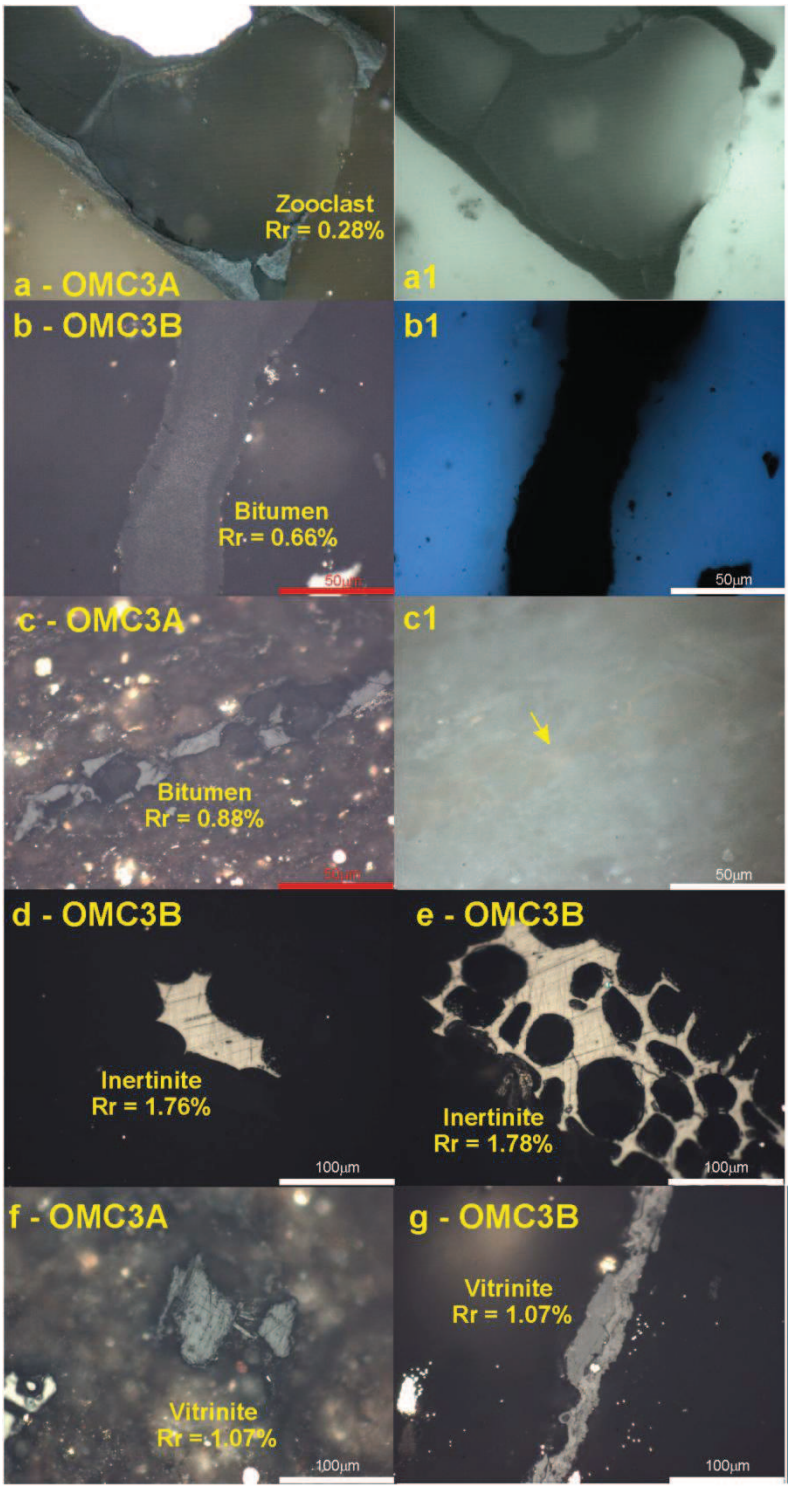
Figure(s)

Figure 4



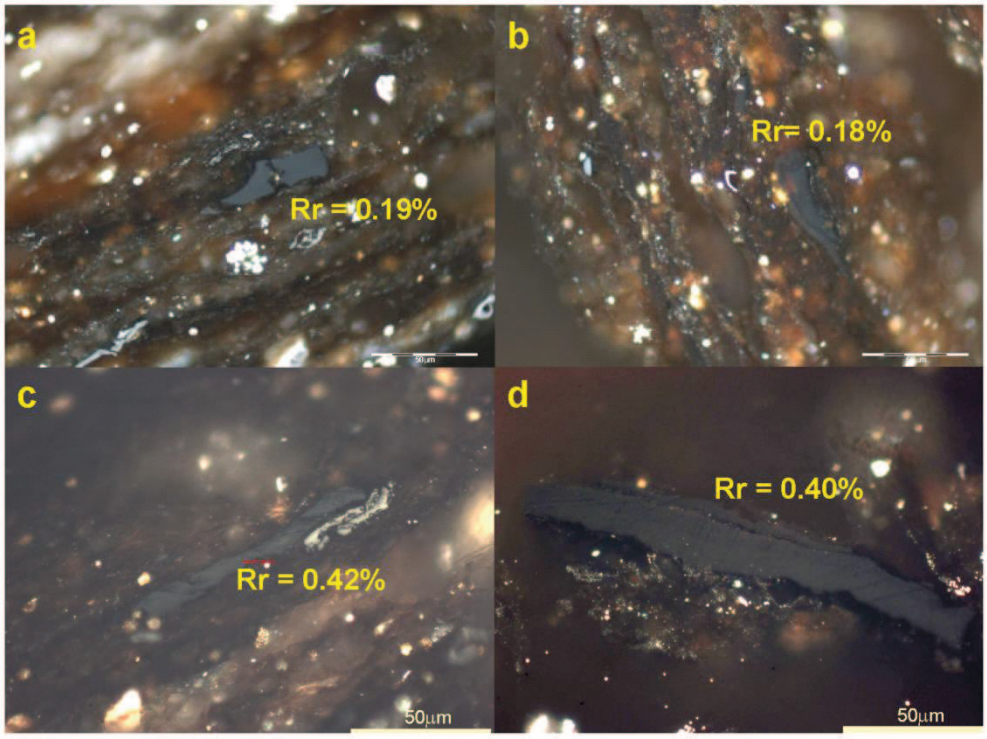
Figure(s)

Figure 5



Figure(s)

Figure 6



Figure(s)

Figure 7

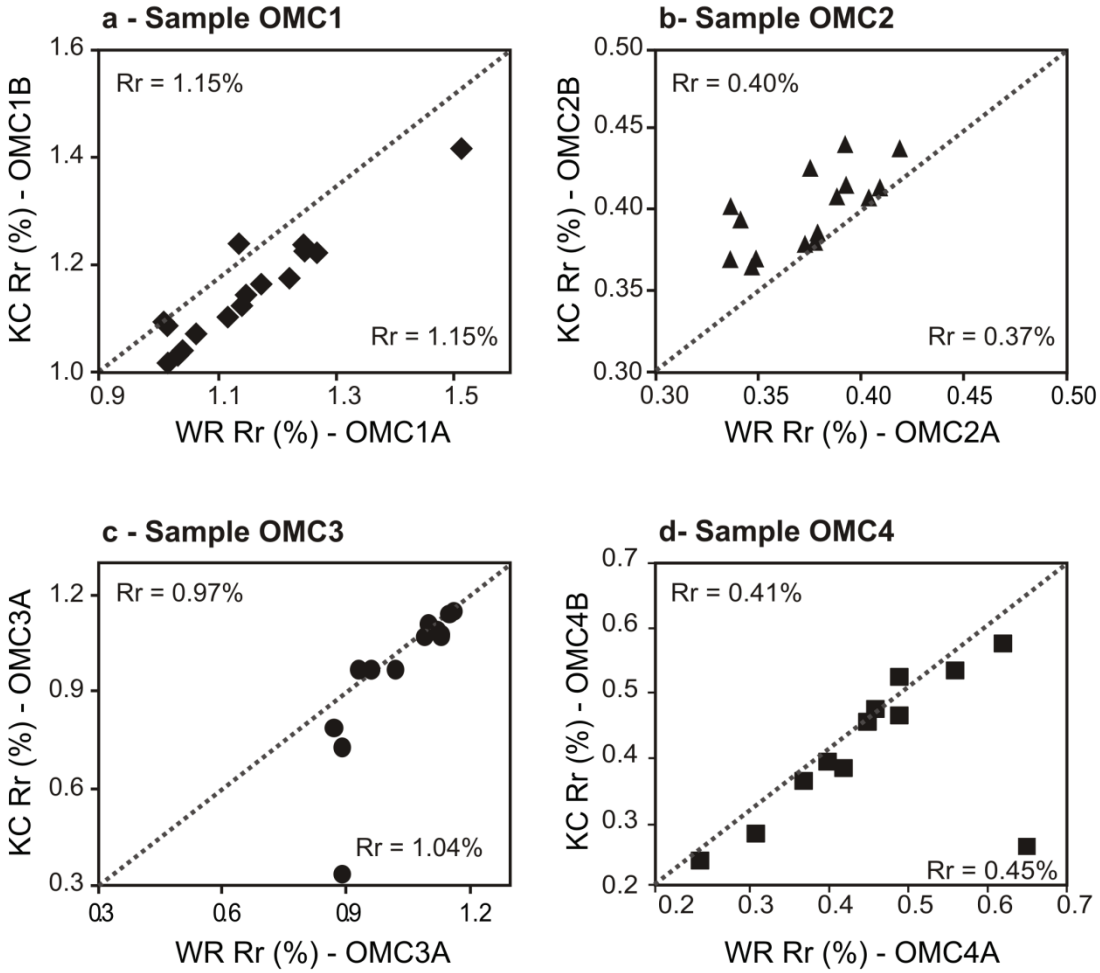


Figure 8

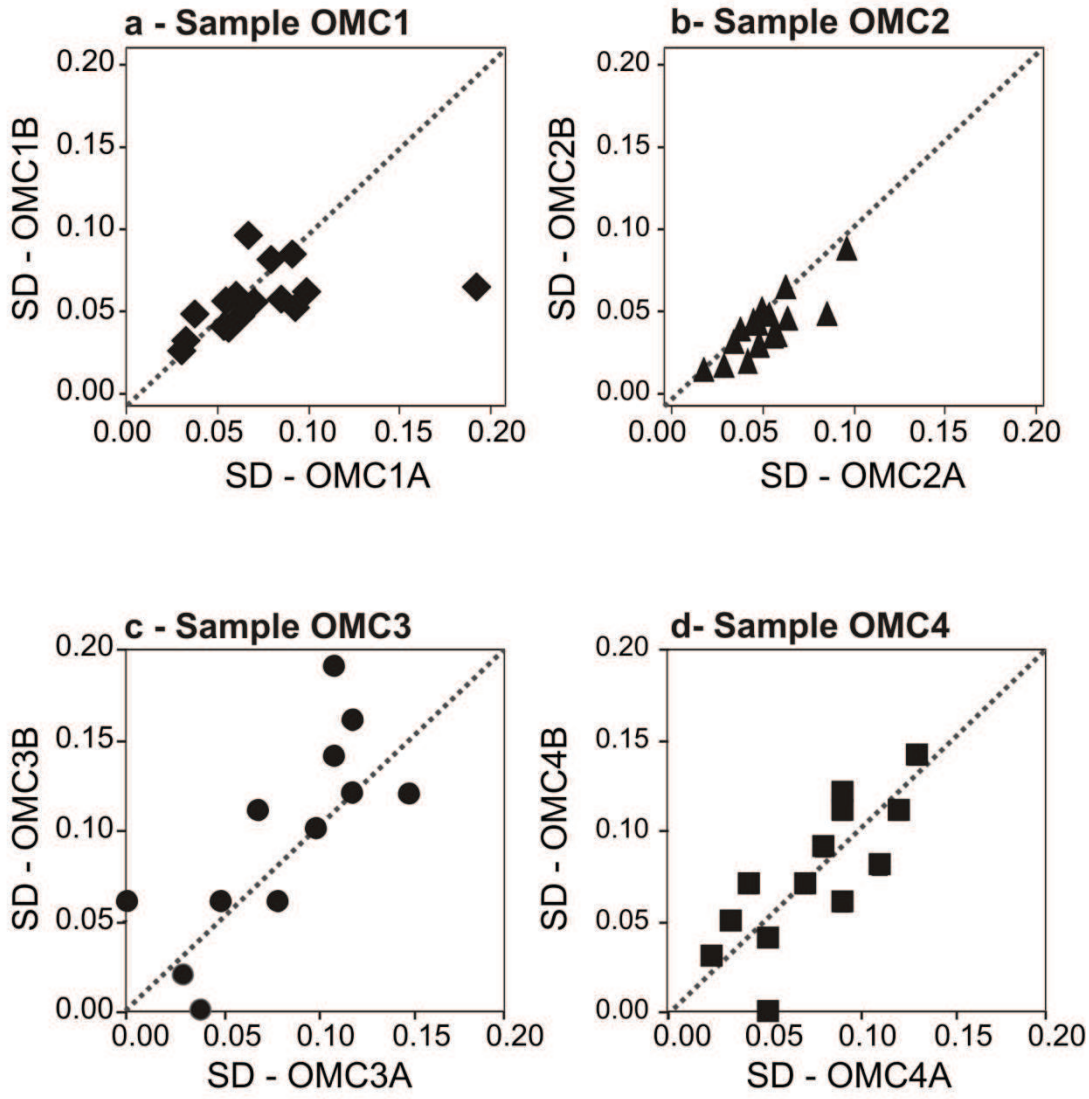
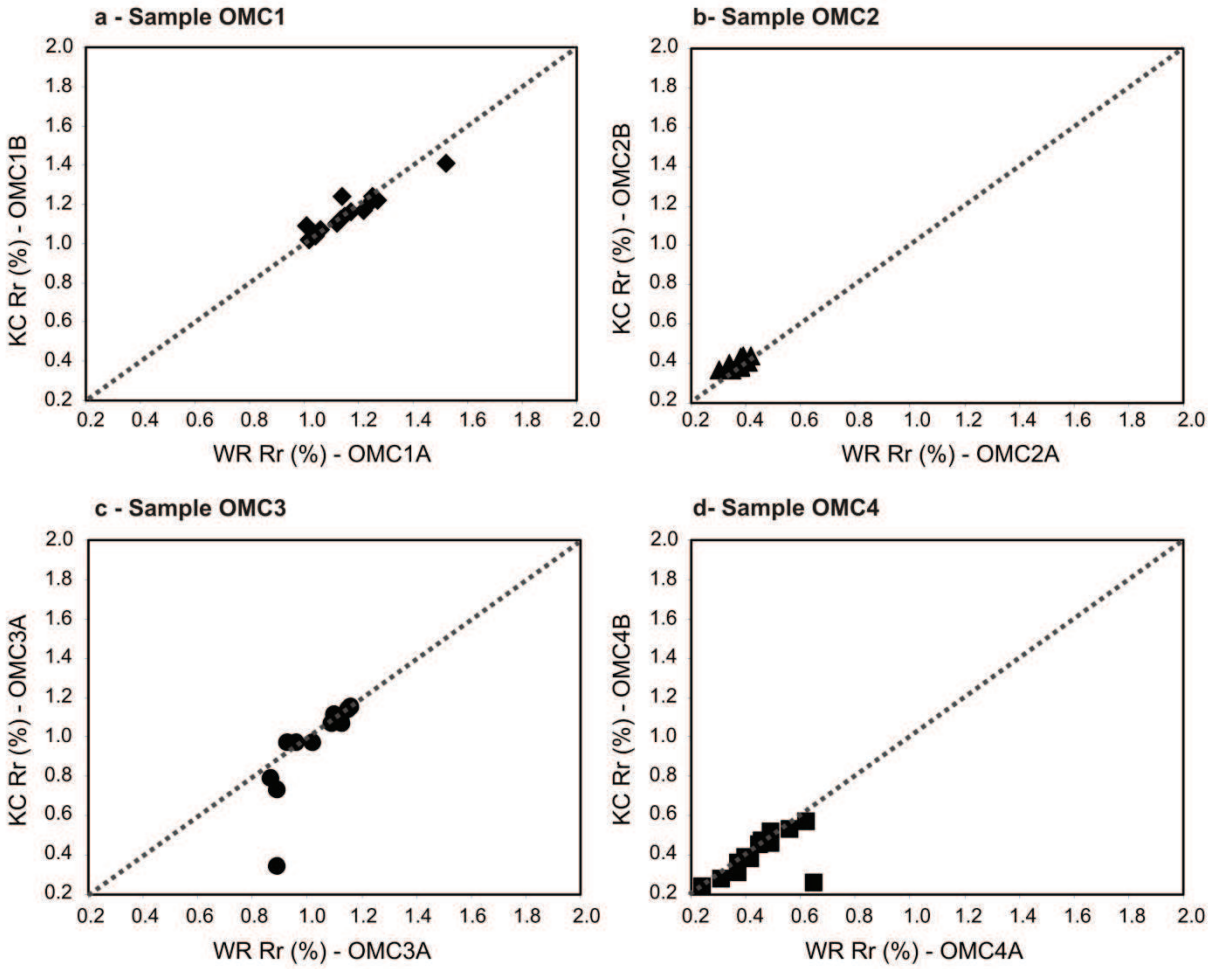

a - Sample OMC1
SD - OMC1B
SD - OMC1A
0.00
0.05
0.10
0.15
0.20
b- Sample OMC2
SD - OMC2B
SD - OMC2A
c - Sample OMC3
SD - OMC3B
SD - OMC3A
d- Sample OMC4
SD - OMC4B
SD - OMC4A

Figure 9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KC Rr (%) - OMC1B
WR Rr (%) - OMC1A
b- Sample OMC2
KC Rr (%) - OMC2B
WR Rr (%) - OMC2A
c - Sample OMC3
KC Rr (%) - OMC3A
WR Rr (%) - OMC3A
d- Sample OMC4
KC Rr (%) - OMC4B
WR Rr (%) - OMC4A
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

Figure(s)

Figure 10

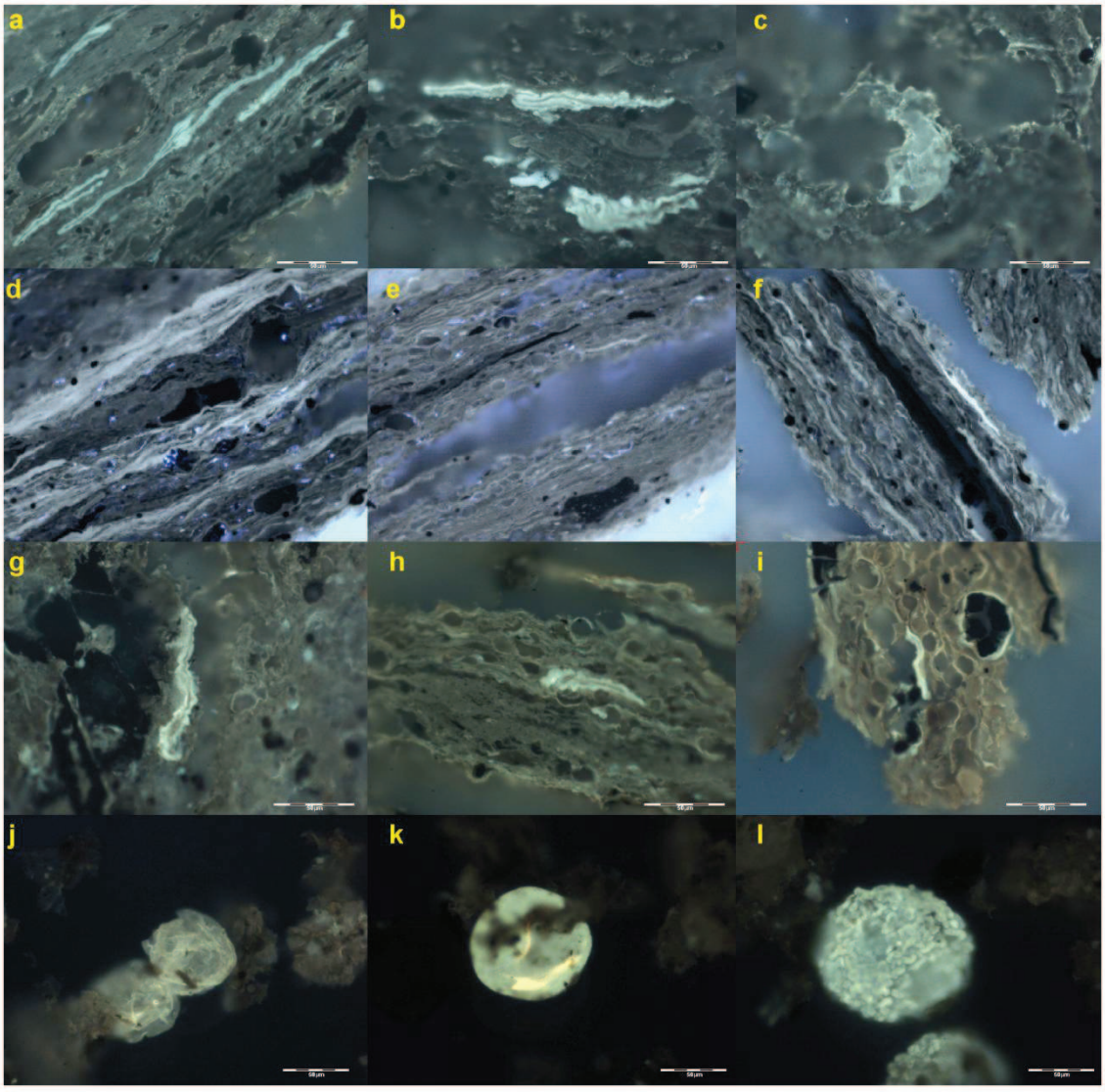
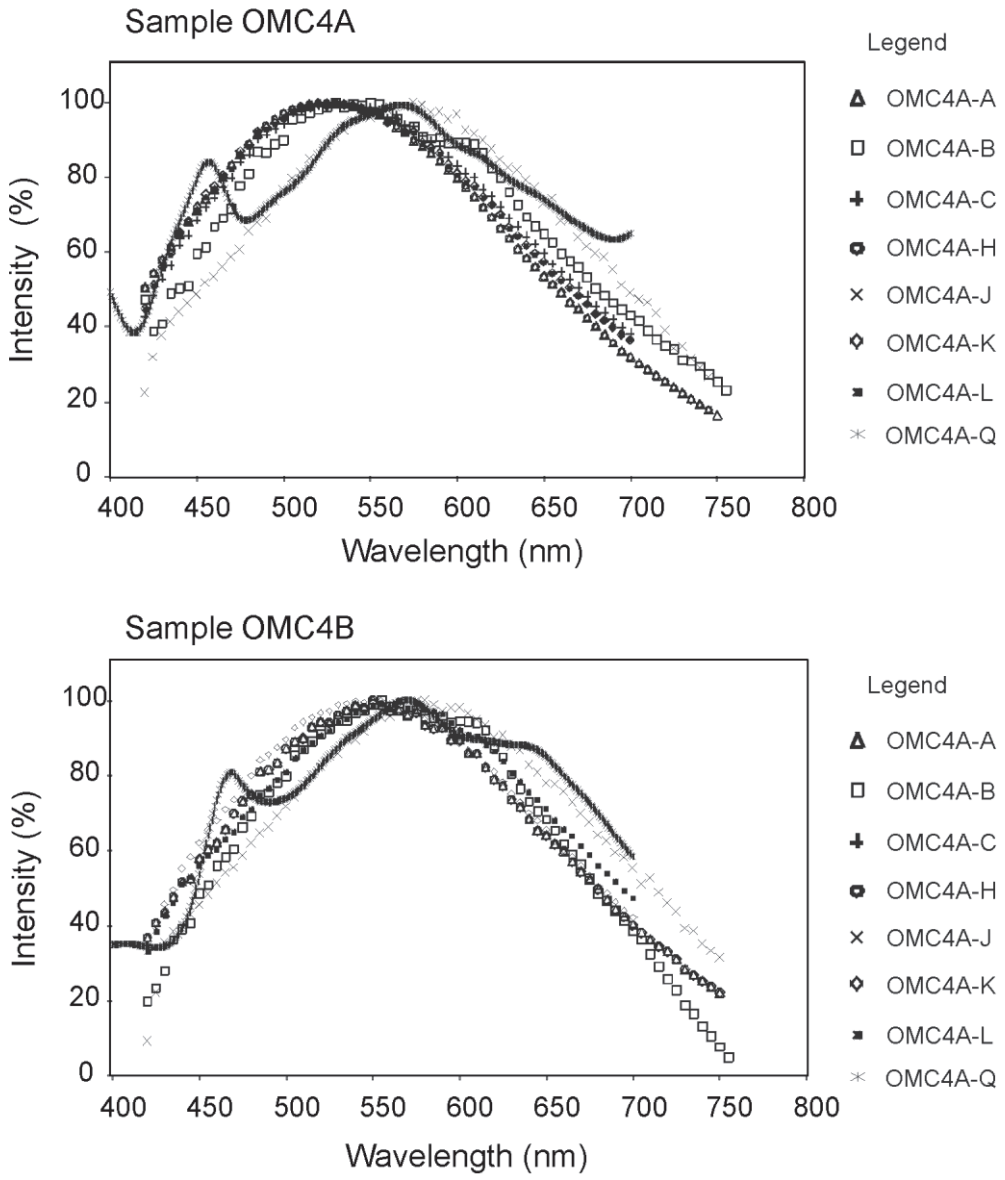


Figure 11


Sample OMC4A
Intensity (%)
Wavelength (nm)
Legend
OMC4A-A
OMC4A-B
OMC4A-C
OMC4A-H
OMC4A-J
OMC4A-K
OMC4A-L
OMC4A-Q
Sample OMC4B
Intensity (%)
Wavelength (nm)
Legend
OMC4A-A
OMC4A-B
OMC4A-C
OMC4A-H
OMC4A-J
OMC4A-K
OMC4A-L
OMC4A-Q