1   **Diagenetic thermal evolution of organic matter by Raman spectroscopy**

2   Andrea Schito [a], Claudia Romano [a], Sveva Corrado [a], Domenico Grigo [b], Brent Poe [c]

3   [a] Dipartimento di Scienze, Sezione di Scienze Geologiche, Università degli Studi Roma Tre, L.go S.
4   Leonardo Murialdo 1, 00146, Roma, Italy
5   [b] Eni SpA e Exploration & Production Division, Via Emilia, San Donato Milanese, MI, 20097, Italy
6   [c] Dipartimento di Geotecnologie per l'Ambiente ed il Territorio, Università degli Studi "G. d'Annunzio" –
7   Chieti, Via dei Vestini 30, 66013 Chieti Scalo, Italy

8

9   **Corresponding author.**

10   E-mail address:**andrea.schito@uniroma3.it**

11

12   **Keywords:** thermal maturity; dispersed organic matter; Raman spectroscopy; diagenesis

13

14   **Abstract**

15   Vitrinite reflectance is considered one of the most reliable indicators of thermal maturity in sedimentary
16   basins and is widely used to calibrate numerical models that assess hydrocarbon generation/expulsion from
17   source rocks. Nevertheless, ambiguities in vitrinite reflectance can occur from variations in composition and
18   preservation state of **organic facies**, temperature/ pressure conditions and **the abundance of** organic matter
19   resulting in incorrect or uncertain assessments of petroleum systems.
20   **This study** presents an original application of Raman spectroscopy to assess the diagenesis - catagenesis of
21   kerogen between the immature and mid-mature stages of hydrocarbon generation. Kerogens were isolated
22   from 33 intervals of drill cuttings from a 5 km thick Oligocene-Miocene siliciclastic section of the Malembo
23   Formation (Lower Congo Basin, Angola). Their Raman spectra were obtained and derived parameters were
24   compared to depth and to previously reported equivalent vitrinite reflectance values. The best correlations
25   between thermal maturity and Raman parameters were found for D-G band distance; FWHM of the G band;
26   D/G area ratio; RA2 ratio (calculated as S+Dl+SD/Dr+Gl+G band ratio) and the D/G width ratio. The
27   Raman parameters were not influenced by varying kerogen composition (mixed type II/III). The technique
28   offers the potential to reduce the risk of source rock thermal maturity assessment even when organic facies
29   rich in amorphous organic matter are present.

30

31

32   **1 Introduction**

33   Quantitative evaluation of the thermal maturity of organic matter (OM) dispersed in sediments is a key
34   element **in assessing the processes of** hydrocarbon (HC) generation/expulsion in petroleum systems. It is
35   linked to the thermal evolution of sedimentary basins and orogenic belts (**Corrado et al., 2010**; Allen and
36   Allen, 2013; Hackley and Cardott, 2016). Vitrinite reflectance analysis is considered a highly reliable and

reproducible measure of thermal maturity of coals. Its application to organic matter dispersed in sediments is a common practice, but there are inherent limitations that can lower the accuracy of the measurement. In many marine sediments, primary vitrinite macerals are absent or very sparse and it is often difficult to obtain **good results** without interference from eroded, secondary sources. Vitrinite reflectance in dispersed organic matter can also be effected **by other processes such as** oxidation during transport, preservation, and retardation and/or suppression. Numerical models calibrated against ambiguous vitrinite reflectance data can yield inaccurate or biased results. Alternative analytical techniques based on the analysis of both the organic and inorganic fraction of sediments can minimize these limitations (e.g., Aldega et al. 2007; Corrado et al., 2009; Federici et al., 2010; Di Paolo et al., 2012; Cantarelli et al., 2013; Andreucci et al., 2014; Schito et al., 2016).

Raman spectroscopy is a potential powerful non-destructive tool to quantitatively evaluate thermal maturity of organic matter (e.g., Beyssac et al., 2002; Quirico et al., 2005; Guedes et al., 2010, 2012; Lahfid et al., 2010; Liu et al., 2012, Hinrichs et al., 2014; Wilkins et al., 2014; Zhou et al., 2014; Lünsdorf, 2016; Mum and Inan, 2016; Ferralis et al., 2016). Advances in instrumentation and data processing have spurred increased applications,and the technique is now simple, fast and can be performed directly on standard petrographic thin sections or on bulk kerogen.

Specifically, two bands on Raman spectra, **namely G** (graphitic) and D (disordered), are related to the growth of the ordered domains with respect to the disordered ones in the organic matter (Tuinstra & Koenig, 1970). Parameters linked to D and G bands have been used to show reliable correlations with paleotemperatures between 200 °C **and 650 °C** (Wopenka and Pasteris, 1993; Beyssac et al., 2002; Aoya et al., 2010; Lahfid et al., 2010; Endo et al., 2012) and against thermal maturity between 1 and 5-6 R_o% (Kelemen and Fang, 2001; Jehlička et al., 2003; Quirico et al., 2005; Guedes et al., 2010; 2012; Liu et al., 2012; Hinrichs et al., 2014; Wilkins et al., 2014; Zhou et al., 2014; Lünsdorf, 2016; Mum and Inan, 2016).

The range of thermal maturity spanning **the** diagenetic to mid-catagenesic stages (corresponding to R_o% 0.4-1.2) has been explored systematically in only a **few studies** (Wilkins et al., 2014; Hinrichs et al., 2016; Lünsdorf, 2016). These report considerable uncertainties at the **low** maturity stages, which are usually the most critical in constraining basin models.

In this **study,** we examine the applicability of Raman spectroscopy as a thermal indicator in the range between the immature and middle mature stages of HC generation, when applied to type II/III kerogen composed mainly **of** amorphous organic matter (AOM). We present the procedures and **analytical results** of the first order Raman spectra performed on Cenozoic organic matter dispersed in sediments of the Malembo Formation drilled in Lower Congo Basin (Angola) that records this maturity range. We demonstrate that robust parameterization of the thermal maturity of dispersed organic matter is possible using Raman indicators.

2 Methods and Materials

74 *2.1 Kerogen and thermal maturity*

75 Kerogen is the insoluble macromolecular fraction of sedimentary organic matter (Vandenbroucke and

76 Largeau, 2007) and is the precursor of oil and gas resources. Dispersed OM is usually highly heterogeneous

77 and reflects differences in its origin and preservation state. Different classifications of kerogen exist, based

78 on optical analyses performed in reflected and transmitted light or rooted on bulk parameters, such as H/C

79 and O/C atomic ratios or Hydrogen and Oxygen indexes derived from pyrolysis yields and TOC values.

80 In this work, we mainly refer to classifications based on optical organic petrography using transmitted light

81 microscopy (Teichmüller, 1986; Tyson, 1995**).** Kerogen composition is classified into four classes from

82 which the abundance and distribution of hydrogen-rich macerals can be discerned: 1) AOM: amorphous

83 organic matter; 2) MPH: marine phytoplankton; 3) CWF: continental wooden organic matter, namely

84 phytoclasts; and 4) CHF: continental herbaceous fragments.

85 Analyses were performed on 33 samples originating from cuttings taken from a 5000 meter thick section

86 drilled offshore Angola (Malembo Formation - Lower Congo Basin). The succession ranges from Oligocene

87 to Upper Miocene and is composed mainly of organic-rich shales interbedded by nearshore to deepwater

88 sandstones (Schito et al., 2016).

89 **Organic matter** of different origin and preservation state, detected through transmitted light analyses, were

90 found in the upper section of the well (depth: 1290-3360m) where woody fragments (CWF) and herbaceous

91 fragments (CHF) of **terrigenous** origin coexist with amorphous organic matter (AOM) and marine

92 phytoplankton (MPH). In contrast, the lower part of the well (depth: 3600-4950 m) is mainly composed of

93 amorphous organic matter with traces of bitumen (Table 1, Schito et al., 2016). Reflected light analyses on

94 kerogen indicate that organic matter of woody fragments of continental origin are represented by vitrinite

95 group macerals, whereas inertinite group macerals are totally absent (Table 1, Schito et al., 2016).

96 The maturation pattern of the well ranges between about 0.35 and 1.5 expressed as vitrinite reflectance

97 values (R_o%) as reported in Corrado et al. (2016) and Schito et al. (2016).

98

99 *2.2 Sample preparation*

100 Kerogens were extracted using a wet-chemical acid demineralization **technique** according to Robl and Davis

101 (1993) and Schimmelmann et al. (1999). Samples were lightly ground in an agate mortar for about 1 minute.

102 Carbonates were dissolved by adding HCl on the dried samples. The HCl was added in small increments to

103 prevent excessive foaming. Digestion of remaining silicates was done by adding a **mixture composed in equal**

104 **parts by distilled water and HF concentrated at 40% weight percent** (45 ml) to 5 g of sample and placed on

105 a shaker table for 2 hours. Kerogen isolates plus any acid-resistant minerals were recovered and washed 5-6

106 times with distilled water.

107

108 *2.3 **Raman Spectroscopy and curve fitting***

109 Raman spectroscopy was performed on the kerogen isolates using a Jobin Yvon micro-Raman LabRam system

110 in a backscattering geometry. Data were collected over the range of 700-2300 cm^{-1} (first order Raman

111   spectrum) using a 600 grooves/mm spectrometer gratings and CCD detector. A Neodimium-Yag laser at 532 nm

112   (green laser) was used as the light source and optical filters adjusted the power of the laser (<0.4mW). The

113   Raman backscattering was recorded after an integration time of 20 seconds for 6 repetitions for each

114   measurement. This, together with the use of green laser and optical filters, allowed us to reduce the fluorescence

115   background to minimal values. Between ten and fifteen measurements were performed for each samples to

116   ensure reproducibility of measurements. Each organic grain was analysed with a 2 μm diameter spot using a

117   50× optical power objective.

118   **Raman spectra of** highly disordered carbon materials, are affected by interference due to high fluorescence

119   caused by the diffuse presence of hydrogen or residual mineral matter. The first step **in the analysis of** the

120   spectra is the removal of the high fluorescence background by a baseline subtraction procedure. Once the

121   procedure is optimized, it then must be reproduced for the entire set of samples.

122   Baseline subtraction was performed using a third order polynomial curve that best followed the real trend of the

123   fluorescence in the most immature samples with high fluorescence background. In order to avoid errors induced

124   by differences in the spectra range considered by the subtraction, we fixed baseline points at 1000 and 1850 cm^{-1}

125   for all spectra. A polynomial curve was chosen with respect to the linear baseline because the latter tends to

126   overestimate the D and G peaks intensities. We observed that the maximum difference resulting from baseline

127   correction was detected for the D band intensity, whose values tend to be higher by 10-15 %.

128   After **removal of the background**, the spectra were deconvoluted using LabSpec 6 software by Horiba. As the

129   Raman spectra of OM in diagenetic conditions show broad overlapping bands and multiple curve-fitting

130   solutions exist (Lünsdorf and Lünsdorf, 2016), we **found** that the best solution using the minimum number of

131   components was attained using a six band deconvolution with a mixed Gaussian-Lorentzian band profile. **The**

132   **goodness of fit** is defined by the minimum values of the χ^2 value (less than 3 according to Sadezky et al., 2005).

133   Several attempts to use only five bands fitting systematically provided χ^2 values two or three times higher than

134   those obtained with a six bands approach. All spectra were deconvoluted using the six peak deconvolution

135   procedure.

136

137   *2.4 Band assignment for Raman spectra in dispersed organic matter*

138   The Raman spectral signal of kerogen is recorded in a "first order" region between 1000 and 2000 cm^{-1} and

139   "second order" region between 2000 and 3500 cm^{-1}. Bands in the second order region are generally hidden

140   by fluorescence for low mature samples (Beyssac et al., 2002) and were not observed in this study. The first

141   order Raman spectra for **carbonaceous** materials consist of two main bands known as the D and G bands

142   (Tuinstra and Koenig, 1970; Friedel and Carlson, 1972) and other bands that vary depending on the rank (Li,

143   2007; Potgieter-Vermaak et al., 2011). The G band is the only Raman active vibration in crystalline graphite

144   at 1582 cm^{-1} (Tuinstra and Koenig, 1972; Reich and Thomsen, 2004; Pimenta, 2007) and is related to the in-

145   plane vibration of the carbon atoms in the graphene sheets.

146   The D band at 1350 cm^{-1} becomes active in disordered graphite and its frequency depends on the excitation

147   laser (Pócsik et al., 1998). Its origin has been interpreted as a results of a double resonant Raman scattering

148 process (Pócsik et al., 1998; Reich and Thomsen, 2004; and Pimenta et al., 2007). Alternatively, the

149 collective intensity of the D band **has been related** to the ring breathing vibration in the graphite sub-unit or

150 polycyclic aromatic compounds (PAHs) (Negri et al., 2002;2004; Castiglioni et al., 2004; Di Donato et al.,

151 2004; and Lünsdorf 2016) or to aromatics with 6 rings **or more** (Li, 2007).

152 When dealing with disordered materials, the contribution of other spectral features at 1100-1200 cm^{-1} and

153 1400-1500 cm^{-1} cannot be neglected and even the assignment of the G and D bands to graphite vibrational

154 modes is questionable. Unfortunately**, there have only been a few** attempt to explain the origin of these

155 bands in disordered materials and these studies are often contradictory (Nemanich and Solin, 1979; Beny-

156 Bassez and Rouzaud, 1985; Ferrari and Robertson, 2000; Castiglioni et al. 2004; Negri et al., 2004; Li et al.,

157 2007; Rebelo et al. 2016). For this reason the assignment of Raman bands for disordered material is still a

158 matter of debate.

159 In high-rank coals, Beyssac et al. (2002) observed the presence of two additional bands in the Raman

160 spectrum: the D2 band, appearing as a right end shoulder of the G band at approximately 1620 cm^{-1} and the

161 D3 band, a wide band residing at approximately 1500 cm^{-1}. These bands have been attributed to out-of-plane

162 defects from tetrahedral carbons (Bèny-Bassez and Rouzaud, 1985), or to small crystallite size (Nemanich

163 and Solin, 1979). Working on carbon material matured at lower temperatures (about 200-320°C), Lahfid et

164 al. (2010) and Sadezky et al. (2005) proposed the presence of an additional band called D4 at about 1200 cm^{-1}

165 , attributed to sp^3-sp^2 bonds or C–C and C=C stretching vibrations of polyene-like structures.

166 In a recent study, Ferralis et al. (2016) found the presence of two bands as a broad shoulder of the D bands,

167 called D4 at 1150 cm^{-1} and D5 at 1250 cm^{-1}. In Ferralis et al.'s (2016) work, the two bands **have been**

168 **related to CH species in aliphatic hydrocarbon chains**. The authors confirm this hypothesis by showing a

169 strong correlation between the intensity of D5 or D5+D4 band with the increase of the atomic ratio H:C in

170 the range between almost pure graphite (H:C = 0.01) and weak metamorphosed kerogen (H:C = 0.65).

171 In low maturity coals, the Raman spectra of highly disordered carbonaceous matter are more complex.

172 In Li et al. (2006) and Li (2007), Raman spectra were deconvoluted into 10 bands. The authors attributed a

173 band at about 1700 cm^{-1} (Gl band) to a carbonyl group C=O, while the Gr (1540 cm^{-1}), Vl (1465 cm^{-1}) and

174 Vr band (1380 cm^{-1}) which represent the "overlap" between D and G were assigned to mainly amorphous

175 carbon structures in char, especially smaller ring systems (e.g., with 3-5 fused benzene rings). At lower

176 wavenumbers, they found that the S band (1185 cm^{-1}), together with Sl band (~1220 cm^{-1}), acts as the

177 shoulder of the **D band (1230 cm^{-1}) and mainly represents $C_{aromatic}$–C_{alkyl}, aromatic (aliphatic) ethers**, C–

178 C on hydroaromatic rings, hexagonal diamond carbon sp^3 and C–H on aromatic rings. Finally, the Sr band

179 (1060 cm^{-1}) is assigned to C-H on aromatic rings and the R band (960-800 cm^{-1}) to C-C on alkanes and

180 cyclic alkanes and/or C-H on aromatic rings.

181 **Similarly, based on analyses of carbon nanotubes, Rebelo et al. (2016) proposed new assignments for the**

182 **first order Raman spectra. In their work the G band is fitted with a Lorentzian shape at ~1580 cm^{-1}**

183 **surrounded by a Loretzian Gr peak at ~1610 cm^{-1} and a Gaussian Gl peak near 1500 cm^{-1} . Gl band**

184 **correspond to the same vibration of the G band in low size aromatic (Heise et al., 2009). The "D region"**

185   **is deconvoluted to a central Lorentzian D band at 1350 cm^{-1} and two satellites Gaussian band called Dl**

186   **and Dr (left and right) respectively at ~1250 and ~1400 cm^{-1} that were assigned to identical vibrations of**

187   **the D band, but in low size aromatic domains. Finally, a further band, the S band, was used to fit a**

188   **relatively small feature on the left side of the spectra at around 1120cm^{-1}.**

189   Bands S and Gl were assigned to a fingerprint of polyacetylene-like structures or areas of conjugated double

190   bonds mainly present along the borders of structures where aromaticity has been broken upon functionalization

191   (Shirakawa et al., 1973).

192

193   *2.5 Raman thermal maturity parameters*

194   Debate still exists on how to relate Raman spectral features to carbonization ranks at low thermal maturity levels

195   (Rantish et al., 2016). Tuinstra and Koenig (1970) proposed the relation ID/IG = C(υL)/La (TK relation), to

196   study the **thermal evolution of carbonaceous materials**. ID/IG is the ratio between the intensities of the D and

197   G peaks, La is the lateral dimension (parallel to the graphene planes) of the nanocrystal and $C(υL)$ is a constant

198   which depends on the laser frequency. Taking IG as a reference value, which **is independent** of the size of the

199   crystal (Cançado et al., 2008), Tuinstra and Koenig (1970) found an inverse relation between the intensities of

200   the D band and the crystal dimensions. Following the TK correlation, Wopenka & Pasteris (1993) correlated

201   **certain** Raman parameters with metamorphic zonation as **determined** by mineral assemblages.

202   Subsequently, Yui et al. (1996) demonstrated the high sensitivity of some Raman parameters to metamorphic

203   grade from low-grade to greenschist facies, while Beyssac et al. (2002) developed the so called RSCM

204   geothermometer (Raman Spectroscopy of Carbonaceous Material). RSCM, which expresses a relationship

205   between the Raman parameter R2 (R2 = D/([G + D + D2] area ratio) and metamorphic temperature, was

206   initially calibrated in a range between 330-640°C, and later extended to contact- metamorphic rocks (Aoya et

207   al., 2010) and low-grade metamorphism (Lahfid et al., 2010, RA1 and RA2 parameters; Lünsdorf, 2016).

208   **Given** the low temperature interval **covering** the sub-bituminous coal to the anthracite ranks, spectral features

209   and **carbonization** are not so clearly correlated. In general, FWHM, **positions of** the G and D bands and D/G

210   area ratio are the most **sensitive** parameters to maturation (Sadezky et al., 2005; Jehlicka et al., 2009; Marques

211   et al., 2009; Guedes et al., 2010; Zhou et al., 2014; Hinrichs et al., 2016; Lünsdorf, 2016). Romero-Sarmiento et

212   al. (2014) suggested that the FWHM of the G band shows the best correlation against **Rock-Eval** Tmax values

213   in a set of samples from the Barnett shales (US), and Liu et al. (2012) determined thermal maturity by using the

214   D-G distance in mature to highly mature carbonized samples of solid organic matter.

215

216

217   **3 Results**

218   *3.1 Raman spectra*

219   From a first qualitative assessment of spectral features, we **observed** a regular decrease of the fluorescence

220   signal, **resulting in the reduction** of the slope of the spectra (Fig. 1), and a corresponding narrowing of the G

221   bands along the same trend. We refer to Rebelo et al. (2016) for band nomenclature. Position and bands names

are shown in Figure 2a for **low maturity** OM and in Figure 2b for high maturity OM. Best fit results were
achieved by considering S, Dl and Dr as purely Gaussian, and D, G and Gl as more mixed Gaussian-Lorentzian
functions. **Generally**, in **response to increasing** thermal maturity, the width of the G band decreases, the D-G
peak position difference increases and the Gl area decreases.

3.2 Correlation of Raman parameters against thermal maturity - Malembo Formation

To correlate spectral features with thermal maturity, the following parameters were calculated: D and G
position, D-G distance, full width at half maximum of the D and G bands (FWHM) and D/G intensity, area and
full width at maximum height ratio. Moreover, we redefined the parameters RA1 and RA2 following the work
of Lahfid et al. (2010), calculated as follows:

  1) RA1 = area (S+Dl+D) / area (S+Dl+D+Dr+Gl+G);
  2) RA2 = area (S+Dl+D) / area (Dr+Gl+G).

The D band position decreases slightly with depth from about 1380 cm^{-1} to 1360 cm^{-1}, while the G band position
(Fig. 3a) shows no trends with depth, ranging between 1590 **cm^{-1}** and 1600 cm^{-1} (Fig. 3b). As a consequence, the
D-G difference increases slightly with depth from about 220 **cm^{-1}** to 240 cm^{-1} (Fig 3c).

The full width at half maximum (FWHM) of the D band ranges between 90 cm^{-1} and 110 cm^{-1} with no defined
trend, while the full width at half maximum (FWHM) of the G band decreases from about 90 cm^{-1} to 55 cm^{-1}
(Fig.3d-e). The intensity ratio between the D and G bands does not show any correlation with depth (Fig. 3f),
while the D/G area ratio and full width at maximum height ratio shows a trend of increasing values with depth,
ranging from about 0.5 to 1.0 and 1.0 and 1.8, respectively (Fig. 3g-h). Both RA1 and RA2 show values ranging
from 0.35 to 0.50 for RA1 and from about 0.55 to 1.10 for RA2 (Fig. 3i-j). **The** best correlations with depth are
provided by the D-G difference (Fig. 3c), the FWHM of peak G (Fig. 3e), the D/G area ratio (Fig. 3g), D/G
width ratio (Fig. 3h) and the RA2 parameter (Fig. 3j).

We plotted these parameters against the maturity profile of the well expressed in R_o% (for details see Schito
et al., 2016) in Fig. 4. A power equation was used to fit the D/G area ($R^2 = 0.93$), RA2 ($R^2 = 0.95$) and D/G
width ($R^2 = 0.96$) parameters (Fig.4c-d-e), FWHM-G parameter ($R^2 = 0.91$) and the D-G distance ($R^2 = 0.94$)
were fitted according to a second order polynomial equation (Fig. a-b).

4 Discussions

We observed good correlations between Raman parameters and well depth for kerogens from the Cenozoic
Malembo Formation (Lower Congo Basin, Angola) **in our study**. The Raman parameters also correlate very
well with vitrinite reflectance values reported by Schito et al. (2016), which range from about 0.3**%** to about
1.5**%** R_o. In the investigated well, Raman spectral features vary continuously with depth independent of
kerogen composition. This is in general agreement with Chen et al. (2012) **who showed that** differences in
parameters derived from micro-FT-IR analyses on vitrinite and liptinite macerals (e.g., AOM) were

7

258 negligible. Raman spectra parameters that best correlate against thermal maturity are: 1) D and G band

259 position difference; 2) G band FWHM and 3) D and G bands area/width ratio (including the RA2 parameter).

260

261 *4.1 Distance between D and G bands*

262 The shift in position of the D and G bands is related to processes that occur at different carbonization ranks.

263 According to Ferrari and Robertson (2000), the D band shift toward lower wavenumbers is attributable to the

264 increase of larger aromatic clusters passing from disordered to more ordered materials.

265 The increase of the D-G distance with thermal maturity is mainly driven by the shift of the D position toward

266 lower wavenumbers (Fig. 3a), while no apparent trend is visible for the G position (Figure 3b). This

267 observations are in agreement with those made others (Ferrari and Robertson, 2000; Kelemen and Fang,

268 2001; Nestler et al., 2003; Quirico et al., 2005; Guedes et al., 2010; and Liu et al, 2012). The D-G distance is

269 one of the best parameters to correlate against vitrinite reflectance (Fig. 4a). Our results are in agreement

270 with Kelemen and Fang (2001) and Liu et al. (2012) (for samples with R_o% varying between 0.5% and **4%**).

271

272 *4.2 Full Width at Half Maximum of the G band*

273 According to Ferrari and Robertson (2000), the width of the G peak increases as a function of the bond-angle disorder at

274 sp^2 sites (in aromatic rings and olefinic) and its values are the greatest for high sp^3 sites content (aliphatic chains) in

275 highly disordered materials. This parameter increases as a function of decreasing temperature or thermal maturity in

276 regional metamorphism (Beyssac et al., 2002; Lahfid et al., 2010) and progressive coalification (Ferrari and Robertson,

277 2000; **Kelemen and Fang, 2001**; Jehlička et al., 2003; **Quirico et al., 2005;** Marques et al., 2009; **Guedes et al., 2010a**

278 ; Wilkins et al., 2014, Hinrichs et al., 2016). In agreement with existing studies, we observed a decrease of FWHM-G as

279 a function of increasing R_o% (Figs. 4b). According to spectra deconvolution, the overall decrease in the

280 integrated intensity of the G region is attributable to both a decrease in the FWHM of the G band and to a

281 decrease in area of the Gl band (Fig. 5). This is in good agreement with the assignment of the Gl band to

282 polyacetylene-like structures (e.g., polyene chains) **which** are expected to decrease as thermal maturity

283 increases (**Castiglioni et al., 2004**; Rebelo et al., 2016). Similar behaviour **is seen in** the Gr (1540 cm^{-1}) and

284 Vl (1465 cm^{-1}) of Li et al. (2007), assigned to mainly amorphous carbon structures in char, especially smaller

285 ring systems (e.g., with 3-5 fused benzene rings) **which** also are expected to decrease as thermal maturity

286 increases.

287

288 *4.3 Area and width ratio parameters (D/G area, RA2, D/G width)*

289 **The intensity ratio between D and G bands**, is related to the in-plane crystallite size (Tuinstra and

290 Koening, 1976) in disordered graphite and shows an inverse correlation against paleotemperatures between

291 330-650 °C (Beyssac et al., 2002).The same relationship is not **seen at low temperatures** (Ferrari and

292 Robertson, 2000) and the area ratio of D and G bands and parameters related to this ratio (RA1 and RA2,

293 Lahfid et al., 2010) correlate **better** against temperature and thermal maturity (Kelemen and Fang, 2001;

294 Jehlička et al., 2003; Quirico et al., 2005; Sadezky et al., 2005; Marques et al., 2009; Guedes et al., 2010; Liu

295   et al., 2012). This is probably due to the fact that while the intensity ratio behaves similarly to the D/G area

296   ratio for disordered graphite, this correlation is no longer valid for amorphous carbon where the width of

297   both bands are related to the disorder in the structure (Ferrari and Robertson, 2000).

298   We observe that the ID/IG ratio does not correlate with depth (Fig. 3f) or R_o% while D/G area and width

299   ratio (Figs. 3g) and RA1 and RA2 parameters (Figs. 3i - j) increase linearly with thermal maturity. The

300   increase in D/G area and width ratio and in RA1 and RA2 parameters are partially attributable to the thinning

301   of the G band due to the clustering of the aromatic rings (Ferrari and Robertson, 2000; Li et al., 2007) and

302   also to the decrease in intensity of peak Gl (Fig. 5). However, other contributions may **also** be important to

303   consider. For this reason, in order to understand and isolate the contribution of each single band to the

304   RA1and RA2 variation in our set of samples, we normalized each band to the G band intensity in Figure 6,

305   where the ratio between the G band intensity and the area of the D, S, Dl and Dr bands against an increasing

306   maturation pattern on the x axes is presented. **No significant** variations are observed in the IG/S area or in

307   the IG/Dl area ratio, while a decrease in the IG/D area (e.g., D area band increase) and an increase of the

308   IG/Dr area ratio (e.g., Dr band area decrease) are clearly visible.

309   We conclude that the increase in RA2 ratio is attributed to the decrease in width and intensity of G and Gl

310   bands and to the decrease of the satellite band Dr. **This is** accompanied by a corresponding increase in D

311   band area (IG/D area decrease) **which is mostly** due to an increase in FWHM of the D band (Fig 3d).

312   While the D band increases, the G, Gl and Dr decrease with increasing structural ordering, in agreement with

313   the interpretations already proposed by Ferrari and Robertson (2000), Li et al., (2007) and Rebelo et al.

314   (2015). The interpretation of the Dr and S bands is not straightforward. Rebelo et al. (2015) assign these

315   bands (S and Dl) to the same vibrational modes and to the same structural units of Gl and Dr bands,

316   respectively; thus, we would expect similar coupled behaviour for these bands at increasing temperature.

317   However, we observe a decoupling between S and Gl and Dl and Dr bands with temperature.

318   A similar decoupling was observed by Ferralis et al. (2016) who suggested a different origin for the S and Dl

319   bands (called the D4 and D5 bands in Ferralis et al., 2016). The authors observed that in the 1200 **cm^{-1}** 1300

320   cm^{-1} region the D4 and D5 bands are **related** to deformation modes of C-C (D4) and CH (D5) species

321   associated with long saturated and unsaturated alkane chains. These bands show an intensity increase with

322   the increase of H:C ratio from weakly metamorphosed kerogen to graphite.

323   On the other hand, no trend is observed for the S and Dl bands in Figure 6. This could be due to the different

324   composition of the OM in the upper part of the well (**varying terrigenous OM** and AOM enrichment)

325   generating different responses of the excitation bands with increasing thermal maturity. The variation of C-C

326   and C-H associated with aliphatic at low maturity stages (R_o% < 1.5) is not straightforward and depends on

327   complex chemical changes that occur simultaneously, such as shortening of aliphatic chains, decreased

328   branching of aliphatic chains and formation of cyclic compounds (Lis et al., 2005). Therefore, we infer that

329   the assignment of the S and Dl bands is still unclear and further investigations are strongly needed to fully

330   address this issue.

331

332 *4.3 Raman spectra evolution in Organic matter*

333 Comparing our results with those obtained at higher degrees of maturation (Beyssac et al., 2002; Lahfid et

334 al., 2010 and Rantish et al., 2016), we can trace the evolution of Raman spectra of the OM over a wide range

335 of paleotemperatures. Using data from previous studies, we observed the **following changes going from**

336 **anthracite to graphite ranks** (i.e. typically greenschist facies and above, see Wopenka and Pasteris, 1993;

337 Beyssac et al., 2002): a decrease in the D band area, a shrinking of the G band and a shift of the G band

338 toward the triperiodic graphite position (Fig. 7). **Conversely, going from low volatile bituminous coal to**

339 **anthracite ranks, we observed from the works of Lahfid et al., (2010), Hinrichs et al., (2016) and**

340 **Lünsdorf, (2016) an increase of the D band and a progressive disappearance of the minor bands.**

341 **From results from this work, we found that changes in Raman spectra in diagenesis consist mainly in a**

342 **narrowing of the G band region and a small increase of the D band area.** The decrease of the G band

343 area is due to a progressive **shrinking** of the G band and to the decrease in the area of the Gl and Dr bands

344 assigned to small aromatic rings and small polyene domains present only in kerogen at low thermal maturity

345 levels (Castiglioni et al., 2004; Li et al., 2007; Rebelo et al., 2016).

346

347

348 **5 Conclusions**

349 Raman spectroscopic measurements **were performed** on shalescollected **from** a 5 km deep well drilled

350 across the Miocene-Oligocene Malembo Formation in the Lower Congo Basin (offshore of Angola). **Bulk**

351 kerogens, with a thermal maturity **range** increasing from about 0.3 R_o% at the top of the well to about 1.5

352 R_o% at the bottom were analysed.

353 The best correlations of Raman spectral parameters against the increase of thermal maturity are: D-G band

354 distance; FWHM of the G band; D/G area ratio; RA2 ratio (calculated as S+Dl+SD/Dr+Gl+G band ratio) and

355 the D/G width ratio.

356 These results demonstrate that, at low diagenetic stages (between **the** immature and mid-mature stages of

357 hydrocarbon generation) changes in Raman spectra of undifferentiated dispersed organic matter **show**

358 quantifiable changes in response to thermal maturation and can be used to successfully parameterize the

359 thermal evolution of a sedimentary succession.

360

368

369

370 **References**

371

372 Aldega, L., Corrado, S., Grasso, M., Maniscalco, R., 2007. Correlation of diagenetic data from organic and
373 inorganic studies in the Apenninic-Maghrebian fold-and-thrust belt: a case study from eastern Sicily. The
374 Journal of Geology 115, 335-353.
375
376 Allen, P. A., Allen, J. R., 2013. Basin Analysis: Principles and Application to Petroleum Play Assessment,
377 third ed. John Wiley & Sons, Hoboken, NJ, USA.
378
379 Andreucci, B., Castelluccio, A., Corrado, S., Jankowski, L., Mazzoli, S., Szaniawski, R., Zattin, M., 2015.
380 Interplay between the thermal evolution of an orogenic wedge and its retro-wedge basin: An example from
381 the Ukrainian Carpathians. Geological Society of America Bulletin 127, 410-427.
382
383 Aoya, M., Kouketsu, Y., Endo, S., Shimizu H., Mizukami, T., Nakamura, D., Wallis, S., 2010. Extending the
384 applicability of the Raman carbonaceous-material geothermometer using data from contact metamorphic
385 rocks. Journal of Metamorphic Geology 28, 895-914.
386
387 Beny-Bassez, C., Rouzaud, J., 1985. Characterization of carbonaceous materials by correlated electron and
388 optical microscopy and Raman microspectroscopy. Scanning Electron Microscopy 1, 119-132.
389
390 Beyssac, O., Goffé, B., Chopin, C., Rouzaud, J., 2002. Raman spectra of carbonaceous material in
391 metasediments: a new geothermometer. Journal of metamorphic Geology 20, 859-871.
392
393 Beyssac, O., Goffé, B., Petitet, J.-P., Froigneux, E., Moreau, M., Rouzaud, J.-N., 2003. On the
394 characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy.
395 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 59, 2267-2276.
396
397 **Cançado, L., Takai, K., Enoki, T., Endo, M., Kim, Y., Mizusaki, H., Speziali, N., Jorio, A., Pimenta,**
398 **M., 2008. Measuring the degree of stacking order in graphite by Raman spectroscopy. Carbon 46, 272-**
399 **275.**
400
401 Cantarelli, V., Aldega, L., Corrado, S., Invernizzi, C., Casas-Sainz, A., 2013. Thermal history of the Aragón-
402 Béarn Basin (Late Paleozoic, western Pyrenees, Spain); insights into basin tectonic evolution. Italian Journal
403 of Geosciences 132, 443-462.
404
405 Caricchi, C., Corrado, S., Di Paolo, L., Aldega, L., Grigo, D., 2016. Thermal maturity of Silurian deposits in
406 the Baltic Syneclise (on-shore Polish Baltic Basin): contribution to unconventional resources assessment.
407 Italian Journal of Geosciences 135, 383-393.
408
409 Carr, A.D., 2000. Suppression and retardation of vitrinite reflectance, Part 1. Formation and significance for
410 hydrocarbon generation. Journal of Petroleum Geology 23, 313-343.
411
412 Castiglioni, C., Tommasini, M., Zerbi, G., 2004. Raman spectroscopy of polyconjugated molecules and
413 materials: confinement effect in one and two dimensions: Philosophical Transactions of the Royal Society of
414 London. Series A. Mathematical, Physical and Engineering Sciences 362, 2425-2459.
415
416 Corrado, S., Aldega, L., Balestrieri, M.L., Maniscalco, R., Grasso, M., 2009. Structural evolution of the
417 sedimentary accretionary wedge of the Alpine system in eastern Sicily: thermal and thermochronological
418 constraints. Geological Society of America Bulletin 121, 1475–1490.
419
420 Corrado, S., Aldega, L., Zattin, M., 2010. Sedimentary vs. tectonic burial and exhumation along the
421 Apennines (Italy). Journal of the Virtual Explorer 36,1-37.
422
423 Corrado, S., Schito, A., Aldega, L. Grigo, D., 2016. A quantitative multi-method approach to assess thermal
424 evolution of the Lower Congo Basin (Angola). Rendiconti Online della Società Geologica Italiana 40,
425 pp.525.
426

427 Di Paolo, L., Aldega, L., Corrado, S., Mastalerz, M., 2012. Maximum burial and unroofing of Mt. Judica
428 recess area in Sicily: implication for the Apenninic–Maghrebian wedge dynamics. Tectonophysics 530, 193-
429 207.
430
431 **Di Donato, E., Tommasini, M., Fustella, G., Brambilla, L., Castiglioni, C., Zerbi, G., Simpson, C.D.,**
432 **Müllen, K., Negri, F., 2004. Wavelength-dependent Raman activity of D2h symmetry polycyclic**
433 **aromatic hydrocarbons in the D-band and acoustic phonon regions. Chemical Physics 301, 81–93.**
434
435 **Endo, S., Wallis, S. R., Tsuboi, M., Torres De Leòn, R., Solari, L. A., 2012. Metamorphic evolution of**
436 **lawsonite eclogites from the southern Motagua fault zone, Guatemala: insights from phase equilibria**
437 **and Raman spectroscopy. Journal of Metamorphic Geology 30, 143-164.**
438
439 **Federici, I., Cavazza, W., Okay, A. I., Beyssac, O., Zattin, M., Corrado, S. Dellisanti, F., 2010.**
440 **Thermal Evolution of the Permo-Triassic Karakaya Subduction-accretion Complex between the Biga**
441 **Peninsula and the Tokat Massif (Anatolia). Turkish Journal of Earth Sciences 19, 409-429.**
442
443 **Ferrari, A.C., Robertson, J., 2000. Interpretation of Raman spectra of disordered and amorphous**
444 **carbon: Physical Review B 61, 14095-14107.**
445
446 Ferrari, A. C., Robertson, J., 2004. Raman spectroscopy of amorphous, nanostructured, diamond–like
447 carbon, and nanodiamond. Philosophical Transactions of the Royal Society of London A: Mathematical,
448 Physical and Engineering Sciences 362, 2477-2512.
449
450 Friedel, R., Carlson, G., 1972. Difficult carbonaceous materials and their infra-red and Raman spectra.
451 Reassignments for coal spectra. Fuel 51, 194-198.
452
453 Guedes, A., Valentim, B., Prieto, A. C., Rodrigues, S., Noronha, F., 2010. Micro-Raman spectroscopy of
454 collotelinite, fusinite and macrinite. International Journal of Coal Geology 83, 415-422.
455
456 Guedes, A., Valentim, B., Prieto, A., Noronha F., 2012. Raman spectroscopy of coal macerals and fluidized
457 bed char morphotypes. Fuel 97, 443-449.
458
459 Hackley, P. C., Cardott, B. J., 2016. Application of organic petrography in North American shale petroleum
460 systems: A review. International Journal of Coal Geology 163, 8-51.
461
462 **Heise, H., Kuckuk, R., Ojha, A., Srivastava, A., Srivastava, V., Asthana, B., 2009. Characterisation of**
463 **carbonaceous materials using Raman spectroscopy: a comparison of carbon nanotube filters,**
464 **single-and multi-walled nanotubes, graphitised porous carbon and graphite. Journal of Raman**
465 **Spectroscopy 40, 344-353.**
466
467 Jehlička, J., Urban, O., Pokorný, J., 2003. Raman spectroscopy of carbon and solid bitumens in sedimentary
468 and metamorphic rocks. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 59, 2341-
469 2352.
470
471 Jehlička, J., Šťastná, A., Přikryl, R., 2009. Raman spectral characterization of dispersed carbonaceous matter
472 in decorative crystalline limestones.Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy
473 73, 404-409.
474
475 Kelemen, S., Fang, H., 2001, Maturity trends in Raman spectra from kerogen and coal. Energy & Fuels 15,
476 653-658.
477
478 Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., Goffé, B., 2010. Evolution of the Raman
479 spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps (Switzerland). Terra
480 Nova 22, 354-360.
481

482   Li, C.-Z., 2007. Some recent advances in the understanding of the pyrolysis and gasification behaviour of
483   Victorian brown coal. Fuel 86, 1664-1683.

485   Lis, G. P., Mastalerz, M., and Schimmelmann, A., 2008, Increasing maturity of kerogen type II reflected by
486   alkylbenzene distribution from pyrolysis-gas chromatography–mass spectrometry: Organic Geochemistry 39,
487   440-449.

489   Liu, D., Xiao, X., Tian, H., Min, Y., Zhou, Q., Cheng, P., Shen, J., 2012. Sample maturation calculated using
490   Raman spectroscopic parameters for solid organics: Methodology and geological applications. Chinese
491   Science Bulletin 58, 1285-1298.

493   Lünsdorf, N. K., 2016. Raman spectroscopy of dispersed vitrinite - Methodical aspects and correlation with
494   reflectance. International Journal of Coal Geology 153, 75-86.

496   Marques, M., Suárez-Ruiz, I., Flores, D., Guedes, A., Rodrigues, S., 2009. Correlation between optical,
497   chemical and micro-structural parameters of high-rank coals and graphite. International Journal of Coal
498   Geology 77, 377-382.

500   Mumm, A. S., İnan, S., 2016. Microscale Organic Maturity determination of Graptolites using
501   Raman Spectroscopy. International Journal of Coal Geology 162, 96-107.

503   Negri, F., di Donato, E., Tommasini, M., Castiglioni, C., Zerbi, G., Müllen, K., 2004. Resonance Raman
504   contribution to the D band of carbon materials: modeling defects with quantum chemistry. Journal of
505   Chemical Physics 120, 11889–11900.

507   Nemanich, R., Solin, S., 1979. First-and second-order Raman scattering from finite-size crystals of graphite.
508   Physical Review B 20, 392.

510   Nestler, K., Dietrich, D., Witke, K., Rößler, R., Marx, G., 2003. Thermogravimetric and Raman
511   spectroscopic investigations on different coals in comparison to dispersed anthracite found in permineralized
512   tree fern *Psaronius* sp. Journal of Molecular Structure 661, 357-362.

514   Petersen, H., Rosenberg, P., 1998. Reflectance retardation (suppression) and source rock properties related to
515   hydrogen enriched vitrinite in middle Jurassic coals, Danish North Sea. Journal of Petroleum Geology 21,
516   247-263.

518   Potgieter-Vermaak, S., Maledi, N., Wagner, N., Van Heerden, J., Van Grieken, R., Potgieter, J., 2011.
519   Raman spectroscopy for the analysis of coal: a review. Journal of Raman Spectroscopy 42, 123-129.

521   Pócsik, I., Hundhausen, M., Koós, M., Ley, L., 1998. Origin of the D peak in the Raman spectrum of
522   microcrystalline graphite. Journal of Non-Crystalline Solids 227, 1083-1086.

524   Price, L. C., Barker, C. E., 1985. Suppression of vitrinite reflectance in amorphous rich kerogen--a major
525   unrecognized problem. Journal of Petroleum Geology 8, p. 59-84.

527   Quirico, E., Rouzaud, J. N., Bonal, L., Montagnac, G., 2005. Maturation grade of coals as revealed by
528   Raman spectroscopy: progress and problems. Spectrochimica Acta Part A: Molecular and Biomolecular
529   Spectroscopy 61, 2368-2377.

531   Rantitsch, G., Lämmerer, W., Fisslthaler, E., Mitsche, S., Kaltenböck, H., 2016. On the discrimination of
532   semi-graphite and graphite by Raman spectroscopy. International Journal of Coal Geology 159, 48–56.

534   Rebelo, S. L., Guedes, A., Szefczyk, M. E., Pereira, A. M., Araújo, J. P., Freire, C., 2016. Progress in the
535   Raman spectra analysis of covalently functionalized multiwalled carbon nanotubes: unraveling disorder in
536   graphitic materials. Physical Chemistry Chemical Physics 18, 12784-12796.

537

538 Robl, T. L., Davis, B. H., 1993. Comparison of the HF-HCl and HF-BF 3 maceration techniques and the
539 chemistry of resultant organic concentrates. Organic Geochemistry 20, 249-255.
540
541 Romero-Sarmiento, M.-F., Rouzaud, J.-N., Bernard, S., Deldicque, D., Thomas, M., Littke, R., 2014.
542 Evolution of Barnett Shale organic carbon structure and nanostructure with increasing maturation. Organic
543 Geochemistry 71, 7-16.
544
545 Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., Pöschl, U., 2005. Raman microspectroscopy of
546 soot and related carbonaceous materials: Spectral analysis and structural information. Carbon 43, 1731-1742.
547
548 **Schito, A., Corrado, S., Aldega, L., Grigo, D., 2016. Overcoming pitfalls of vitrinite reflectance**
549 **measurements in the assessment of thermal maturity: the case history of the lower Congo basin.**
550 **Marine and Petroleum Geology 74, 59-70.**
551
552 Scott, A. C., Glasspool, I. J., 2007. Observations and experiments on the origin and formation of inertinite
553 group macerals. International Journal of Coal Geology 70, 53-66.
554
555 Shirakawa, H., Ito, T., Ikeda, S., 1973. Raman scattering and electronic spectra of poly (acetylene). Polymer
556 Journal 4, 460-462.
557
558 Taylor, G. H., 1998. Organic petrology: A new handbook incorporating some revised parts of Stach's
559 textbook of coal petrology, Gebruder Borntraeger Verlagsbuchhandlung, Stuttgart, Germany.
560
561 Tyson, R. V., 1995. Organic facies and palynofacies, In: Sedimentary organic matter, Springer Netherlands,
562 pp. 81-118
563
564 Teichmüller, M., 1986. Organic petrology of source rocks, history and state of the art. Organic Geochemistry
565 10, 581-599.
566
567 Tuinstra, F., Koenig, J. L., 1970. Raman spectrum of graphite. The Journal of Chemical Physics 53, 1126-
568 1130
569 Vandenbroucke, M., Largeau, C., 2007. Kerogen origin, evolution and structure. Organic Geochemistry 38,
570 719-833.
571
572 Wilkins, R. W., Boudou, R., Sherwood, N., Xiao, X., 2014. Thermal maturity evaluation from inertinites by
573 Raman spectroscopy: The 'RaMM'technique. International Journal of Coal Geology 128, 143-152.
574
575 Wopenka, B., Pasteris, J. D., 1993. Structural characterization of kerogens to granulite-facies graphite:
576 applicability of Raman microprobe spectroscopy. The American Mineralogist 78, 533-557.
577
578 Yui, T. F., Huang, E., Xu, J..1996. Raman spectrum of carbonaceous material: a possible metamorphic grade
579 indicator for low-grade metamorphic rocks. Journal of Metamorphic Geology 14, 115-124.
580
581 Zhou, Q., Xiao, X., Pan, L., Tian, H., 2014. The relationship between micro-Raman spectral parameters and
582 reflectance of solid bitumen. International Journal of Coal Geology 121, 19-25.
583
584
585 **Figure captions**
586
587
588 Figure 1. Examples of Raman spectra measured on organic matter extracted from cuttings at different
589 stratigraphic depth. The stratigraphic column is redrawn after Schito et al. (2016)
590
591

Figure 2. Example of bands and bands position obtained by Raman analysis on dispersed organic matter for: low matured samples collected at the top of the well (a) and high matured samples collected at the bottom of the well (b)

Figure 3. Trends with depth of: position of the D band (a), position of the G band (b), difference between G band and D band positions (c), width at half height of the D band (d), the width at half height of the G band (e), intensities ratios between D and G bands (f), area ratios between D and G bands(g), full width at maximum height of the D and G bands (h), RA1 parameter (i) and RA2 parameter (j). Grey dots indicate terrestrial derived organic matter rich kerogen, black dots amorphous organic matter rich kerogen. Bars indicate standard deviation for each samples

Figure 4 Correlation between $R_o\%_{eq.}$ calculated based on clay mineralogy and FT-IR analyses and distance between D and G band (a), width at half height of the G band (b), area ratio between D and G bands (c); RA2 parameter (d) and width ratio between D and G ratio (e)

Figure 5. Schematic evolution of the Gl and the G bands

Figure 6. Ratio of G intensity against: S band area (a), Dl band area (b), D band area (c) and Dr band area (d) for all sample (not average per each depth) of the analysed well

Figure 7. Evolution of the Raman spectra from high metamorphic stages to the immature stage of HC generation. Raman spectra for temperatures higher than 170 °C are redrawn from Lahfid et al. (2010) and Beyssac et al. (2002). Temperature for samples from this work were carried out from thermal model by Schito et al. (2016).

Table 1. Organic matter composition and Raman parameters for each depth interval analysed. Acronyms: AOM amorphous organic matter; MPH marine phytoplankton; CHF continental herbaceous fragments; CWF continental wooden fragments; stdv: standard deviation; pD: position of the D band (cm^{-1}); pG: position of the G band (cm^{-1}); wD: full width at maximum height of the D band (cm^{-1}); wG: full width at maximum height of the D band (cm^{-1}); Δ D-G: difference between G band and D band position (cm^{-1}); ID/IG: intensity ratio between D and G bands; aD/aG: area ratio between D and G bands; RA1: area (S+Dl+D) / area (S+Dl+D+Dr+Gl+G); RA2: area (S+Dl+D) / area (Dr+Gl+G); wD/wG: ratio between full width at maximum height of D and G bands; s.d: standard deviation

1   **Diagenetic thermal evolution of organic matter by Raman spectroscopy**

2   Andrea Schito [a], Claudia Romano [a], Sveva Corrado [a], Domenico Grigo [b], Brent Poe [c]

3   [a] Dipartimento di Scienze, Sezione di Scienze Geologiche, Università degli Studi Roma Tre, L.go S.
4   Leonardo Murialdo 1, 00146, Roma, Italy
5   [b] Eni SpA e Exploration & Production Division, Via Emilia, San Donato Milanese, MI, 20097, Italy
6   [c] Dipartimento di Geotecnologie per l'Ambiente ed il Territorio, Università degli Studi "G. d'Annunzio" –
7   Chieti, Via dei Vestini 30, 66013 Chieti Scalo, Italy

8

9   **Corresponding author.**

10   E-mail address:**andrea.schito@uniroma3.it**

11

12   **Keywords:** thermal maturity; dispersed organic matter; Raman spectroscopy; diagenesis

13

14   **Abstract**
15   Vitrinite reflectance is considered one of the most reliable indicators of thermal maturity in sedimentary
16   basins and is widely used to calibrate numerical models that assess hydrocarbon generation/expulsion from
17   source rocks. Nevertheless, ambiguities in vitrinite reflectance can occur from variations in composition and
18   preservation state of organic facies, temperature/ pressure conditions and the abundance of organic matter
19   resulting in incorrect or uncertain assessments of petroleum systems.
20   This study presents an original application of Raman spectroscopy to assess the diagenesis - catagenesis of
21   kerogen between the immature and mid-mature stages of hydrocarbon generation. Kerogens were isolated
22   from 33 intervals of drill cuttings from a 5 km thick Oligocene-Miocene siliciclastic section of the Malembo
23   Formation (Lower Congo Basin, Angola). Their Raman spectra were obtained and derived parameters were
24   compared to depth and to previously reported equivalent vitrinite reflectance values. The best correlations
25   between thermal maturity and Raman parameters were found for D-G band distance; FWHM of the G band;
26   D/G area ratio; RA2 ratio (calculated as S+Dl+SD/Dr+Gl+G band ratio) and the D/G width ratio. The
27   Raman parameters were not influenced by varying kerogen composition (mixed type II/III). The technique
28   offers the potential to reduce the risk of source rock thermal maturity assessment even when organic facies
29   rich in amorphous organic matter are present.

30
31

32   **1 Introduction**

33   Quantitative evaluation of the thermal maturity of organic matter (OM) dispersed in sediments is a key
34   element in assessing the processes of hydrocarbon (HC) generation/expulsion in petroleum systems. It is
35   linked to the thermal evolution of sedimentary basins and orogenic belts (Corrado et al., 2010; Allen and
36   Allen, 2013; Hackley and Cardott, 2016). Vitrinite reflectance analysis is considered a highly reliable and

reproducible measure of thermal maturity of coals. Its application to organic matter dispersed in sediments is a common practice, but there are inherent limitations that can lower the accuracy of the measurement. In many marine sediments, primary vitrinite macerals are absent or very sparse and it is often difficult to obtain good results without interference from eroded, secondary sources. Vitrinite reflectance in dispersed organic matter can also be effected by other processes such as oxidation during transport, preservation, and retardation and/or suppression. Numerical models calibrated against ambiguous vitrinite reflectance data can yield inaccurate or biased results. Alternative analytical techniques based on the analysis of both the organic and inorganic fraction of sediments can minimize these limitations (e.g., Aldega et al. 2007; Corrado et al., 2009; Federici et al., 2010; Di Paolo et al., 2012; Cantarelli et al., 2013; Andreucci et al., 2014; Schito et al., 2016).

Raman spectroscopy is a potential powerful non-destructive tool to quantitatively evaluate thermal maturity of organic matter (e.g., Beyssac et al., 2002; Quirico et al., 2005; Guedes et al., 2010, 2012; Lahfid et al., 2010; Liu et al., 2012, Hinrichs et al., 2014; Wilkins et al., 2014; Zhou et al., 2014; Lünsdorf, 2016; Mum and Inan, 2016; Ferralis et al., 2016). Advances in instrumentation and data processing have spurred increased applications,and the technique is now simple, fast and can be performed directly on standard petrographic thin sections or on bulk kerogen.

Specifically, two bands on Raman spectra, namely G (graphitic) and D (disordered), are related to the growth of the ordered domains with respect to the disordered ones in the organic matter (Tuinstra & Koenig, 1970). Parameters linked to D and G bands have been used to show reliable correlations with paleotemperatures between 200 °C and 650 °C (Wopenka and Pasteris, 1993; Beyssac et al., 2002; Aoya et al., 2010; Lahfid et al., 2010; Endo et al., 2012) and against thermal maturity between 1 and 5-6 R_o% (Kelemen and Fang, 2001; Jehlička et al., 2003; Quirico et al., 2005; Guedes et al., 2010; 2012; Liu et al., 2012; Hinrichs et al., 2014; Wilkins et al., 2014; Zhou et al., 2014; Lünsdorf, 2016; Mum and Inan, 2016).

The range of thermal maturity spanning the diagenetic to mid-catagenesic stages (corresponding to R_o% 0.4-1.2) has been explored systematically in only a few studies (Wilkins et al., 2014; Hinrichs et al., 2016; Lünsdorf, 2016). These report considerable uncertainties at the low maturity stages, which are usually the most critical in constraining basin models.

In this study, we examine the applicability of Raman spectroscopy as a thermal indicator in the range between the immature and middle mature stages of HC generation, when applied to type II/III kerogen composed mainly of amorphous organic matter (AOM). We present the procedures and analytical results of the first order Raman spectra performed on Cenozoic organic matter dispersed in sediments of the Malembo Formation drilled in Lower Congo Basin (Angola) that records this maturity range. We demonstrate that robust parameterization of the thermal maturity of dispersed organic matter is possible using Raman indicators.

2 Methods and Materials

74 *2.1 Kerogen and thermal maturity*

75 Kerogen is the insoluble macromolecular fraction of sedimentary organic matter (Vandenbroucke and

76 Largeau, 2007) and is the precursor of oil and gas resources. Dispersed OM is usually highly heterogeneous

77 and reflects differences in its origin and preservation state. Different classifications of kerogen exist, based

78 on optical analyses performed in reflected and transmitted light or rooted on bulk parameters, such as H/C

79 and O/C atomic ratios or Hydrogen and Oxygen indexes derived from pyrolysis yields and TOC values.

80 In this work, we mainly refer to classifications based on optical organic petrography using transmitted light

81 microscopy (Teichmüller, 1986; Tyson, 1995**).** Kerogen composition is classified into four classes from

82 which the abundance and distribution of hydrogen-rich macerals can be discerned: 1) AOM: amorphous

83 organic matter; 2) MPH: marine phytoplankton; 3) CWF: continental wooden organic matter, namely

84 phytoclasts; and 4) CHF: continental herbaceous fragments.

85 Analyses were performed on 33 samples originating from cuttings taken from a 5000 meter thick section

86 drilled offshore Angola (Malembo Formation - Lower Congo Basin). The succession ranges from Oligocene

87 to Upper Miocene and is composed mainly of organic-rich shales interbedded by nearshore to deepwater

88 sandstones (Schito et al., 2016).

89 Organic matter of different origin and preservation state, detected through transmitted light analyses, were

90 found in the upper section of the well (depth: 1290-3360m) where woody fragments (CWF) and herbaceous

91 fragments (CHF) of terrigenous origin coexist with amorphous organic matter (AOM) and marine

92 phytoplankton (MPH). In contrast, the lower part of the well (depth: 3600-4950 m) is mainly composed of

93 amorphous organic matter with traces of bitumen (Table 1, Schito et al., 2016). Reflected light analyses on

94 kerogen indicate that organic matter of woody fragments of continental origin are represented by vitrinite

95 group macerals, whereas inertinite group macerals are totally absent (Table 1, Schito et al., 2016).

96 The maturation pattern of the well ranges between about 0.35 and 1.5 expressed as vitrinite reflectance

97 values (R_o%) as reported in Corrado et al. (2016) and Schito et al. (2016).

98

99 *2.2 Sample preparation*

100 Kerogens were extracted using a wet-chemical acid demineralization technique according to Robl and Davis

101 (1993) and Schimmelmann et al. (1999). Samples were lightly ground in an agate mortar for about 1 minute.

102 Carbonates were dissolved by adding HCl on the dried samples. The HCl was added in small increments to

103 prevent excessive foaming. Digestion of remaining silicates was done by adding a mixture composed in equal

104 parts by distilled water and HF concentrated at 40% weight percent (45 ml) to 5 g of sample and placed on a

105 shaker table for 2 hours. Kerogen isolates plus any acid-resistant minerals were recovered and washed 5-6 times

106 with distilled water.

107

108 *2.3 Raman Spectroscopy and curve fitting*

109 Raman spectroscopy was performed on the kerogen isolates using a Jobin Yvon micro-Raman LabRam system

110 in a backscattering geometry. Data were collected over the range of 700-2300 cm^{-1} (first order Raman

3

spectrum) using a 600 grooves/mm spectrometer gratings and CCD detector. A Neodimium-Yag laser at 532 nm (green laser) was used as the light source and optical filters adjusted the power of the laser (<0.4mW). The Raman backscattering was recorded after an integration time of 20 seconds for 6 repetitions for each measurement. This, together with the use of green laser and optical filters, allowed us to reduce the fluorescence background to minimal values. Between ten and fifteen measurements were performed for each samples to ensure reproducibility of measurements. Each organic grain was analysed with a 2 μm diameter spot using a 50× optical power objective.

Raman spectra of highly disordered carbon materials, are affected by interference due to high fluorescence caused by the diffuse presence of hydrogen or residual mineral matter. The first step in the analysis of the spectra is the removal of the high fluorescence background by a baseline subtraction procedure. Once the procedure is optimized, it then must be reproduced for the entire set of samples.

Baseline subtraction was performed using a third order polynomial curve that best followed the real trend of the fluorescence in the most immature samples with high fluorescence background. In order to avoid errors induced by differences in the spectra range considered by the subtraction, we fixed baseline points at 1000 and 1850 cm^{-1} for all spectra. A polynomial curve was chosen with respect to the linear baseline because the latter tends to overestimate the D and G peaks intensities. We observed that the maximum difference resulting from baseline correction was detected for the D band intensity, whose values tend to be higher by 10-15 %.

After removal of the background, the spectra were deconvoluted using LabSpec 6 software by Horiba. As the Raman spectra of OM in diagenetic conditions show broad overlapping bands and multiple curve-fitting solutions exist (Lünsdorf and Lünsdorf, 2016), we found that the best solution using the minimum number of components was attained using a six band deconvolution with a mixed Gaussian-Lorentzian band profile. The goodnessof fit is defined by the minimum values of the χ^2 value (less than 3 according to Sadezky et al., 2005). Several attempts to use only five bands fitting systematically provided χ^2 values two or three times higher than those obtained with a six bands approach. All spectra were deconvoluted using the six peak deconvolution procedure.

2.4 Band assignment for Raman spectra in dispersed organic matter

The Raman spectral signal of kerogen is recorded in a "first order" region between 1000 and 2000 cm^{-1} and "second order" region between 2000 and 3500 cm^{-1}. Bands in the second order region are generally hidden by fluorescence for low mature samples (Beyssac et al., 2002) and were not observed in this study. The first order Raman spectrafor carbonaceous materials consist of two main bands known as the D and G bands (Tuinstra and Koenig, 1970; Friedel and Carlson, 1972) and other bands that vary depending on the rank (Li, 2007; Potgieter-Vermaak et al., 2011). The G band is the only Raman active vibration in crystalline graphite at 1582 cm^{-1} (Tuinstra and Koenig, 1972; Reich and Thomsen, 2004; Pimenta, 2007) and is related to the in-plane vibration of the carbon atoms in the graphene sheets.

The D band at 1350 cm^{-1} becomes active in disordered graphite and its frequency depends on the excitation laser (Pócsik et al., 1998). Its origin has been interpreted as a results of a double resonant Raman scattering

148 process (Pócsik et al., 1998; Reich and Thomsen, 2004; and Pimenta et al., 2007). Alternatively, the

149 collective intensity of the D band has been related to the ring breathing vibration in the graphite sub-unit or

150 polycyclic aromatic compounds (PAHs) (Negri et al., 2002;2004; Castiglioni et al., 2004; Di Donato et al.,

151 2004; and Lünsdorf 2016) or to aromatics with 6 rings or more (Li, 2007).

152 When dealing with disordered materials, the contribution of other spectral features at 1100-1200 cm^{-1} and

153 1400-1500 cm^{-1} cannot be neglected and even the assignment of the G and D bands to graphite vibrational

154 modes is questionable. Unfortunately, there have only been a few attempt to explain the origin of these bands

155 in disordered materials and these studies are often contradictory (Nemanich and Solin, 1979; Beny-Bassez

156 and Rouzaud, 1985; Ferrari and Robertson, 2000; Castiglioni et al. 2004; Negri et al., 2004; Li et al., 2007;

157 Rebelo et al. 2016). For this reason the assignment of Raman bands for disordered material is still a matter of

158 debate.

159 In high-rank coals, Beyssac et al. (2002) observed the presence of two additional bands in the Raman

160 spectrum: the D2 band, appearing as a right end shoulder of the G band at approximately 1620 cm^{-1} and the

161 D3 band, a wide band residing at approximately 1500 cm^{-1}. These bands have been attributed to out-of-plane

162 defects from tetrahedral carbons (Bèny-Bassez and Rouzaud, 1985), or to small crystallite size (Nemanich

163 and Solin, 1979). Working on carbon material matured at lower temperatures (about 200-320°C), Lahfid et

164 al. (2010) and Sadezky et al. (2005) proposed the presence of an additional band called D4 at about 1200 cm^{-1}

165 , attributed to sp^3-sp^2 bonds or C–C and C=C stretching vibrations of polyene-like structures.

166 In a recent study, Ferralis et al. (2016) found the presence of two bands as a broad shoulder of the D bands,

167 called D4 at 1150 cm^{-1} and D5 at 1250 cm^{-1}. In Ferralis et al.'s (2016) work, the two bands have been related

168 to CH species in aliphatic hydrocarbon chains. The authors confirm this hypothesis by showing a strong

169 correlation between the intensity of D5 or D5+D4 band with the increase of the atomic ratio H:C in the range

170 between almost pure graphite (H:C = 0.01) and weak metamorphosed kerogen (H:C = 0.65).

171 In low maturity coals, the Raman spectra of highly disordered carbonaceous matter are more complex.

172 In Li et al. (2006) and Li (2007), Raman spectra were deconvoluted into 10 bands. The authors attributed a

173 band at about 1700 cm^{-1} (Gl band) to a carbonyl group C=O, while the Gr (1540 cm^{-1}), Vl (1465 cm^{-1}) and

174 Vr band (1380 cm^{-1}) which represent the "overlap" between D and G were assigned to mainly amorphous

175 carbon structures in char, especially smaller ring systems (e.g., with 3-5 fused benzene rings). At lower

176 wavenumbers, they found that the S band (1185 cm^{-1}), together with Sl band (~1220 cm^{-1}), acts as the

177 shoulder of the D band (1230 cm^{-1}) and mainly represents $C_{aromatic}$–C_{alkyl}, aromatic (aliphatic) ethers, C–C on

178 hydroaromatic rings, hexagonal diamond carbon sp^3 and C–H on aromatic rings. Finally, the Sr band (1060

179 cm^{-1}) is assigned to C-H on aromatic rings and the R band (960-800 cm^{-1}) to C-C on alkanes and cyclic

180 alkanes and/or C-H on aromatic rings.

181 Similarly, based on analyses of carbon nanotubes, Rebelo et al. (2016) proposed new assignments for the first

182 order Raman spectra. In their work the G band is fitted with a Lorentzian shape at ~1580 cm^{-1} surrounded by a

183 Loretzian Gr peak at ~1610 cm^{-1} and a Gaussian Gl peak near 1500 cm^{-1} . Gl band correspond to the same

184 vibration of the G band in low size aromatic (Heise et al., 2009). The "D region" is deconvoluted to a central

185 Lorentzian D band at 1350 cm^{-1} and two satellites Gaussian band called Dl and Dr (left and right) respectively at

186 ~1250 and ~1400 cm^{-1} that were assigned to identical vibrations of the D band, but in low size aromatic

187 domains. Finally, a further band, the S band, was used to fit a relatively small feature on the left side of the

188 spectra at around 1120cm^{-1}.

189 Bands S and Gl were assigned to a fingerprint of polyacetylene-like structures or areas of conjugated double

190 bonds mainly present along the borders of structures where aromaticity has been broken upon functionalization

191 (Shirakawa et al., 1973).

192

193 *2.5 Raman thermal maturity parameters*

194 Debate still exists on how to relate Raman spectral features to carbonization ranks at low thermal maturity levels

195 (Rantish et al., 2016). Tuinstra and Koenig (1970) proposed the relation ID/IG = C(υL)/La (TK relation), to

196 study the thermal evolution of carbonaceous materials. ID/IG is the ratio between the intensities of the D and G

197 peaks, La is the lateral dimension (parallel to the graphene planes) of the nanocrystal and $C(\upsilon L)$ is a constant

198 which depends on the laser frequency. Taking IG as a reference value, which is independent of the size of the

199 crystal (Cançado et al., 2008), Tuinstra and Koenig (1970) found an inverse relation between the intensities of

200 the D band and the crystal dimensions. Following the TK correlation, Wopenka & Pasteris (1993) correlated

201 certain Raman parameters with metamorphic zonation as determined by mineral assemblages.

202 Subsequently, Yui et al. (1996) demonstrated the high sensitivity of some Raman parameters to metamorphic

203 grade from low-grade to greenschist facies, while Beyssac et al. (2002) developed the so called RSCM

204 geothermometer (Raman Spectroscopy of Carbonaceous Material). RSCM, which expresses a relationship

205 between the Raman parameter R2 (R2 = D/([G + D + D2] area ratio) and metamorphic temperature, was

206 initially calibrated in a range between 330-640°C, and later extended to contact- metamorphic rocks (Aoya et

207 al., 2010) and low-grade metamorphism (Lahfid et al., 2010, RA1 and RA2 parameters; Lünsdorf, 2016).

208 Given the low temperature interval covering the sub-bituminous coal to the anthracite ranks, spectral features

209 and carbonization are not so clearly correlated. In general, FWHM, positions of the G and D bands and D/G area

210 ratio are the most sensitive parameters to maturation (Sadezky et al., 2005; Jehlicka et al., 2009; Marques et al.,

211 2009; Guedes et al., 2010; Zhou et al., 2014; Hinrichs et al., 2016; Lünsdorf, 2016). Romero-Sarmiento et al.

212 (2014) suggested that the FWHM of the G band shows the best correlation against Rock-Eval Tmax values in a

213 set of samples from the Barnett shales (US), and Liu et al. (2012) determined thermal maturity by using the D-G

214 distance in mature to highly mature carbonized samples of solid organic matter.

215

216

217 **3 Results**

218 *3.1 Raman spectra*

219 From a first qualitative assessment of spectral features, we observed a regular decrease of the fluorescence

220 signal, resulting in the reduction of the slope of the spectra (Fig. 1), and a corresponding narrowing of the G

221 bands along the same trend. We refer to Rebelo et al. (2016) for band nomenclature. Position and bands names

222 are shown in Figure 2a for low maturity OM and in Figure 2b for high maturity OM. Best fit results were

223 achieved by considering S, Dl and Dr as purely Gaussian, and D, G and Gl as more mixed Gaussian-Lorentzian

224 functions. Generally, in response to increasing thermal maturity, the width of the G band decreases, the D-G

225 peak position difference increases and the Gl area decreases.

226

227 *3.2 Correlation of Raman parameters against thermal maturity - Malembo Formation*

228 To correlate spectral features with thermal maturity, the following parameters were calculated: D and G

229 position, D-G distance, full width at half maximum of the D and G bands (FWHM) and D/G intensity, area and

230 full width at maximum height ratio. Moreover, we redefined the parameters RA1 and RA2 following the work

231 of Lahfid et al. (2010), calculated as follows:

    1) RA1 = area (S+Dl+D) / area (S+Dl+D+Dr+Gl+G);

    2) RA2 = area (S+Dl+D) / area (Dr+Gl+G).

234 The D band position decreases slightly with depth from about 1380 cm^{-1} to 1360 cm^{-1}, while the G band position

235 (Fig. 3a) shows no trends with depth, ranging between 1590 cm^{-1} and 1600 cm^{-1} (Fig. 3b). As a consequence, the

236 D-G difference increases slightly with depth from about 220 cm^{-1} to 240 cm^{-1} (Fig 3c).

237 The full width at half maximum (FWHM) of the D band ranges between 90 cm^{-1} and 110 cm^{-1} with no defined

238 trend, while the full width at half maximum (FWHM) of the G band decreases from about 90 cm^{-1} to 55 cm^{-1}

239 (Fig.3d-e). The intensity ratio between the D and G bands does not show any correlation with depth (Fig. 3f),

240 while the D/G area ratio and full width at maximum height ratio shows a trend of increasing values with depth,

241 ranging from about 0.5 to 1.0 and 1.0 and 1.8, respectively (Fig. 3g-h). Both RA1 and RA2 show values ranging

242 from 0.35 to 0.50 for RA1 and from about 0.55 to 1.10 for RA2 (Fig. 3i-j). The best correlations with depth are

243 provided by the D-G difference (Fig. 3c), the FWHM of peak G (Fig. 3e), the D/G area ratio (Fig. 3g), D/G

244 width ratio (Fig. 3h) and the RA2 parameter (Fig. 3j).

245 We plotted these parameters against the maturity profile of the well expressed in R_o% (for details see Schito

246 et al., 2016) in Fig. 4. A power equation was used to fit the D/G area ($R^2 = 0.93$), RA2 ($R^2 = 0.95$) and D/G

247 width ($R^2 = 0.96$) parameters (Fig.4c-d-e), FWHM-G parameter ($R^2 = 0.91$) and the D-G distance ($R^2 = 0.94$)

248 were fitted according to a second order polynomial equation (Fig. a-b).

249

250

4 Discussions

252 We observed good correlations between Raman parameters and well depth for kerogens from the Cenozoic

253 Malembo Formation (Lower Congo Basin, Angola) in our study. The Raman parameters also correlate very

254 well with vitrinite reflectance values reported by Schito et al. (2016), which range from about 0.3% to about

255 1.5% R_o. In the investigated well, Raman spectral features vary continuously with depth independent of

256 kerogen composition. This is in general agreement with Chen et al. (2012) who showed that differences in

257 parameters derived from micro-FT-IR analyses on vitrinite and liptinite macerals (e.g., AOM) were

258 negligible. Raman spectra parameters that best correlate against thermal maturity are: 1) D and G band

259 position difference; 2) G band FWHM and 3) D and G bands area/width ratio (including the RA2 parameter).

260

261 *4.1 Distance between D and G bands*

262 The shift in position of the D and G bands is related to processes that occur at different carbonization ranks.

263 According to Ferrari and Robertson (2000), the D band shift toward lower wavenumbers is attributable to the

264 increase of larger aromatic clusters passing from disordered to more ordered materials.

265 The increase of the D-G distance with thermal maturity is mainly driven by the shift of the D position toward

266 lower wavenumbers (Fig. 3a), while no apparent trend is visible for the G position (Figure 3b). This

267 observations are in agreement with those made others (Ferrari and Robertson, 2000; Kelemen and Fang,

268 2001; Nestler et al., 2003; Quirico et al., 2005; Guedes et al., 2010; and Liu et al, 2012). The D-G distance is

269 one of the best parameters to correlate against vitrinite reflectance (Fig. 4a). Our results are in agreement

270 with Kelemen and Fang (2001) and Liu et al. (2012) (for samples with R_o% varying between 0.5% and 4%).

271

272 *4.2 Full Width at Half Maximum of the G band*

273 According to Ferrari and Robertson (2000), the width of the G peak increases as a function of the bond-angle disorder at

274 sp^2 sites (in aromatic rings and olefinic) and its values are the greatest for high sp^3 sites content (aliphatic chains) in

275 highly disordered materials. This parameter increases as a function of decreasing temperature or thermal maturity in

276 regional metamorphism (Beyssac et al., 2002; Lahfid et al., 2010) and progressive coalification (Ferrari and Robertson,

277 2000;; Kelemen and Fang, 2001; Jehlička et al., 2003; Quirico et al., 2005; Marques et al., 2009; Guedes et al., 2010a ;

278 Wilkins et al., 2014, Hinrichs et al., 2016). In agreement with existing studies, we observed a decrease of FWHM-G as

279 a function of increasing R_o% (Figs. 4b). According to spectra deconvolution, the overall decrease in the

280 integrated intensity of the G region is attributable to both a decrease in the FWHM of the G band and to a

281 decrease in area of the Gl band (Fig. 5). This is in good agreement with the assignment of the Gl band to

282 polyacetylene-like structures (e.g., polyene chains) which are expected to decrease as thermal maturity

283 increases (Castiglioni et al., 2004; Rebelo et al., 2016). Similar behaviour is seen in the Gr (1540 cm^{-1}) and

284 Vl (1465 cm^{-1}) of Li et al. (2007), assigned to mainly amorphous carbon structures in char, especially smaller

285 ring systems (e.g., with 3-5 fused benzene rings) which also are expected to decrease as thermal maturity

286 increases.

287

288 *4.3 Area and width ratio parameters (D/G area, RA2, D/G width)*

289 The intensity ratio between D and G bands, is related to the in-plane crystallite size (Tuinstra and Koening,

290 1976) in disordered graphite and shows an inverse correlation against paleotemperatures between 330-650

291 °C (Beyssac et al., 2002).The same relationship is not seen at low temperatures (Ferrari and Robertson,

292 2000) and the area ratio of D and G bands and parameters related to this ratio (RA1 and RA2, Lahfid et al.,

293 2010) correlate better against temperature and thermal maturity (Kelemen and Fang, 2001; Jehlička et al.,

294 2003; Quirico et al., 2005; Sadezky et al., 2005; Marques et al., 2009; Guedes et al., 2010; Liu et al., 2012).

295   This is probably due to the fact that while the intensity ratio behaves similarly to the D/G area ratio for

296   disordered graphite, this correlation is no longer valid for amorphous carbon where the width of both bands

297   are related to the disorder in the structure (Ferrari and Robertson, 2000).

298   We observe that the ID/IG ratio does not correlate with depth (Fig. 3f) or R_o% while D/G area and width

299   ratio (Figs. 3g) and RA1 and RA2 parameters (Figs. 3i - j) increase linearly with thermal maturity. The

300   increase in D/G area and width ratio and in RA1 and RA2 parameters are partially attributable to the thinning

301   of the G band due to the clustering of the aromatic rings (Ferrari and Robertson, 2000; Li et al., 2007) and

302   also to the decrease in intensity of peak Gl (Fig. 5). However, other contributions may also be important to

303   consider. For this reason, in order to understand and isolate the contribution of each single band to the

304   RA1and RA2 variation in our set of samples, we normalized each band to the G band intensity in Figure 6,

305   where the ratio between the G band intensity and the area of the D, S, Dl and Dr bands against an increasing

306   maturation pattern on the x axes is presented. No significant variations are observed in the IG/S area or in the

307   IG/Dl area ratio, while a decrease in the IG/D area (e.g., D area band increase) and an increase of the IG/Dr

308   area ratio (e.g., Dr band area decrease) are clearly visible.

309   We conclude that the increase in RA2 ratio is attributed to the decrease in width and intensity of G and Gl

310   bands and to the decrease of the satellite band Dr. This is accompanied by a corresponding increase in D

311   band area (IG/D area decrease) which is mostly due to an increase in FWHM of the D band (Fig 3d).

312   While the D band increases, the G, Gl and Dr decrease with increasing structural ordering, in agreement with

313   the interpretations already proposed by Ferrari and Robertson (2000), Li et al., (2007) and Rebelo et al.

314   (2015). The interpretation of the Dr and S bands is not straightforward. Rebelo et al. (2015) assign these

315   bands (S and Dl) to the same vibrational modes and to the same structural units of Gl and Dr bands,

316   respectively; thus, we would expect similar coupled behaviour for these bands at increasing temperature.

317   However, we observe a decoupling between S and Gl and Dl and Dr bands with temperature.

318   A similar decoupling was observed by Ferralis et al. (2016) who suggested a different origin for the S and Dl

319   bands (called the D4 and D5 bands in Ferralis et al., 2016). The authors observed that in the 1200 cm^{-1} 1300

320   cm^{-1} region the D4 and D5 bands are related to deformation modes of C-C (D4) and CH (D5) species

321   associated with long saturated and unsaturated alkane chains. These bands show an intensity increase with

322   the increase of H:C ratio from weakly metamorphosed kerogen to graphite.

323   On the other hand, no trend is observed for the S and Dl bands in Figure 6. This could be due to the different

324   composition of the OM in the upper part of the well (varying terrigenous OM and AOM enrichment)

325   generating different responses of the excitation bands with increasing thermal maturity. The variation of C-C

326   and C-H associated with aliphatic at low maturity stages (R_o% < 1.5) is not straightforward and depends on

327   complex chemical changes that occur simultaneously, such as shortening of aliphatic chains, decreased

328   branching of aliphatic chains and formation of cyclic compounds (Lis et al., 2005). Therefore, we infer that

329   the assignment of the S and Dl bands is still unclear and further investigations are strongly needed to fully

330   address this issue.

331

9

332 *4.3 Raman spectra evolution in Organic matter*

333 Comparing our results with those obtained at higher degrees of maturation (Beyssac et al., 2002; Lahfid et

334 al., 2010 and Rantish et al., 2016), we can trace the evolution of Raman spectra of the OM over a wide range

335 of paleotemperatures. Using data from previous studies, we observed the following changes going from

336 anthracite to graphite ranks (i.e. typically greenschist facies and above, see Wopenka and Pasteris, 1993;

337 Beyssac et al., 2002): a decrease in the D band area, a shrinking of the G band and a shift of the G band

338 toward the triperiodic graphite position (Fig. 7). Conversely, going from low volatile bituminous coal to

339 anthracite ranks, we observed from the works of Lahfid et al., (2010), Hinrichs et al., (2016) and Lünsdorf,

340 (2016) an increase of the D band and a progressive disappearance of the minor bands. From results from this

341 work, we found that changes in Raman spectra in diagenesis consist mainly in a narrowing of the G band

342 region and a small increase of the D band area. The decrease of the G band area is due to a progressive

343 shrinking of the G band and to the decrease in the area of the Gl and Dr bands assigned to small aromatic

344 rings and small polyene domains present only in kerogen at low thermal maturity levels (Castiglioni et al.,

345 2004; Li et al., 2007; Rebelo et al., 2016).

346

347

348 **5 Conclusions**

349 Raman spectroscopic measurements were performed on shalescollected from a 5 km deep well drilled across

350 the Miocene-Oligocene Malembo Formation in the Lower Congo Basin (offshore of Angola). Bulk kerogens,

351 with a thermal maturity range increasing from about 0.3 R_o% at the top of the well to about 1.5 R_o% at the

352 bottom were analysed.

353 The best correlations of Raman spectral parameters against the increase of thermal maturity are: D-G band

354 distance; FWHM of the G band; D/G area ratio; RA2 ratio (calculated as S+Dl+SD/Dr+Gl+G band ratio) and

355 the D/G width ratio.

356 These results demonstrate that, at low diagenetic stages (between the immature and mid-mature stages of

357 hydrocarbon generation) changes in Raman spectra of undifferentiated dispersed organic matter show

358 quantifiable changes in response to thermal maturation and can be used to successfully parameterize the

359 thermal evolution of a sedimentary succession.

360

368
369
370 **References**
371

372 Aldega, L., Corrado, S., Grasso, M., Maniscalco, R., 2007. Correlation of diagenetic data from organic and
373 inorganic studies in the Apenninic-Maghrebian fold-and-thrust belt: a case study from eastern Sicily. The
374 Journal of Geology 115, 335-353.

376 Allen, P. A., Allen, J. R., 2013. Basin Analysis: Principles and Application to Petroleum Play Assessment,
377 third ed. John Wiley & Sons, Hoboken, NJ, USA.

379 Andreucci, B., Castelluccio, A., Corrado, S., Jankowski, L., Mazzoli, S., Szaniawski, R., Zattin, M., 2015.
380 Interplay between the thermal evolution of an orogenic wedge and its retro-wedge basin: An example from
381 the Ukrainian Carpathians. Geological Society of America Bulletin 127, 410-427.

383 Aoya, M., Kouketsu, Y., Endo, S., Shimizu H., Mizukami, T., Nakamura, D., Wallis, S., 2010. Extending the
384 applicability of the Raman carbonaceous-material geothermometer using data from contact metamorphic
385 rocks. Journal of Metamorphic Geology 28, 895-914.

387 Beny-Bassez, C., Rouzaud, J., 1985. Characterization of carbonaceous materials by correlated electron and
388 optical microscopy and Raman microspectroscopy. Scanning Electron Microscopy 1, 119-132.

390 Beyssac, O., Goffé, B., Chopin, C., Rouzaud, J., 2002. Raman spectra of carbonaceous material in
391 metasediments: a new geothermometer. Journal of metamorphic Geology 20, 859-871.

393 Beyssac, O., Goffé, B., Petitet, J.-P., Froigneux, E., Moreau, M., Rouzaud, J.-N., 2003. On the
394 characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy.
395 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 59, 2267-2276.

397 Cançado, L., Takai, K., Enoki, T., Endo, M., Kim, Y., Mizusaki, H., Speziali, N., Jorio, A., Pimenta, M.,
398 2008. Measuring the degree of stacking order in graphite by Raman spectroscopy. Carbon 46, 272-275.

400 Cantarelli, V., Aldega, L., Corrado, S., Invernizzi, C., Casas-Sainz, A., 2013. Thermal history of the Aragón-
401 Béarn Basin (Late Paleozoic, western Pyrenees, Spain); insights into basin tectonic evolution. Italian Journal
402 of Geosciences 132, 443-462.

404 Caricchi, C., Corrado, S., Di Paolo, L., Aldega, L., Grigo, D., 2016. Thermal maturity of Silurian deposits in
405 the Baltic Syneclise (on-shore Polish Baltic Basin): contribution to unconventional resources assessment.
406 Italian Journal of Geosciences 135, 383-393.

408 Carr, A.D., 2000. Suppression and retardation of vitrinite reflectance, Part 1. Formation and significance for
409 hydrocarbon generation. Journal of Petroleum Geology 23, 313-343.

411 Castiglioni, C., Tommasini, M., Zerbi, G., 2004. Raman spectroscopy of polyconjugated molecules and
412 materials: confinement effect in one and two dimensions: Philosophical Transactions of the Royal Society of
413 London. Series A. Mathematical, Physical and Engineering Sciences 362, 2425-2459.

415 Corrado, S., Aldega, L., Balestrieri, M.L., Maniscalco, R., Grasso, M., 2009. Structural evolution of the
416 sedimentary accretionary wedge of the Alpine system in eastern Sicily: thermal and thermochronological
417 constraints. Geological Society of America Bulletin 121, 1475–1490.

419 Corrado, S., Aldega, L., Zattin, M., 2010. Sedimentary vs. tectonic burial and exhumation along the
420 Apennines (Italy). Journal of the Virtual Explorer 36,1-37.

422 Corrado, S., Schito, A., Aldega, L. Grigo, D., 2016. A quantitative multi-method approach to assess thermal
423 evolution of the Lower Congo Basin (Angola). Rendiconti Online della Società Geologica Italiana 40,
424 pp.525.
425

426 Di Paolo, L., Aldega, L., Corrado, S., Mastalerz, M., 2012. Maximum burial and unroofing of Mt. Judica
427 recess area in Sicily: implication for the Apenninic–Maghrebian wedge dynamics. Tectonophysics 530, 193-
428 207.
429
430 Di Donato, E., Tommasini, M., Fustella, G., Brambilla, L., Castiglioni, C., Zerbi, G., Simpson, C.D., Müllen,
431 K., Negri, F., 2004. Wavelength-dependent Raman activity of D2h symmetry polycyclic aromatic
432 hydrocarbons in the D-band and acoustic phonon regions. Chemical Physics 301, 81–93.
433
434 Endo, S., Wallis, S. R., Tsuboi, M., Torres De Leòn, R., Solari, L. A., 2012. Metamorphic evolution of
435 lawsonite eclogites from the southern Motagua fault zone, Guatemala: insights from phase equilibria and
436 Raman spectroscopy. Journal of Metamorphic Geology 30, 143-164.
437
438 Federici, I., Cavazza, W., Okay, A. I., Beyssac, O., Zattin, M., Corrado, S. Dellisanti, F., 2010.
439 Thermal Evolution of the Permo-Triassic Karakaya Subduction-accretion Complex between the Biga
440 Peninsula and the Tokat Massif (Anatolia). Turkish Journal of Earth Sciences 19, 409-429.
441
442 Ferrari, A.C., Robertson, J., 2000. Interpretation of Raman spectra of disordered and amorphous carbon:
443 Physical Review B 61, 14095-14107.
444
445 Ferrari, A. C., Robertson, J., 2004. Raman spectroscopy of amorphous, nanostructured, diamond–like
446 carbon, and nanodiamond. Philosophical Transactions of the Royal Society of London A: Mathematical,
447 Physical and Engineering Sciences 362, 2477-2512.
448
449 Friedel, R., Carlson, G., 1972. Difficult carbonaceous materials and their infra-red and Raman spectra.
450 Reassignments for coal spectra. Fuel 51, 194-198.
451
452 Guedes, A., Valentim, B., Prieto, A. C., Rodrigues, S., Noronha, F., 2010. Micro-Raman spectroscopy of
453 collotelinite, fusinite and macrinite. International Journal of Coal Geology 83, 415-422.
454
455 Guedes, A., Valentim, B., Prieto, A., Noronha F., 2012. Raman spectroscopy of coal macerals and fluidized
456 bed char morphotypes. Fuel 97, 443-449.
457
458 Hackley, P. C., Cardott, B. J., 2016. Application of organic petrography in North American shale petroleum
459 systems: A review. International Journal of Coal Geology 163, 8-51.
460
461 Heise, H., Kuckuk, R., Ojha, A., Srivastava, A., Srivastava, V., Asthana, B., 2009. Characterisation of
462 carbonaceous materials using Raman spectroscopy: a comparison of carbon nanotube filters, single-and
463 multi-walled nanotubes, graphitised porous carbon and graphite. Journal of Raman Spectroscopy 40, 344-
464 353.
465
466 Jehlička, J., Urban, O., Pokorný, J., 2003. Raman spectroscopy of carbon and solid bitumens in sedimentary
467 and metamorphic rocks. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 59, 2341-
468 2352.
469
470 Jehlička, J., Šťastná, A., Přikryl, R., 2009. Raman spectral characterization of dispersed carbonaceous matter
471 in decorative crystalline limestones.Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy
472 73, 404-409.
473
474 Kelemen, S., Fang, H., 2001, Maturity trends in Raman spectra from kerogen and coal. Energy & Fuels 15,
475 653-658.
476
477 Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., Goffé, B., 2010. Evolution of the Raman
478 spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps (Switzerland). Terra
479 Nova 22, 354-360.
480

481 Li, C.-Z., 2007. Some recent advances in the understanding of the pyrolysis and gasification behaviour of
482 Victorian brown coal. Fuel 86, 1664-1683.
483
484 Lis, G. P., Mastalerz, M., and Schimmelmann, A., 2008, Increasing maturity of kerogen type II reflected by
485 alkylbenzene distribution from pyrolysis-gas chromatography–mass spectrometry: Organic Geochemistry 39,
486 440-449.
487
488 Liu, D., Xiao, X., Tian, H., Min, Y., Zhou, Q., Cheng, P., Shen, J., 2012. Sample maturation calculated using
489 Raman spectroscopic parameters for solid organics: Methodology and geological applications. Chinese
490 Science Bulletin 58, 1285-1298.
491
492 Lünsdorf, N. K., 2016. Raman spectroscopy of dispersed vitrinite - Methodical aspects and correlation with
493 reflectance. International Journal of Coal Geology 153, 75-86.
494
495 Marques, M., Suárez-Ruiz, I., Flores, D., Guedes, A., Rodrigues, S., 2009. Correlation between optical,
496 chemical and micro-structural parameters of high-rank coals and graphite. International Journal of Coal
497 Geology 77, 377-382.
498
499 Mumm, A. S., İnan, S., 2016. Microscale Organic Maturity determination of Graptolites using
500 Raman Spectroscopy. International Journal of Coal Geology 162, 96-107.
501
502 Negri, F., di Donato, E., Tommasini, M., Castiglioni, C., Zerbi, G., Müllen, K., 2004. Resonance Raman
503 contribution to the D band of carbon materials: modeling defects with quantum chemistry. Journal of
504 Chemical Physics 120, 11889–11900.
505
506 Nemanich, R., Solin, S., 1979. First-and second-order Raman scattering from finite-size crystals of graphite.
507 Physical Review B 20, 392.
508
509 Nestler, K., Dietrich, D., Witke, K., Rößler, R., Marx, G., 2003. Thermogravimetric and Raman
510 spectroscopic investigations on different coals in comparison to dispersed anthracite found in permineralized
511 tree fern *Psaronius* sp. Journal of Molecular Structure 661, 357-362.
512
513 Petersen, H., Rosenberg, P., 1998. Reflectance retardation (suppression) and source rock properties related to
514 hydrogen enriched vitrinite in middle Jurassic coals, Danish North Sea. Journal of Petroleum Geology 21,
515 247-263.
516
517 Potgieter-Vermaak, S., Maledi, N., Wagner, N., Van Heerden, J., Van Grieken, R., Potgieter, J., 2011.
518 Raman spectroscopy for the analysis of coal: a review. Journal of Raman Spectroscopy 42, 123-129.
519
520 Pócsik, I., Hundhausen, M., Koós, M., Ley, L., 1998. Origin of the D peak in the Raman spectrum of
521 microcrystalline graphite. Journal of Non-Crystalline Solids 227, 1083-1086.
522
523 Price, L. C., Barker, C. E., 1985. Suppression of vitrinite reflectance in amorphous rich kerogen--a major
524 unrecognized problem. Journal of Petroleum Geology 8, p. 59-84.
525
526 Quirico, E., Rouzaud, J. N., Bonal, L., Montagnac, G., 2005. Maturation grade of coals as revealed by
527 Raman spectroscopy: progress and problems. Spectrochimica Acta Part A: Molecular and Biomolecular
528 Spectroscopy 61, 2368-2377.
529
530 Rantitsch, G., Lämmerer, W., Fisslthaler, E., Mitsche, S., Kaltenböck, H., 2016. On the discrimination of
531 semi-graphite and graphite by Raman spectroscopy. International Journal of Coal Geology 159, 48–56.
532
533 Rebelo, S. L., Guedes, A., Szefczyk, M. E., Pereira, A. M., Araújo, J. P., Freire, C., 2016. Progress in the
534 Raman spectra analysis of covalently functionalized multiwalled carbon nanotubes: unraveling disorder in
535 graphitic materials. Physical Chemistry Chemical Physics 18, 12784-12796.
536

537 Robl, T. L., Davis, B. H., 1993. Comparison of the HF-HCl and HF-BF 3 maceration techniques and the
538 chemistry of resultant organic concentrates. Organic Geochemistry 20, 249-255.
539
540 Romero-Sarmiento, M.-F., Rouzaud, J.-N., Bernard, S., Deldicque, D., Thomas, M., Littke, R., 2014.
541 Evolution of Barnett Shale organic carbon structure and nanostructure with increasing maturation. Organic
542 Geochemistry 71, 7-16.
543
544 Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., Pöschl, U., 2005. Raman microspectroscopy of
545 soot and related carbonaceous materials: Spectral analysis and structural information. Carbon 43, 1731-1742.
546
547 Schito, A., Corrado, S., Aldega, L., Grigo, D., 2016. Overcoming pitfalls of vitrinite reflectance
548 measurements in the assessment of thermal maturity: the case history of the lower Congo basin. Marine and
549 Petroleum Geology 74, 59-70.
550
551 Scott, A. C., Glasspool, I. J., 2007. Observations and experiments on the origin and formation of inertinite
552 group macerals. International Journal of Coal Geology 70, 53-66.
553
554 Shirakawa, H., Ito, T., Ikeda, S., 1973. Raman scattering and electronic spectra of poly (acetylene). Polymer
555 Journal 4, 460-462.
556
557 Taylor, G. H., 1998. Organic petrology: A new handbook incorporating some revised parts of Stach's
558 textbook of coal petrology, Gebruder Borntraeger Verlagsbuchhandlung, Stuttgart, Germany.
559
560 Tyson, R. V., 1995. Organic facies and palynofacies, In: Sedimentary organic matter, Springer Netherlands,
561 pp. 81-118
562
563 Teichmüller, M., 1986. Organic petrology of source rocks, history and state of the art. Organic Geochemistry
564 10, 581-599.
565
566 Tuinstra, F., Koenig, J. L., 1970. Raman spectrum of graphite. The Journal of Chemical Physics 53, 1126-
567 1130
568 Vandenbroucke, M., Largeau, C., 2007. Kerogen origin, evolution and structure. Organic Geochemistry 38,
569 719-833.
570
571 Wilkins, R. W., Boudou, R., Sherwood, N., Xiao, X., 2014. Thermal maturity evaluation from inertinites by
572 Raman spectroscopy: The 'RaMM' technique. International Journal of Coal Geology 128, 143-152.
573
574 Wopenka, B., Pasteris, J. D., 1993. Structural characterization of kerogens to granulite-facies graphite:
575 applicability of Raman microprobe spectroscopy. The American Mineralogist 78, 533-557.
576
577 Yui, T. F., Huang, E., Xu, J..1996. Raman spectrum of carbonaceous material: a possible metamorphic grade
578 indicator for low-grade metamorphic rocks. Journal of Metamorphic Geology 14, 115-124.
579
580 Zhou, Q., Xiao, X., Pan, L., Tian, H., 2014. The relationship between micro-Raman spectral parameters and
581 reflectance of solid bitumen. International Journal of Coal Geology 121, 19-25.
582
583
584 **Figure captions**
585
586
587 Figure 1. Examples of Raman spectra measured on organic matter extracted from cuttings at different
588 stratigraphic depth. The stratigraphic column is redrawn after Schito et al. (2016)
589
590

14

Figure 2. Example of bands and bands position obtained by Raman analysis on dispersed organic matter for: low matured samples collected at the top of the well (a) and high matured samples collected at the bottom of the well (b)

Figure 3. Trends with depth of: position of the D band (a), position of the G band (b), difference between G band and D band positions (c), width at half height of the D band (d), the width at half height of the G band (e), intensities ratios between D and G bands (f), area ratios between D and G bands(g), full width at maximum height of the D and G bands (h), RA1 parameter (i) and RA2 parameter (j).
Grey dots indicate terrestrial derived organic matter rich kerogen, black dots amorphous organic matter rich kerogen. Bars indicate standard deviation for each samples

Figure 4 Correlation between $R_o\%_{eq.}$ calculated based on clay mineralogy and FT-IR analyses and distance between D and G band (a), width at half height of the G band (b), area ratio between D and G bands (c); RA2 parameter (d) and width ratio between D and G ratio (e)

Figure 5. Schematic evolution of the Gl and the G bands

Figure 6. Ratio of G intensity against: S band area (a), Dl band area (b), D band area (c) and Dr band area (d) for all sample (not average per each depth) of the analysed well

Figure 7. Evolution of the Raman spectra from high metamorphic stages to the immature stage of HC generation. Raman spectra for temperatures higher than 170 °C are redrawn from Lahfid et al. (2010) and Beyssac et al. (2002). Temperature for samples from this work were carried out from thermal model by Schito et al. (2016).
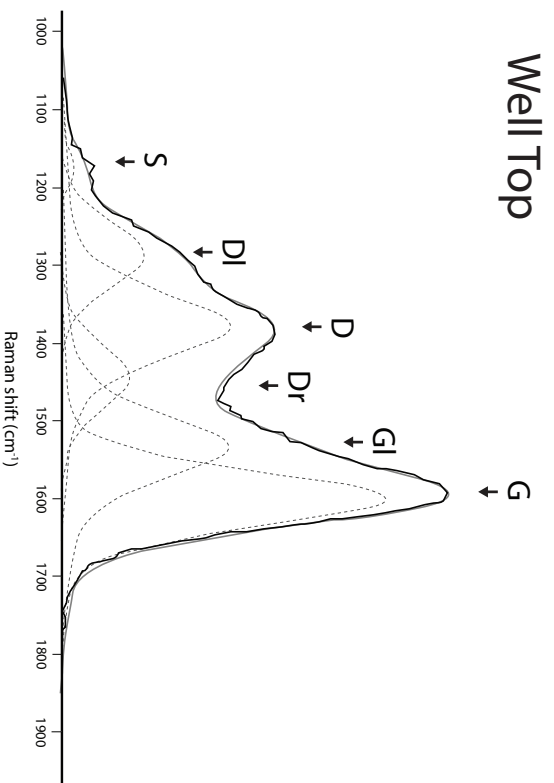
Table 1. Organic matter composition and Raman parameters for each depth interval analysed. Acronyms: AOM amorphous organic matter; MPH marine phytoplankton; CHF continental herbaceous fragments; CWF continental wooden fragments; stdv: standard deviation; pD: position of the D band (cm^{-1}); pG: position of the G band (cm^{-1}); wD: full width at maximum height of the D band (cm^{-1}); wG: full width at maximum height of the D band (cm^{-1}); Δ D-G: difference between G band and D band position (cm^{-1}); ID/IG: intensity ratio between D and G bands; aD/aG: area ratio between D and G bands; RA1: area (S+Dl+D) / area (S+Dl+D+Dr+Gl+G); RA2: area (S+Dl+D) / area (Dr+Gl+G); wD/wG: ratio between full width at maximum height of D and G bands; s.d: standard deviation
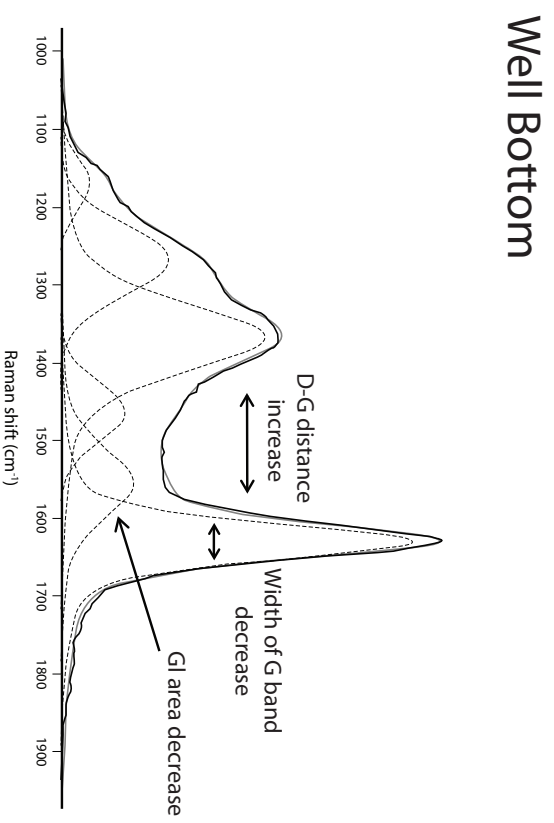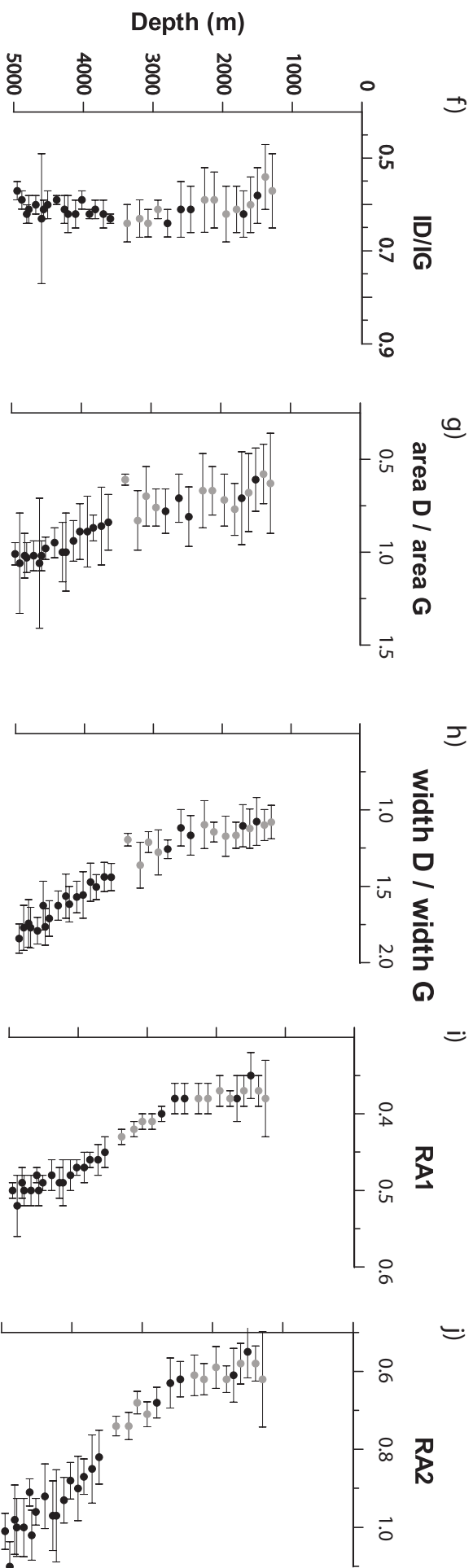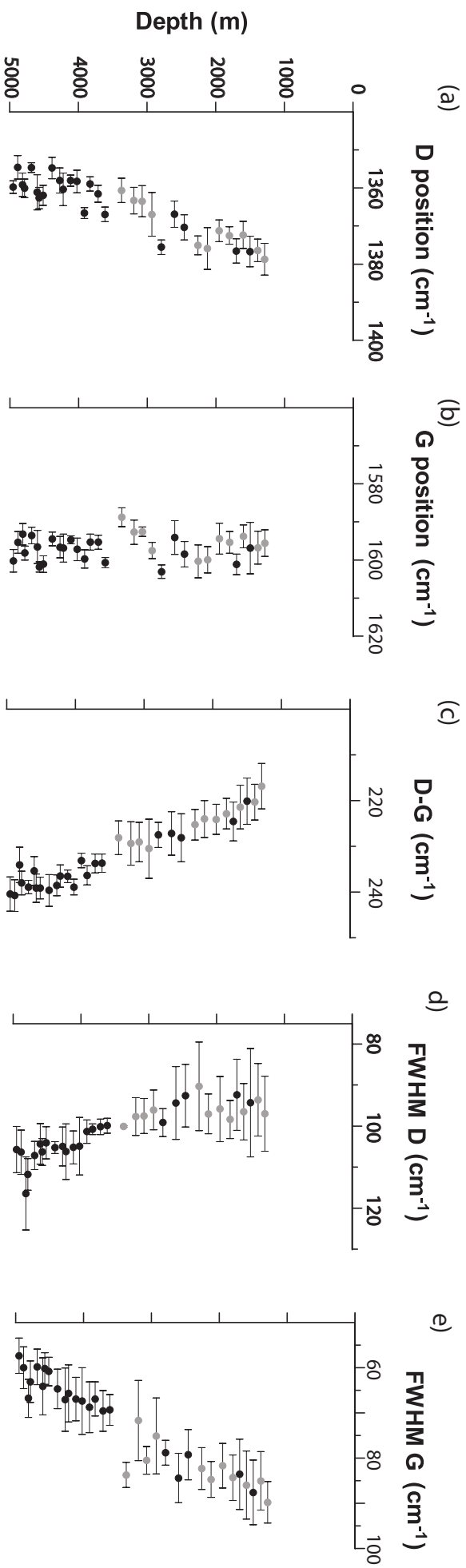
15

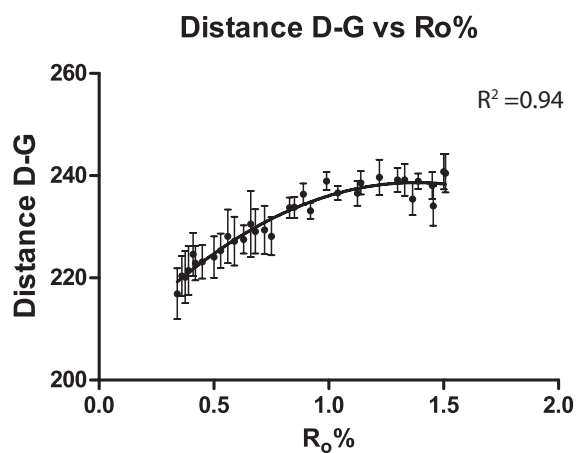Depth

Plio-Pleist	600
Upper Mioc.	800
	1000
	1200
Mid. Mioc	1400
	1600
	1800
Lower Miocene	2000
	2200
	2400
	2600
	2800
	3000
	3200
Oligocene	3400
	3600
	3800
	4000
	4200
	4400
	4600
	4800
	5000

?

1290 m

2120 m

3180 m

4110 m

4950 m

700   800   900   1 000   1 100   1 200   1 300   1 400   1 500   1 600   1 700   1 800   1 900   2 000   2 100   2 200

Raman Shift (cm^{-1})

a) Well Top

S
Dl
D
Dr
Gl
G

Raman shift (cm⁻¹)

b) Well Bottom

D-G distance increase

Width of G band decrease

Gl area decrease

Raman shift (cm⁻¹)

a)

Distance D-G vs Ro%

$R^2 = 0.94$

Distance D-G vs $R_o\%$ scatter plot with fitted curve. Y-axis: Distance D-G (200 to 260). X-axis: $R_o\%$ (0.0 to 2.0).

b)

FWHM-G vs Ro%

$R^2 = 0.91$

FWHM-G vs $R_o\%$ scatter plot with fitted curve. Y-axis: FWHM-G (50 to 100). X-axis: $R_o\%$ (0.0 to 2.0).

c)

D area / G area vs Ro%

$R^2 = 0.93$

D area / G area vs $R_o\%$ scatter plot with fitted curve. Y-axis: D area / G area (0.0 to 1.5). X-axis: $R_o\%$ (0.0 to 2.0).

d)

RA2 vs Ro%

$R^2 = 0.95$

RA2 vs $R_o\%$ scatter plot with fitted curve. Y-axis: RA2 (0.0 to 1.5). X-axis: $R_o\%$ (0.0 to 2.0).

e)

D width/G width vs Ro%

$R^2 = 0.96$

D width/G width vs $R_o\%$ scatter plot with fitted curve. Y-axis: D width/G width (0.0 to 2.5). X-axis: $R_o\%$ (0.0 to 2.0).
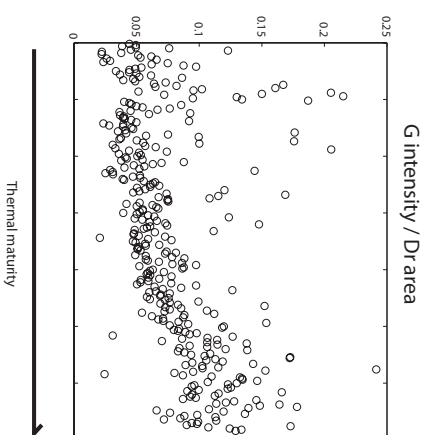
Low thermal maturity signal

High thermal maturity signal

Gl band area

Width at half heigth of G band

700 ° C

600 ° C
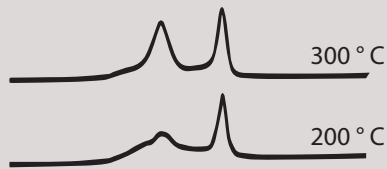
540 ° C

400 ° C
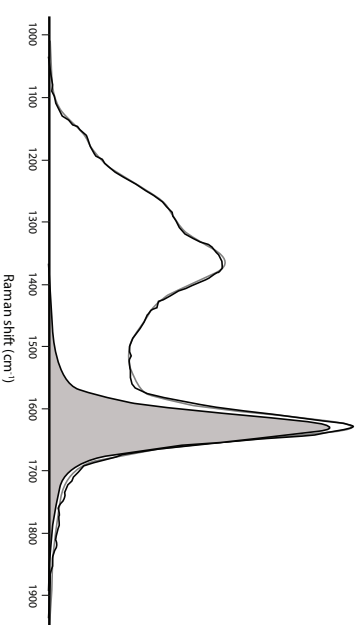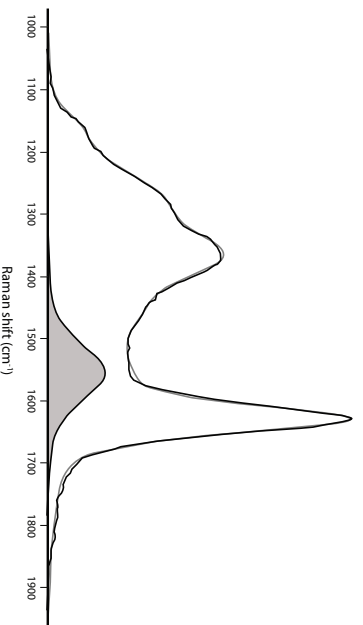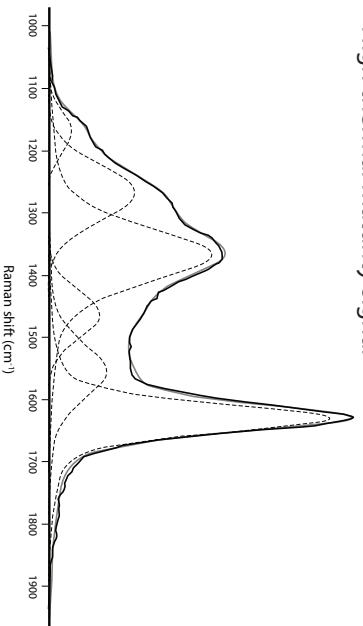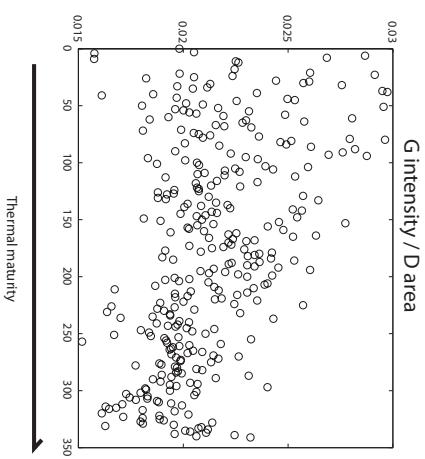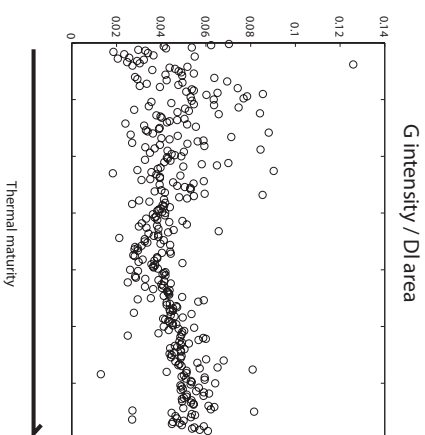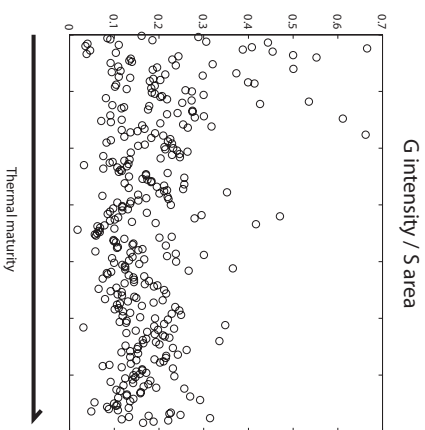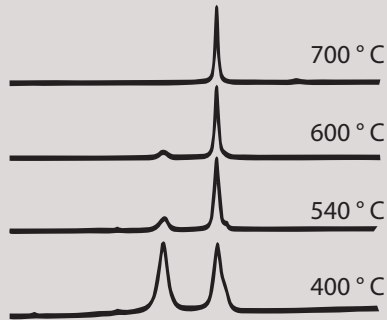
Coal ranks

Antracite to Graphite

Driven mechanism with Temperature increase

Decrease of the D band area and decraese of the full

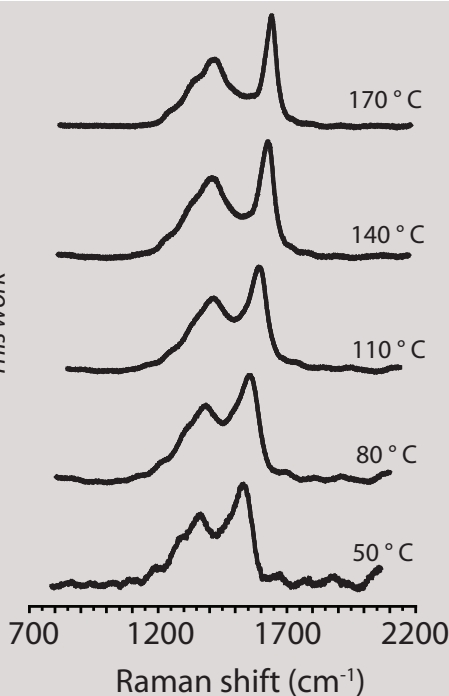width at maximum height of the G band

300 ° C

200 ° C

Coal ranks

Low volatile bituminous coal to antracite

Driven mechanism with Temperature increase

Increase of the D band area and progressive desappearance

of the minor bands

170 ° C

140 ° C

110 ° C

80 ° C

50 ° C

700   1200   1700   2200

Raman shift (cm^{-1})

Coal ranks

Subituminous coals to medium volatile bituminous coal

Driven mechanism with Temperature increase

Decrease of the G band area due to a progressive shirnking

of the G band and to the decreaes in the area of the Dl band

assigned by recent work (Rebelo et al., 2016) to small aromatic

rings and small polyene domains present only in kerogene at

lo thermal maturity

Depth (m)	Kerogen composition	pD	s.d. pD	pG	s.d. pG	wD	s.d. wD	wG	s.d. wG	Δ D−G	s.d. Δ D−G
1290	$AOM_{10}CHF_{25}CWF_{65}$	1378.71	4.14	1595.58	3.48	96.96	9.15	89.82	4.60	1378.33	4.97
1390	$AOM_5MPH_5CHF_{30}CWF_{60}$	1376.38	2.98	1596.75	4.34	93.57	8.84	85.07	6.48	1376.02	3.91
1500	$AOM_{80}CHF_{15}CWF_5$	1376.70	4.01	1596.85	6.73	94.29	13.22	87.63	7.18	1376.35	5.08
1600	$AOM_{70}CHF_{20}CWF_{10}$	1372.34	3.54	1593.79	3.02	96.48	6.85	86.00	7.53	1371.98	4.79
1700	$AOM_{70}CHF_{25}CWF_5$	1376.55	3.18	1601.14	2.69	92.35	8.66	83.61	7.78	1376.17	4.23
1800	$AOM_{10}MPH_5CHF_{25}CWF_{60}$	1372.48	2.30	1595.36	2.84	98.37	4.65	84.37	5.02	1372.09	3.34
1950	$AOM_{20}MPH_{10}CHF_{25}CWF_{45}$	1371.25	2.86	1594.40	4.04	95.80	7.94	81.72	4.94	1370.87	3.28
2120	$AOM_{60}CHF_{15}CWF_{25}$	1375.91	5.47	1599.96	3.45	97.02	4.85	84.76	3.96	1375.53	4.05
2260	$AOM_{10}MPH_{10}CHF_{15}CWF_{65}$	1375.04	2.46	1600.35	4.29	90.29	10.81	82.33	4.64	1374.66	3.36
2460	$AOM_{80}MPH_5CHF_{10}CWF_5$	1370.33	3.32	1598.46	3.35	92.54	7.64	79.28	5.55	1369.95	5.25
2600	$AOM_{90}CHF_5CWF_5$	1366.90	3.43	1594.10	4.40	94.35	8.88	84.44	5.47	1366.51	4.76
2790	$AOM_{80}MPH_{15}CHF_{10}CWF_5$	1375.53	1.91	1603.05	1.77	99.12	3.40	78.84	2.74	1375.13	2.75
2930	$AOM_{40}CHF_{20}CWF_{40}$	1366.95	5.75	1597.50	2.11	96.04	4.82	75.14	8.42	1366.54	6.47
3070	$AOM_{90}CHF_5CWF_5$	1363.48	4.10	1592.56	1.22	97.53	4.27	80.53	3.08	1363.08	4.33
3190	$AOM_{25}CHF_{35}CWF_{40}$	1363.32	3.49	1592.70	3.16	97.67	4.59	71.74	8.87	1362.90	4.75
3370	$AOM_{35}CHF_{15}CWF_{50}$	1360.63	3.21	1588.77	2.49	100.04	0.22	83.77	2.79	1360.20	3.71
3610	$AOM_{60}CHF_{25}CWF_{15}$	1366.95	1.90	1600.68	1.36	99.86	1.82	69.37	3.38	1366.50	1.99
3710	$AOM_{80}MPH_{10}CHF_5CWF_5$	1361.53	2.21	1595.32	1.81	100.16	1.92	69.61	4.50	1361.07	2.06
3830	$AOM_{90}CHF_5CWF_5$	1358.91	1.88	1595.29	2.12	100.73	1.30	66.94	3.78	1358.45	2.07
3910	$AOM_{10}CHF_{20}BIT_{70}$	1366.58	1.40	1599.71	2.42	101.30	2.85	68.79	5.61	1366.11	1.57
4020	$AOM_{85}CHF_{15}$	1358.27	2.97	1597.20	2.98	104.89	7.01	67.39	7.39	1357.80	1.73
4110	AOM_{100}	1358.07	1.45	1594.67	1.03	105.18	4.00	66.98	4.80	1357.59	1.39
4220	—	1360.34	4.27	1596.89	3.67	106.20	6.79	65.71	6.30	1359.85	2.43
4270	AOM_{100}	1358.01	3.29	1596.61	2.79	104.93	4.76	67.08	6.99	1357.52	2.28
4380	AOM_{100}	1354.77	2.79	1594.43	1.80	105.20	1.46	64.73	4.39	1354.29	3.47
4510	—	1361.91	2.62	1601.08	2.19	104.07	3.91	60.87	3.16	1361.42	2.37
4570	AOM_{100}	1362.64	2.82	1601.82	1.34	106.27	3.26	60.23	3.49	1362.14	3.10
4600	AOM_{100}	1361.13	4.60	1596.56	4.35	104.32	4.98	64.14	6.32	1360.66	3.18
4680	AOM_{100}	1354.64	1.28	1593.58	2.16	107.15	3.44	59.84	3.93	1354.14	1.49
4780	—	1360.10	2.41	1598.16	1.82	111.75	3.88	63.13	4.61	1359.60	2.61
4810	AOM_{100}	1359.13	3.08	1593.21	2.84	116.39	8.92	66.81	4.19	1358.63	3.87
4880	AOM_{100}	1354.58	3.09	1595.37	2.83	106.33	5.39	60.04	4.63	1354.06	3.46
4950		1359.74	1.64	1600.22	2.97	105.69	5.64	57.38	3.90	1359.24	3.75

Depth (m)	Kerogen composition	ID/IG	s.d. ID/IG	aD/aG	s.d. aD/aG	RA1	s.d. RA1	RA2	s.d. RA2	wD/wG	s.d. wD/wG
1290	$AOM_{10}CHF_{25}CWF_{65}$	0.57	0.08	0.63	0.27	0.38	0.05	0.62	0.12	1.08	0.11
1390	$AOM_5MPH_5CHF_{30}CWF_{60}$	0.54	0.07	0.58	0.16	0.37	0.02	0.58	0.05	1.10	0.10
1500	$AOM_{80}CHF_{15}CWF_5$	0.58	0.06	0.61	0.17	0.35	0.03	0.55	0.07	1.08	0.16
1600	$AOM_{70}CHF_{20}CWF_{10}$	0.60	0.06	0.68	0.21	0.37	0.02	0.58	0.05	1.12	0.13
1700	$AOM_{70}CHF_{25}CWF_5$	0.62	0.05	0.71	0.25	0.38	0.03	0.61	0.07	1.10	0.14
1800	$AOM_{10}MPH_5CHF_{25}CWF_{60}$	0.61	0.05	0.77	0.14	0.38	0.01	0.62	0.03	1.17	0.09
1950	$AOM_{20}MPH_{10}CHF_{25}CWF_{45}$	0.62	0.06	0.72	0.14	0.37	0.02	0.59	0.05	1.17	0.13
2120	$AOM_{60}CHF_{15}CWF_{25}$	0.59	0.06	0.67	0.13	0.38	0.02	0.62	0.04	1.14	0.06
2260	$AOM_{10}MPH_{10}CHF_{15}CWF_{65}$	0.59	0.07	0.67	0.20	0.38	0.02	0.61	0.05	1.10	0.16
2460	$AOM_{80}MPH_5CHF_{10}CWF_5$	0.61	0.05	0.81	0.16	0.38	0.02	0.62	0.05	1.17	0.13
2600	$AOM_{90}CHF_5CWF_5$	0.61	0.06	0.71	0.13	0.38	0.02	0.63	0.06	1.12	0.12
2790	$AOM_{80}MPH_5CHF_{10}CWF_5$	0.64	0.03	0.78	0.12	0.40	0.01	0.68	0.04	1.26	0.06
2930	$AOM_{40}CHF_{20}CWF_{40}$	0.61	0.02	0.76	0.10	0.41	0.01	0.71	0.03	1.28	0.15
3070	$AOM_{90}CHF_5CWF_5$	0.64	0.03	0.70	0.16	0.41	0.01	0.68	0.03	1.21	0.07
3190	$AOM_{25}CHF_{35}CWF_{40}$	0.63	0.04	0.83	0.16	0.42	0.01	0.74	0.04	1.36	0.15
3370	$AOM_{35}CHF_{15}CWF_{50}$	0.64	0.04	0.61	0.03	0.43	0.01	0.74	0.02	1.19	0.04
3610	$AOM_{60}CHF_{25}CWF_{15}$	0.63	0.01	0.84	0.15	0.45	0.02	0.82	0.07	1.44	0.09
3710	$AOM_{80}MPH_{10}CHF_5CWF_5$	0.62	0.03	0.86	0.21	0.46	0.02	0.85	0.09	1.44	0.10
3830	$AOM_{90}CHF_5CWF_5$	0.61	0.02	0.87	0.07	0.46	0.01	0.87	0.05	1.50	0.08
3910	$AOM_{10}CHF_{20}BIT_{70}$	0.62	0.01	0.89	0.19	0.47	0.02	0.90	0.08	1.47	0.12
4020	$AOM_{85}CHF_{15}$	0.59	0.02	0.89	0.15	0.47	0.01	0.88	0.05	1.56	0.15
4110	AOM_{100}	0.62	0.03	0.94	0.11	0.48	0.02	0.93	0.06	1.57	0.10
4220	–	0.62	0.04	1.00	0.21	0.49	0.03	0.97	0.12	1.62	0.12
4270	AOM_{100}	0.61	0.03	1.00	0.16	0.49	0.02	0.97	0.09	1.56	0.14
4380	AOM_{100}	0.59	0.01	0.95	0.08	0.48	0.02	0.92	0.08	1.63	0.10
4510	–	0.60	0.03	0.98	0.06	0.49	0.01	0.96	0.03	1.71	0.12
4570	AOM_{100}	0.61	0.02	1.02	0.08	0.50	0.02	1.02	0.06	1.76	0.12
4600	AOM_{100}	0.63	0.14	1.06	0.35	0.48	0.01	0.91	0.03	1.63	0.16
4680	AOM_{100}	0.60	0.02	1.02	0.08	0.50	0.02	1.00	0.07	1.79	0.09
4780	–	0.61	0.03	1.03	0.08	0.50	0.02	1.00	0.07	1.77	0.13
4810	AOM_{100}	0.62	0.02	1.02	0.12	0.49	0.02	0.98	0.09	1.74	0.16
4880	AOM_{100}	0.59	0.02	1.06	0.27	0.52	0.04	1.10	0.06	1.77	0.15
4950		0.57	0.02	1.01	0.06	0.50	0.01	1.01	0.05	1.84	0.10

Highlights

- We analysed kerogen from a well from the offshore Angola with Raman spectroscopy

- Thermal maturity ranges between immature and mature stages of HC generation

- Raman parameters show good trends with depth in the well

- We found a good correlation between thermal maturity trend and Raman parameters

- We discuss the physical-chemical meaning of Raman spectra variations in diagenesis