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# New insights into the structure and formation of coals, terrestrial and extraterrestrial kerogens from resonant UV Raman spectroscopy

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1 **New insights into the structure and formation of coals, terrestrial and**  
2 **extraterrestrial kerogens from resonant UV Raman spectroscopy.**

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## **ABSTRACT**

Resonant UV (244 nm-excitation) Raman spectroscopy was used to characterize a series of coals, type II kerogens, Insoluble Organic Matter (IOM) extracted from primitive chondrites and two stratospheric Interplanetary Dust Particles. UV-Raman spectra of immature terrestrial kerogens and coals are distinct from those of extraterrestrial kerogens extracted from type 1 and 2 primitive chondrites, allowing unambiguous identification. The degree of disorder in the refractory carbonaceous matter in the considered IDPs is found to be higher than in primitive chondrites, confirming former interpretation of visible (514 nm-excitation) Raman spectra of IDPs. Spectral and structural features of laboratory analogues of chondritic organic matter formed in cold plasma reactors at 500-700 °C differ from those of natural samples, challenging the hypothesis that chondritic organic matter within the protosolar disk may form through plasma reactions. Finally, UV Raman data shed new light in the structural evolution of coals during maturation and support the presence of an  $sp^2$  structural transition at vitrinite reflectance  $R_o \sim 0.4-0.5\%$ . Comparison with former visible Raman and infrared spectroscopic data confirms the existence of this structural transition, which is related to a dramatic drop of oxygenated species (carboxyl, hydroxyl, ketone and ether groups). Oxygen thus plays an indirect but significant role in the control of the Raman spectra of polyaromatic materials. A potential application of this technique is the determination of the biotic versus abiotic origin of kerogens in ancient rocks on Earth, and of soils and rocks on Mars that is otherwise difficult with classical visible-excitation Raman spectroscopy.

## 40 1. INTRODUCTION

41 On Earth, kerogens and coals are formed by the slow thermal degradation of living  
42 organisms. Their structure, at least in the first stages of their maturation, retains a memory of  
43 the polyaromatic structure and composition of their precursors (Van Krevelen, 1993;  
44 Vandembroucke and Largeau, 2007). Extraterrestrial kerogens recovered from primitive  
45 chondrites were formed in local interstellar medium (ISM) or the protosolar disk through  
46 abiotic processes. There is no consensus to date on their formation process (Alexander et al.,  
47 2017). Their elemental composition is close to that of type III terrestrial kerogens, but their  
48 structure and composition is different. In particular, their polyaromatic structure is based on  
49 highly substituted polyaromatic units (1-4 rings) connected through a ramified aliphatic  
50 linkage with short alkyl chains (Cody and Alexander, 2005; Cody et al., 2002; Gardinier et  
51 al., 2000; Remusat et al., 2005a, 2005b; Wang et al., 2005), while in type III kerogens and  
52 coals the aliphatic linkage is made of longer chains, and overall the structure is less cross-  
53 linked (Vandembroucke and Largeau, 2007).

54 Unravelling the biogenic versus abiotic origin of kerogens is a key issue in several fields  
55 of research. The search of ancient Life on Mars relies on investigations on Martian meteorites  
56 that host tiny refractory carbon inclusions, and in-situ analyses of the Martian soil and rocks  
57 at the surface or in the close subsurface by space missions (Steele et al., 2016, 2018). The  
58 surface of Mars is possibly inseminated by chondritic organic matter, due to meteoritic and  
59 micrometeoritic impacts (Quirico and Bonal, 2019). In this context, distinguishing chondritic  
60 kerogens from putative kerogens issued from a past Martian Life is a major challenge. A  
61 similar issue exists in the interpretation of ancient terrestrial kerogens (> 2 Gyrs), complicated  
62 in that case by the effects of severe thermal metamorphism (Bower et al., 2013; Foucher,  
63 2019).



64 Raman spectroscopy, a versatile technique well suited to characterize solid natural  
65 samples, provides insights into the composition and structure of organic materials (Quirico  
66 and Bonal, 2019). The combined characterization of minerals and molecular species offers a  
67 valuable opportunity to investigate mineral-organic associations at the micrometric scale in  
68 metamorphic and sedimentary rocks, soils, sedimentary organic matter, meteorites and  
69 cometary dusts. Raman spectroscopy has been widely used in the laboratory for mineral and  
70 natural material identification, and is now available as portable instruments allowing field  
71 measurements. This includes two Raman instruments implemented aboard the Mars 2020  
72 rover, which will investigate rocks and soils on the Mars planet: SuperCam, whose Raman  
73 sub-instrument operates at 532 nm and is designed to analyze targets as far as 14 m; and  
74 SHERLOC (Scanning Habitable Environments with Raman and Luminescence for Organics  
75 and Chemicals), holding a Raman sub-instrument operating with a UV 248.6 nm excitation at  
76 a spatial resolution of 50  $\mu\text{m}$  (Beegle et al., 2020; Wiens et al., 2016).

77 Raman spectroscopy has been widely used to characterize the maturation grade of  
78 coals and kerogens, complementing the usual ranking method based on reflectance  
79 measurements (Jehlička et al., 2003; Kelemen and Fang, 2001; Quirico et al., 2005a;  
80 Wopenka and Pasteris, 1993), and to implement carbon thermometers (Beysac et al., 2002;  
81 Lahfid et al., 2010). The structure of carbonaceous matter as determined by Raman spectra is  
82 also influenced by other parameters, such as the nature of the precursor, pressure, oxidation  
83 reactions, and kinetics in the case of short duration thermal events (Bonal et al., 2016; Quirico  
84 et al., 2009, 2018). For instance, terrestrial coals and extraterrestrial kerogens hosted by  
85 primitive chondrites display significant differences in their first-order carbon bands collected  
86 with a 514 nm excitation, which may be due to a precursor effect or post-accretional parent  
87 bodies conditions (Quirico et al., 2009). Disentangling the respective contribution of these  
88 processes is a difficult yet essential step in making Raman spectroscopy a quantitative tool for

89 assessing the conditions of formation and precursors of carbonaceous matter in ancient  
90 terrestrial and extraterrestrial settings.

91 Raman spectroscopy that uses excitation in the deep UV (200-250 nm) has been  
92 shown to present advantages over classical Raman spectroscopy that uses excitation in the  
93 visible to near IR range. UV-Raman spectra are generally devoid of fluorescence, and a  
94 certain number of species have resonant transitions enhancing their detection limit (Asher,  
95 1993). Drawbacks have also been identified, such as sample damage due to photolysis or  
96 annealing, and low scattering yield due to a weak penetration of UV photons. We report a 244  
97 nm Raman survey of a series of terrestrial sedimentary organic matter samples that includes  
98 coals and three type II kerogens, covering a broad range of maturities. Only few UV Raman  
99 spectra have been published so far on sedimentary organic matter, and these data should be  
100 helpful in the context of the study of carbonaceous matter in ancient rocks on Earth,  
101 meteorites and the Mars 2020 mission. We also report new Raman spectra of Insoluble  
102 Organic Matter (IOM) extracted from the Renazzo (CR) and Murray (CM) primitive  
103 chondrites, along with spectra of IOMs and stratospheric IDPs published earlier (Dobrica et  
104 al., 2011; Quirico et al., 2014). We first address technical aspects on the implementation of  
105 244 nm Raman spectroscopy. Then, we report new insights into the structure of these  
106 terrestrial and extraterrestrial kerogens, and discuss four issues: (1) distinguishing terrestrial  
107 biogenic kerogens from abiotic chondritic kerogens; (2) the structure of carbonaceous matter  
108 in IDPs compared to chondrites; (3) the putative formation of chondritic kerogen by plasma  
109 reactions and (4) the investigation of coal maturity and the role of oxygen in the Raman  
110 signature.

111

## 112 2. MATERIALS AND METHODS

113

## 114 2.1 Samples

115 Coal samples were provided by the Penn State data bank ([Table 1](#)). Their maturity is  
116 rated by their mean maximum vitrinite reflectance ( $R_o$ , %), and their elemental ratio H/C and  
117 O/C are also provided. Type II kerogens were provided by Institut Français du Pétrole (Rueil-  
118 Malmaison France; courtesy of Mrs M. Vandenbroucke). They were recovered from different  
119 Toarcian wells and outcrops: MENIL/VAIR, outcrop (K99296); DICKEL4, 1416 m (K20505)  
120 and REHDEN9, 1306 m (K20507). The H/C and O/C elemental ratios were also provided, as  
121 well as the  $R_o$  reflectance of allochthonous vitrinite for K20507 and K20505. Allochthonous  
122 vitrinite is not a fully reliable tracer, because its diagenetic history before incorporation into  
123 the type II kerogen is unknown. For K20505 with respect to K20507, the vitrinite reflectance  
124 of 0.57 and 1.25 %, respectively, are consistent with the H/C values of 1.09 and 0.80,  
125 respectively. As K99296 is obviously more immature than the two other kerogens  
126 ( $H/C=1.23$ ), the maturity of these samples is as following:  $K20507 > K20505 > K99296$ .

127 Chondrites were supplied by the Muséum National d'Histoire Naturelle (MNHN -  
128 Paris, France). Stratospheric IDPs, L2008x3 and W7013I1, were supplied by the NASA-  
129 Johnson Space Center, and were earlier characterized by 514 nm Raman spectroscopy ([Bonal  
130 et al., 2011](#)). The 244 nm Raman spectra of L2008x3 were presented in [Dobrica et al. \(2011\)](#)  
131 but not quantitatively analyzed.

132 IOM samples from Renazzo and Murray were extracted following two methods.  
133 Murray IOM was obtained through protocol very similar to the one described in [Gardinier et  
134 al. \(2000\)](#) and adapted to ~100 mg samples. The sample was ground by hand with a pillar and  
135 mortar, and ~100 mg was introduced into a polypropylene micro-tube. A first step consisted  
136 in the elimination of soluble compounds through: (i) washing in distilled water  $V(H_2O)= 1$   
137 ml, 15 min sonication, centrifugation (30 min 6000 rpm), supernatant removal; followed by  
138 (ii) washing in 0.5 ml  $CH_2Cl_2:CH_3OH$  ( $v/v=1/2$ ), 30 min stirring, centrifugation and

139 supernatant removal. The second step consisted in eliminating carbonates: 37% HCl,  
140  $V(\text{HCl})=V(\text{H}_2\text{O})=0.75$  ml. Sonication for 1 h. Neutralization of the solid residue by addition  
141 of distilled water until getting a 6-7 pH. The third step had for objective the dissolution of  
142 silicates: HCl (37%) and HF (48%),  $V(\text{HF}) = 2V(\text{HCl}/\text{H}_2\text{O} = 1/1) = 0.5$  ml, 8 h sonication and  
143  $\text{N}_2$  bubbling, centrifugation and neutralization, operation executed three times. The fourth step  
144 consisted in the elimination of neoformed minerals (fluorures):  $V(\text{HCl}) = V(\text{H}_2\text{O})=0.75$  ml,  
145  $80^\circ\text{C}$  1 h sonication, repeated 2-3 times. The fifth and last step was similar to the second step,  
146 for removing encaged soluble molecules.

147         Renazzo IOM was obtained with a protocol dedicated to very small amount of sample.  
148 Around ten grains of 100-500  $\mu\text{m}$  of maximum dimension were deposited on an Au foil with  
149 curved edges in order to prevent grain loss. The foil was then inserted in a Teflon holder,  
150 placed in an alumina box covered with a polycarbonate window, which allowed a visual  
151 control of operations with a binocular microscope (Fig. 1a). Inside the reactor, liquids were  
152 simultaneously injected and expelled with a peristaltic pump ( $90.5 \mu\text{l}\cdot\text{min}^{-1}$ ). Viton® tube  
153 were used to carry the liquids, and were hold inside the reactors by two micromanipulators  
154 (Fig. 1b). The reactor was continuously purged with gaseous nitrogen or argon to ensure a  
155 non-oxidizing atmosphere, and to minimize micromanipulators etching. The chemical  
156 procedure was similar to that previously described, except the lack of sonication or  
157 mechanical stirring. Demineralized grains were then recovered from the gold foil, and  
158 transferred on glass slides for Raman analysis (Fig. 1c). The present protocol has been  
159 validated by comparing etched  $\mu\text{m}$ -sized matrix grains, with IOM extracted with the standard  
160 procedure dedicated to macroscopic samples. In both cases, a significant enrichment in carbon  
161 was observed through energy dispersive X-ray spectrometry in a scanning electron  
162 microscope, but with a variety of sulfides that survived the acid attack (detection of S and Fe).  
163

164 *2.2 Raman spectroscopy*

165 Spectra were collected with a JOBIN-YVON-Horiba LabRam system with a  
166 frequency-doubled Ar<sup>+</sup>(244 nm) excitation and a microscope equipped with an OFR™ 40×  
167 objective with a 240-360 nm broad band transmission (> 80%). (Laboratoire de Géologie de  
168 Lyon Terre, Planètes, Environnement/ENS-Lyon France). The laser spot on the sample had a  
169 diameter of 3–5 micrometers. Two gratings were used, 3600 and 600 gr/mm, that allow  
170 covering spectral ranges of 400-1500 and 400-3500 cm<sup>-1</sup>, respectively. In the case of  
171 immature coals (Ro < 1%) and type II kerogens, IOM samples and IDPs, the laser power  
172 delivered to the sample was fixed to 300 μW. For most of the measurements, the acquisition  
173 time was 2x150 s and the 600 gr/mm grating was used. When seeking for faint narrow  
174 spectral features (see below), the acquisition time was increased up to 4x300 s, and both  
175 gratings were used. The mature coals with Ro>1% were measured with a laser power of ~500  
176 μW, acquisition time of 2x300 s and a 3600 gr/mm grating.

177 Sample stability under 244 nm laser irradiation is a critical issue. Photochemical or  
178 thermal damages can be induced by the focused laser beam, depending on the power  
179 deposited on the sample and on its fragility. The presence of a crater or color modification at  
180 the laser spot was visually inspected for each measurement. Measurement conditions (i.e.  
181 laser power, collection time) were optimized through time-resolved measurements at the same  
182 spot location (see [Appendix](#)). Tests were run in air and under argon atmosphere by means of  
183 an environmental cell. Using an inert atmosphere reduces photo-oxidation, which causes  
184 possible fluorescence and evolution of the Raman spectra with time. The gain was however  
185 too small compared to signal loss through the cell window, and spectra were mostly collected  
186 in air. Because laser-induced damages can be almost instantaneous, we also investigated the  
187 effect of exposure time on a coal sample by using a rotating sample holder. We found no  
188 spectral difference with measurements performed under static conditions. In contrast, similar

189 measurements under static and rotating conditions on a cellulose sample revealed dramatic  
190 spectral modification reflecting alteration of the sample for both conditions. Coal samples are  
191 probably more resistant because they underwent metamorphism during burial in the sediment  
192 pile or due to tectonic events, and their most fragile and thermally labile fraction was expelled  
193 or transformed during thermal maturation. However, even for mature coals and kerogens, a  
194 limited photochemical or thermal alteration cannot be ruled out.

195 The raw UV-Raman spectra of terrestrial and extraterrestrial kerogens are available in  
196 the GhoSST/SSHADE spectral database (Quirico, Eric; Montagnac, Gilles (2006a,b)).

197 The Raman spectra were corrected with a linear baseline between 830 and 1925 cm<sup>-1</sup>.  
198 The Raman G- and D-carbon bands were fitted with the so-called Lorentzian-Breit-Wigner-  
199 Fano (LBWF) spectral model following Ferrari and Robertson (2000) (Fig. 2):

$$I(\omega) = I_G \frac{[1 + 2(\omega - \omega_G)/Q \cdot FWHM_G]^2}{1 + [2(\omega - \omega_G)/FWHM_G]^2} + \frac{I_D}{1 + 4(\omega - \omega_D)^2/FWHM_D^2}$$

200  
201  
202 where  $\omega_G$  and  $\omega_D$  are the resonant frequencies (in cm<sup>-1</sup>) of the G and D bands,  $I_G$  and  
203  $I_D$  their peak intensity,  $FWHM_D$  and  $FWHM_G$  their full width at half maximum, and  $Q$  the  
204 coupling coefficient. The fit finally provided, for each sample,  $FWHM_D$ ,  $FWHM_G$ ,  $\omega_G$  and  
205  $\omega_D$ , as well as the ratios of peak intensities ( $I_D/I_G$ ) and integrated intensities  
206 ( $A_{DDG}=A_D/[A_D+A_G]$ ). Note that the peak position of the G band does not correspond to the  
207  $\omega_G$ , and is equal to  $\omega_G+FWHM_G/2Q$ .

208 For the sake of comparison with former studies (Quirico et al. (2014) and Kuga et al.  
209 (2015)) that used a slightly different (with or without constant) LBWF fit, the Raman spectra  
210 from Quirico et al. (2014) have been reanalyzed and the Raman parameters of Kuga et al.  
211 (2015) have been rescaled by applying a correction factor. These earlier studies used similar  
212 experimental conditions as those used here – 300 μW on the sample, 40x objective and 600

213 g/mm grating -, making the comparison possible.

214 The electronic data collected in this study can be freely downloaded from the

215 SSHADE/GHOST spectroscopic database (<https://www.sshade.eu/>), at

216 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20200414\\_001](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20200414_001)

217

## 218 3. RESULTS

219

### 220 3.1 Coal and kerogen samples

221 Raman spectra obtained with 244-nm excitation are different from those collected with  
222 a visible excitation (Fig. 3). This wavelength dependence is due to the resonant process, i.e.  
223 the excitation photon is absorbed before being inelastically scattered. Different photon  
224 energies then lead to probing different fraction of the carbonaceous material (Merlen et al.,  
225 2017). Spectra of immature samples are devoid of the fluorescence background that occurs  
226 with visible excitation, and display an intense and sharp G-band (centred at 1600-1610  $\text{cm}^{-1}$ ),  
227 accompanied by a broad D band centred at 1360-1440  $\text{cm}^{-1}$ , weaker in intensity with respect  
228 to the G band by a factor of  $\sim 2$ -5. A weak feature at  $\sim 1750 \text{ cm}^{-1}$  appears as a shoulder of the  
229 G band, along with other weak and narrow substructures in the D band at  $\sim 1190$ , 1280 and  
230 1450  $\text{cm}^{-1}$  (Figs. 3, 4). Spectral variations with vitrinite reflectance are subtle in the range 0.3-  
231 2 %  $R_o$  and become more significant above this value (Figs. 4,5). The LBWF fit parameters,  
232  $\text{FWHM}_G$ ,  $\omega_D$ ,  $I_D/I_G$  and  $A_{DDG}$  fairly correlate with the vitrinite reflectance for values larger  
233 than  $\sim 1$  %  $R_o$  (Fig. 6; Table 2). In contrast, the peak position of the G band and the width of  
234 the D band are nearly insensitive to maturity variations in the range  $R_o = 1$  to  $\sim 3\%$ . Only the  
235 anthracite sample with the highest maturity shows a clear modification of  $\omega_G$  and  $\text{FWHM}_D$ . In  
236 the range 0.3-0.8 %  $R_o$ ,  $\text{FWHM}_D$ ,  $\text{FWHM}_G$  and  $A_{DDG}$  vary strongly between 0.3 %  $R_o$  and

237 0.5 % Ro and become stable above this value (Fig. 7). In contrast,  $I_D/I_G$ ,  $\omega_G$  and  $\omega_D$  do not  
238 show systematic variation with the vitrinite reflectance in the range 0.3 -0.8%.

239 The spectra of type II kerogens are similar to those of coals (Fig. 5), and do not  
240 present the strong fluorescence that prevents the detection of Raman features in spectra  
241 collected with a 514 nm excitation. At first inspection, the UV Raman spectra of three  
242 kerogen samples are identical. However, fitted parameters reveal significant differences  
243 between these samples (Fig. 8), with a low  $I_D/I_G$  ratio (Fig. 8a) for K20507 and distinct values  
244 of  $FWHM_G$  and  $\omega_G$  among the three samples (K20507, K99296 and K20505, with H/C= 0.80,  
245 1.23 and 1.09, respectively). In these diagrams, kerogens K99296 and K20505 are very close  
246 to the more mature coals (Ro=0.52 and 0.73%).

247

### 248 3.2 IOM and IDPs

249 244 nm Raman spectra with good signal-to-noise ratio could not be obtained from raw  
250 matrix fragments of chondrites, due to the small penetration of incoming UV photons in the  
251 sample (Fig. 9). Therefore, matrix fragments were treated through a HF/HCl acid attack prior  
252 to UV-Raman measurements. At first sight, the spectra share similarities with those of coals  
253 and kerogens (Fig. 10). They display an intense and narrow G band, and a weaker and broader  
254 D band. A weak feature at  $1750\text{ cm}^{-1}$  is sometimes observed. The second-order carbon bands  
255 ( $2500\text{-}3500\text{ cm}^{-1}$ ) could be observed, but they did not provide additional information to those  
256 of the first-order G and D bands. Besides first-order similarities, a major spectral difference  
257 between coal and kerogens and extraterrestrial samples is the shape of the D band. The D-  
258 band looks like a shoulder of the G-band in IOM spectra (Fig. 11d), and the minimum  
259 between the D- and G-bands is much fainter in IOM than in coals. Raman parameters  $I_D/I_G$   
260 (Fig. 11a) and  $\omega_G$  (Fig. 11b) are, with a few exceptions, lower in chondrites than in coals. On  
261 the other hand, type II kerogens plot along with chondrites and coals. Overall, coals, kerogens



262 and chondrites display similar  $\text{FWHM}_G$ . The  $\omega_D$  parameter unambiguously distinguishes  
263 extraterrestrial materials and coals, and type II kerogens display values across those two  
264 groups. The  $A_{\text{DDG}}$  parameter efficiently discriminates extraterrestrial and terrestrial samples  
265 (Fig. 11c).

266 UV-Raman spectra were collected on two stratospheric IDPs: L2008X3 and W70131I,  
267 and were partly published in Dobrică et al. (2011) (Fig. 12). Due to the small size of those  
268 particles, no HF/HCl acid attack was attempted. The signal-to-noise ratio of L2008X3 spectra  
269 is similar to that of IOM extracted from chondrites, but it is too low in W70131I to attempt  
270 spectral fitting. In the latter sample, the peaks at 800-840  $\text{cm}^{-1}$  are attributed to iron-rich  
271 olivine. Accordingly, we infer that the abundance of polyaromatic organic matter is higher in  
272 L2008X3. The IDP L2008X3 displays a much higher value of  $\text{FWHM}_G$  and much lower  
273 value of  $\omega_G$  than chondrites, coals and kerogens (Fig. 11a).

274 The insert in figure 12 shows raw and smoothed spectra in the range 1900-2400  $\text{cm}^{-1}$ ,  
275 pointing to faint features at 2220 and 2325  $\text{cm}^{-1}$ . These features, unobserved in 514 nm  
276 Raman spectra, are likely resonant with a UV excitation wavelength. The band at 2320  $\text{cm}^{-1}$   
277 corresponds to the stretching vibration mode of the  $\text{N}_2$  molecule whose nature, atmospheric  
278 versus adsorbed on the sample (Smudde et al., 1995) cannot be resolved due to the low signal-  
279 to-noise ratio. The atmospheric  $\text{O}_2$  stretching vibration modes at  $\sim 1550 \text{ cm}^{-1}$  was not detected  
280 due to the merging with the carbon G band. The weak feature at 2220  $\text{cm}^{-1}$  is likely due to the  
281 cyanide  $-\text{CN}$  functional group, as proposed by Quirico et al., (2008a). Indeed, no other  
282 organic functional group is plausible in the range 2200-2250  $\text{cm}^{-1}$ , and this band has already  
283 been confidently identified by 244 nm Raman spectroscopy in heated N-rich tholins (Bonnet  
284 et al., 2015). Cyanide groups have been identified in N-rich Ultra-Carbonaceous Antarctic  
285 Micro-Meteorites (UCAMMs) (Dartois et al., 2013), and tentatively detected in Orgueil IOM  
286 by Nuclear Magnetic Resonance (NMR) spectroscopy (Remusat et al., 2005b). The  $-\text{CN}$

287 functional group is known to be thermally labile. Its presence in L2008X3 and absence in  
288 most chondritic IOMs (except possibly Alais), support the view that refractory organics in this  
289 IDP were less thermally processed.

290

## 291 4. DISCUSSION

292

### 293 4.1 Coal and kerogens maturity

294 In the range  $R_o=0.3-1\%$ , several fitted Raman band parameters show a large evolution  
295 below  $0.5\%$  and constant values above (Fig. 7). In Raman spectra acquired with a 514 nm  
296 excitation, a linear correlation between  $FWHM_G$  and  $\omega_G$  is reported for immature coals  
297 (Quirico et al., 2003). Looking back in detail this old dataset, we observe that the data points  
298 cluster into three groups in a  $FWHM_G$  vs.  $\omega_G$  diagram:  $R_o < 0.4\%$ ,  $0.4 < R_o (\%) < 1$  and  $R_o >$   
299  $1\%$  (Fig. 13). It suggests the existence of a small but significant change of the polyaromatic  
300 structure of coals at  $R_o \sim 0.4 \%$ , and points to a significant evolution above  $1 R_o\%$ . Thus in  
301 the maturity range  $R_o < 1\%$ , coals clearly experience a chemical evolution (modifications of  
302 H/C and O/C, Table 1), but also some structural modifications. This point is consistent with  
303 the infrared spectroscopic measurements of Chen et al. (2012) that show that coals with  $R_o <$   
304  $1.5 \%$  experience a progressive aromatization. They also show that the size of the  
305 polyaromatic units (i.e. the degree of aromatic condensation) increases with increasing  $R_o$  in  
306 the range  $0.4-2 \%$ , while no significant variations are observed for  $R_o < 0.4 \%$ . The number  
307 and diversity of oxygenated functions also show a dramatic drop above  $R_o \sim 0.4 - 0.5 \%$   
308 (Petersen et al., 2008). This includes carboxylic, ketone, hydroxyl (essentially phenolic),  
309 quinone and ether groups. Raman spectroscopy probes the  $sp^2$  structure of carbonaceous  
310 material (Ferrari and Robertson, 2000), which in coals is essentially present as aromatic and  
311 polyaromatic units (Van Krevelen, 1993). Phenol and quinone groups are part of the

312 polyaromatic structure, and ether groups may also be involved when bridging polyaromatic  
313 units. In the case of very disordered carbonaceous materials, the parameters that control the  
314 Raman spectra are not only the size of their very small aromatic units, but also the molecular  
315 environment of those units (e.g. degree of substitution, nature of the branched species)  
316 (Ferrari and Robertson, 2000). It results in a complex control of the first order carbon bands,  
317 and sometimes in a degeneracy issue as different carbonaceous materials may exhibit similar  
318 spectra at a given excitation wavelength (Ferrari and Robertson, 2001). In the case of  
319 immature coals, we think it is premature to decipher between polyaromatic units size and  
320 oxygen speciation as controlling parameters of the Raman spectra. Both parameters most  
321 likely play a role. In conclusion, the analysis of spectra acquired at both 244 and 514 nm laser  
322 wavelength supports the view that significant structural changes happen in coals at  $R_o \sim 0.4\%$ .

323         In the range  $R_o > 1\%$ , the  $FWHM_G$  and  $\omega_D$  parameters, and to a lesser extent  $I_D/I_G$  and  
324  $A_{DDG}$  (data points around  $R_o \sim 2\%$  are more scattered), correlate well with the vitrinite  
325 reflectance (Fig. 6). These results are consistent with those obtained with a 514 nm excitation,  
326 in the case of the  $FWHM_G$ ,  $\omega_D$ ,  $I_D/I_G$  and  $A_{DDG}$  parameters (Quirico et al., 2005a).  $FWHM_D$   
327 and  $\omega_G$  provide no significant information, except that the anthracite sample is clearly  
328 different from other coals (Fig. 6). The  $\omega_G$  is found poorly useful with either the 244 or 514  
329 nm excitations.  $FWHM_D$ , which is a very sensitive and powerful maturity tracer of spectra  
330 acquired at 514 nm, is useless with a 244 nm excitation, in this maturity range at least. The  
331 244 nm excitation efficiently traces maturity for  $R_o > 1\%$ . The main parameter that controls  
332 the Raman spectra is likely the size of the aromatic units. Above  $R_o \sim 0.5\%$ , a sharp decrease  
333 of elemental oxygen (i.e., oxygenated groups) is observed (Table 1), leading to a low oxygen  
334 concentration at  $R_o > 1\%$  ( $O/C < 0.04$ ). Only hydroxyl and ether groups remain in the  
335 structure, with variable concentration ratio from one coal to another (Petersen et al., 2008).

336 The UV-Raman spectra of the three kerogens K99296, K20505 and K20507 are close  
337 to those of immature coals. The 244 nm excitation presents a clear advantage for these  
338 samples as no 514 nm Raman spectra could be collected on K99296 and K20505 due to high  
339 fluorescence that is absent with UV excitation. In the graphics  $FWHM_D$  vs.  $I_D/I_G$  and  
340  $FWHM_G$  vs.  $\omega_G$  (Fig. 8), the more mature kerogen K99296 (with H/C = 0.80) plots apart the  
341 other samples. K20505 and K20507 plot at the edge of the area defined by immature coals in  
342 both graphs. The maturity of K20505 and K20507 is rated by allochthonous vitrinite mean  
343 maximum reflectance  $R_o$ , 0.57 and 1.25 %, respectively (Table 1). These two samples do not  
344 plot with coals that have similar  $R_o$  values (Fig. 8), pointing to a possible precursor effect as  
345 type II kerogens and coals originate from different marine (planktonic) and continental  
346 (higher ligno-cellulosic plants) environments. However, caution should be used when using  
347 allochthonous vitrinite reflectance. As their prior history before incorporation into the kerogen  
348 is unknown, they may not properly trace the actual thermal history of the kerogen. In  
349 addition, maturation happens in an open system in the sediments in the case of kerogens, and  
350 a rather closed environment in the case of coals. The carbonization processes may thus play a  
351 role in shaping the different structure and chemistry and coals and kerogens.

352

#### 353 *4.2 Insoluble organic Matter in Chondrites and IDPs*

354 The 244 nm Raman parameters of chondritic IOMs evidence little difference between  
355 IOM of the studied carbonaceous chondrites (Fig. 11).  $I_D/I_G$  may point to a possible  
356 distinction of Murchison/Orgueil/Ivuna from Tagish Lake (heated lithology), as previously  
357 suggested by Quirico et al. (2014). However, they do not confirm the distinction with Cold  
358 Bokkeveld, a CM that experienced a mild heating event (Quirico et al., 2018). Murray (CM)  
359 displays a low  $FWHM_D$  value, and the primitive CR Renazzo plots close to Tagish Lake.  
360  $FWHM_D$  and  $I_D/I_G$  do not clearly discriminate chondrites having experienced mild heating

361 events, and the other parameters do not provide further information. Structural differences are  
362 faint and unconstrained by UV Raman spectroscopy. Visible excitation appears to be more  
363 effective for deciphering the subtle differences in IOM maturity in response to metamorphic  
364 intensity on the different parent bodies (Quirico et al. 2018).

365 The stratospheric IDP L2008X3 is easily distinguished from chondrites, with its large  
366 FWHM<sub>G</sub>, high I<sub>D</sub>/I<sub>G</sub> values, and low ω<sub>G</sub>. This IDP also displays, for data collected at 514 nm,  
367 low FWHM<sub>G</sub> and ω<sub>G</sub> parameters compared to primitive carbonaceous chondrites (Bonal et  
368 al., 2011). Combining 244 nm and 514 nm spectral data shows that the dispersion of the G  
369 band is  $\Delta_G = (\omega_G^{244} - \omega_D^{514}) / (514 - 244) \sim 0.015 \text{ cm}^{-1}/\text{nm}$  slightly above dispersion values  
370 of unheated C2 chondrites ( $\sim 0.010 \text{ cm}^{-1}/\text{nm}$ ; Quirico et al., 2014). The question arises  
371 whether these data can be interpreted in term of differences in structural order. In the case of  
372 pre-graphitic materials, the degree of structural order is assessed through the so-called  
373 Tuinstra and Koenig relationship that connect the I<sub>D</sub>/I<sub>G</sub> ratio with the length of coherent  
374 domains (Tuinstra and Koenig, 1970). However, this relationship does not apply to  
375 amorphous or highly disordered carbon materials, including coals and kerogens.

376 We follow here the framework defined by Ferrari and Robertson (2000) and Ferrari et  
377 al. (2003) that characterizes evolution stages between four end-members as graphite (G),  
378 nano-crystalline graphite (nc-G), amorphous sp<sup>2</sup>-rich (a-C) and sp<sup>3</sup>-rich (ta-C) carbon  
379 materials. These materials are pure or hydrogenated carbon materials formed in the  
380 laboratory. The sp<sup>2</sup>-rich carbon materials (C-sp<sup>3</sup><20%) between nc-G and a-C contain a  
381 growing number of defects (bond angle and length defects) that result in shifting the position  
382 of the G-peak towards low values, increasing the G-peak dispersion and decreasing the I<sub>D</sub>/I<sub>G</sub>  
383 ratio. From a-C to ta-C the increase of sp<sup>3</sup> bonds constitutes an additional source of disorder  
384 (hybridization disorder), resulting in the decrease of I<sub>D</sub>/I<sub>G</sub>, and the increase of ω<sub>G</sub>. Disorder is  
385 experimentally produced through irradiation, or formation conditions at low temperature.

386 Ordering is usually generated through annealing, which tends to increase  $sp^2$  clustering and to  
387 transform any carbon films into nc-G. For instance, the annealing of a ta-C:H film leads to the  
388 sharp drop of its G-peak dispersion, the increase of  $I_D/I_G$  and the decrease of  $FWHM_G$  in both  
389 244 and 514 nm spectra (Ferrari and Robertson, 2001). Thus the G-peak dispersion,  $FWHM_G$   
390 and  $I_D/I_G$  probe the degree of disorder.

391 The low dispersion of the G-peak clearly distinguishes chondritic kerogens from  
392 amorphous a-C, a-C:H and ta-C:H, and points to similarity with rather disordered nc-G. In  
393 addition, the G-band peak position and its width are very similar to those of nc-G. However,  
394 the use of dispersion in chondritic kerogens requires caution because they are not strictly  
395 similar to carbon thin films produced in the laboratory. The abundance of  $sp^2$  (aromatic  
396 carbon) in an unheated primitive chondrite like Murchison is 60-68 % (Cody et al., 2002;  
397 Gardinier et al., 2000). Around 24-28% of aliphatic carbons are detected, with ~ 20%  
398 hybridized to hydrogen, which has no detectable effects on the Raman spectra (Ferrari and  
399 Robertson, 2000). The remaining carbons are located in carbonyl and carboxyl groups (9-11  
400 at%). Thus the presence of oxygen is a major difference with the synthetic carbon films used  
401 by Ferrari and Robertson (2000) and Ferrari et al. (2003). According to results from section  
402 4.1, oxygen has an effect on the Raman spectra (in fact, essentially O atoms tightly linked to  
403  $sp^2$  clusters, e.g. ether bridge), but this effect remains weak.

404 G-peak dispersion of ~ 0.015  $cm^{-1}/nm$  for IDP L2008x3 points to an  $sp^2$  structure very  
405 close to that of nc-G. Its large  $FWHM_G$  and low  $\omega_G$ , in both 244 nm (this study) and 514 nm  
406 data of Bonal et al. (2011) reflect a low degree of order in the decreasing ordering sequence  
407 across ta-C:H, a-C:H and nc-G. In IDP W7013I1, the low signal-to-noise ratio prevents fitting  
408 the 244 nm Raman spectra, but we can estimate the G-band dispersion to ~ 0.02  $cm^{-1}/nm$   
409 using the peak position in raw data and using the 514 nm data of Bonal et al. (2011) (Table 3).  
410 The higher dispersion value points to a higher degree of structural order in the IDP W7013I1

411 than in L2008x3. The 514 nm measurements of [Bonal et al. \(2011\)](#) also provide  $\text{FWHM}_G$  and  
412  $\omega_G$  values that are lower and larger than those of IDP L2008x3, respectively, also indicative  
413 of higher degree of structural order.

414 Systematic measurements on stratospheric IDPs and Antarctic micro-meteorites  
415 (AMMs) collected since the pioneering study of [Wopenka \(1988\)](#) show that (1) the G-band is  
416 weakly dispersive ([Starkey et al., 2013](#)) and (2) 514 nm Raman spectra point to larger  
417  $\text{FWHM}_G$  and lower  $\omega_G$  parameters in comparison to primitive carbonaceous chondrites  
418 ([Battandier et al., 2018](#); [Busemann et al., 2009](#); [Dobrică et al., 2011](#); [Merouane et al., 2013](#);  
419 [Quirico et al., 2005b](#)). These observations, in the light of the discussion above, support the  
420 view that the refractory organic materials in IDPs and AMMs have a lower degree of  
421 structural order than chondritic kerogens, in the definition of [Ferrari and Robertson \(2000\)](#).

422

#### 423 *4.3 Relevance of laboratory analogues*

424 The origin of chondritic organic matter is still a pending issue, and its elucidation  
425 partly relies on experimental simulations that produce disordered carbonaceous materials. A  
426 comprehensive study on a variety of amorphous and disordered carbonaceous materials  
427 ([Ferrari and Robertson, 2000](#)) shows that polymeric a-C:H amorphous carbon displays 244  
428 nm spectra fairly similar to coals, but a much larger G-peak dispersion ([Ferrari and  
429 Robertson, 2001](#)). Heated ta-C:H films (600 °C) display 244 nm Raman spectra akin to those  
430 of chondritic IOM and with a similar G-peak dispersion. This ta-C:H amorphous carbon was  
431 formed in a radio-frequency 13.6 MHz cold plasma chamber, from a  $\text{C}_2\text{H}_2$  gas at  $\sim 10^{-4}$  mbars  
432 ([Morrison et al., 1999](#)). No insight into the  $\text{CH}_3/\text{CH}_2$  cross-linking is provided in this  
433 publication, but the infrared study of carbon films synthesized in a similar chamber from  $\text{CH}_4$   
434 shows a high  $\text{CH}_3/\text{CH}_2$  ratio, as observed in IOM from primitive chondrites ([Mutsukura and  
435 Akita, 1999](#)). This reflects a random growth of the carbon network, containing short alkyl

436 chains, at odd with the coal structure inherited from lignine and cellulose. Such materials then  
437 appear as potential analogues of chondritic IOM, except they do not contain heteroatoms like  
438 oxygen, nitrogen and sulfur.

439 Oxygen-bearing IOM analogues have been synthesized in the cavity of a microwave  
440 (2.45 GHz) plasma reactor, for temperatures ranging between 520 and 730 °C and  
441 characterized by Raman spectroscopy (Kuga et al. (2015)). We have calculated their G-band  
442 dispersion from their Raman spectra collected at 244 and 514 nm (Figs 3 and S2 in Kuga et  
443 al., 2015) and obtained G-band dispersions in the range 0.05-0.09 cm<sup>-1</sup>/nm. These values are  
444 similar to those of the ta-C:H film annealed between 450 and 500 °C in Ferrari and Robertson  
445 (2001), and confirm the key role of temperature in ordering carbonaceous materials.

446 Dispersion values for the synthetic materials (Kuga et al., 2015) are higher than those  
447 of IOM in primitive chondrites (0.01 cm<sup>-1</sup>/nm; Quirico et al. 2014). The 244 nm Raman  
448 parameters of these analogues are also different from those of chondritic IOM, and of  
449 immature coals (Fig. 11). These significant differences point to a different mechanism of  
450 formation and evolution, suggesting that cold plasma reactions may not be a likely route of  
451 formation of chondritic IOM and IDPs or that the formation process was subsequently erased  
452 by metamorphism on the parent bodies of carbonaceous chondrites.

453

#### 454 *4.4 A possible past life tracer for Early Earth and planetary exploration*

455 Complex organics are widespread across the Solar System; they have been found at  
456 the surface of Mars (Freissinet et al., 2015), asteroids (Campins et al., 2010), comets  
457 (Capaccioni et al., 2015), satellites of ice-giants (Cruikshank et al., 2014) and Trans-  
458 Neptunian-Objects (Stern et al., 2015). The presence of organic compounds does not imply  
459 the presence of life, and the identification of chemical biosignatures is a major challenge of



460 Solar System exploration (Quirico and Bonal, 2019), and in the quest of biosignatures in  
461 ancient sediments on Earth.

462 Mars shows plenty of evidence for the action of liquid water, including the presence of  
463 long-lasting bodies of water (i.e. the Gale crater lake, Grotzinger et al. 2014), and is a prime  
464 target for the quest of bio-related organic matter. Organic matter on Mars could have different  
465 endogenous or exogenous origins: (i) terrestrial: brought through successive space  
466 missions/rovers; (ii) chondritic: brought by meteorites and dusts; (iii) synthesized through  
467 biotic or abiotic processes on Mars. The high sensitivity of Raman spectroscopy to  
468 carbonaceous matter has led to the presence of Raman spectrometer onboard of future landed  
469 missions. The payloads of these rovers will include visible Raman (SuperCam/Mars2020-  
470 NASA, RLS/ExoMars/ESA) and UV Raman (SHERLOC/ Mars2020-NASA) spectrometers  
471 operating at the excitation frequency (248.6 nm) close to the one used in the present work  
472 (244 nm) (Beegle et al., 2020; Wiens et al., 2016).

473

474 The 244 nm Raman spectra collected in this study efficiently discriminate chondritic  
475 kerogens from immature coals and type II kerogens (Fig. 11). As far as we know, chondritic  
476 OM has an abiotic origin, in contrast to terrestrial coals and kerogens derived from vascular  
477 ligno-cellulosic plants, and from algae and plankton in marine environments for type II  
478 kerogens, respectively. Comparison of UV and visible Raman spectra may thus prove to be a  
479 valuable tool for deciphering the biotic vs. abiotic nature of organics in old sediments both on  
480 Earth and on Mars, in the event that carbonaceous materials are detected by future rovers.

481 The present study could also be useful for future *in situ* studies on the Martian surface  
482 by showing the strengths and weaknesses of UV Raman to analyze organic signatures in  
483 natural – and thus complex – samples. Obtaining UV spectra for raw carbonaceous chondrites  
484 that typically contain 0.1 - 4 wt. % carbon (Alexander et al., 2017) is challenging. The

485 presence of major amount of silicates in these samples, which are strong UV absorbers, limits  
486 the penetration depth into the samples to the very surface. Spectra of quality were obtained in  
487 some studied IDPs, where the amount of organic carbon (the total carbon abundance in IDPs  
488 is estimated to 15 wt. % in average; [Thomas et al., 1993](#)) is higher than in carbonaceous  
489 chondrites ([Alexander et al., 2017](#)). An advantage of UV Raman is to suppress the often-  
490 present and strong fluorescence background in macromolecular carbon, which may prevent  
491 measurements of the Raman signal in the visible. This applies to investigations of organic  
492 compound signatures, as well as to inorganic compound signatures that may be totally masked  
493 by the fluorescence background. UV Raman may also be used to constrain the thermal history  
494 of the carbonaceous materials. Assessing which sample has been the least modified by  
495 geological processes will help in sample selections for subsequent catching and return to  
496 Earth.

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500

## 501 **5. CONCLUSION**

502

- 503 • 244 nm UV Raman spectroscopy efficiently discriminates immature abiotic  
504 extraterrestrial kerogens (IOM) from terrestrial kerogens and coals, and may help in  
505 recognizing potential biological origin of macromolecular carbonaceous matter  
506 present in the Martian soil or in ancient rocks on Earth for a large range of degree of  
507 maturity.
- 508 • Carbonaceous matter appears more disordered in stratospheric IDPs than in chondrites  
509 from UV 244 nm Raman spectroscopy.

- 510 • The 244 nm excitation Raman spectra show that materials formed in cold plasma  
511 reactors have a different structure than chondritic organic matter, even for rather high  
512 temperature conditions (500-700 °C), suggesting that cold plasma reactions may not  
513 be a likely route for chondritic IOM formation, or that metamorphic reactions on the  
514 parent body overprinted that signature.
- 515 • The maturity of coals is rated by UV Raman spectroscopy with a structural transition  
516 observed around  $R_0 \sim 0.4\%$ , which is attributed to changes in oxygen speciation.
- 517 • UV-Raman spectra of type II kerogens, even those that are highly fluorescent with a  
518 visible excitation, are easily collected. Raman spectroscopy appears here as a potential  
519 tool to provide maturity tracers of type II kerogens.

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525

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532

533

534 **APPENDIX**

535

536 Sample degradation is a critical issue in 244 nm Raman spectroscopy. This technique  
537 has been usually implemented on moving samples to limit the exposure to the laser beam. In  
538 the case of solid samples, a rotating sample holder with or without association to a random  
539 XY movement has been successfully used (Ferrari and Robertson, 2001; Quirico et al.,  
540 2008b). In the case of extraterrestrial material available in minute quantities, this approach is  
541 not suitable. To test the resistance of the sample to the laser beam, we first proceed with time-  
542 resolved measurements over 0-200s, during the focus optimization of the beam. Figure A1  
543 reports tests on pure cellulose, and compare 244 nm spectra collected in this study with FT-  
544 Raman (1064 nm) (Agarwal, 2019). For a collection time of 20s, the cellulose sample starts  
545 degrading, and we observe the emergence of a broad feature at  $\sim 1600\text{ cm}^{-1}$ , while the rest of  
546 the spectrum still resembles that of cellulose. For a collection time of 200s, the sample is fully  
547 degraded. In the case of coals and IOMs, no dramatic evolution of the spectra is observed  
548 during the first tens of seconds. As these materials have experienced thermal processing in  
549 their natural host rocks, we think that the effect of an ultra-fast ( $< 5\text{ s}$ ) processing under the  
550 laser beam is unlikely.

551 Another issue is that of the evolution of the Raman spectra over a longer time, due to  
552 oxidation processes (Quirico et al, 2005a). Figure A2 reports the Raman spectra collected  
553 continuously for a collection time of 150s for each spectrum, under air and in a cell under an  
554 argon atmosphere. The results are qualitatively similar with those obtained with a 514 nm  
555 excitation: a progressive drop of the intensity, and slight spectral changes that lead to changes  
556 of the Raman parameters (Fig. A3). The Ar environment only slightly improves the data, and  
557 we observe that the evolution trend of the Raman parameters is much smaller than the

558 dispersion due to sample heterogeneity or other factors not clearly identified (e.g. sample  
559 topography, porosity, etc.).  
560

561

562 **RESEARCH DATA**

563 Research Data associated with this article can be accessed from through the  
564 SSHADE/GHOST database (<https://www.sshade.eu/>), at  
565 [https://doi.org/10.26302/SSHADE/EXPERIMENT\\_LB\\_20200414\\_001](https://doi.org/10.26302/SSHADE/EXPERIMENT_LB_20200414_001)  
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761

762

## 763 FIGURES CAPTIONS

764

765 **Figure 1:** The experimental set up used to enrich matrix grains in carbonaceous matter by  
766 applying a HF/HCl acid treatment. (a) The alumina chamber purged with Ar, binocular  
767 microscope and a peristaltic pump providing and extracting reagents and distilled water for  
768 neutralization. (b) A Teflon sample holder contain a gold foil onto which matrix grains are  
769 deposited. Inlet for injection and extraction of liquids are handled by two micromanipulator. (c)  
770 Scanning Electron Microscopy image of matrix grains after the HF/HCl treatment.

771

772 **Figure 2:** The Lorentzian-Breit-Wigner-Fano spectral decomposition of the first-order carbon  
773 bands.

774

775 **Figure 3:** Raman spectra of the immature coal PSOC 1532 (left) and of polyaromatic matter  
776 of the Murchison chondrite (right). Top: normalized baseline-corrected spectra. Bottom: raw  
777 spectra. Note the low fluorescence and the lower D-band intensity in 244 nm spectra.

778

779 **Figure 4:** Raman spectra of mature coals ( $R_o > 1\%$ , indicated for each spectrum).

780

781 **Figure 5:** (a): Raman spectra of immature coals ( $R_o < 1\%$ ) (top); (b) type II kerogens; (c):  
782 same spectra vertically shifted to enhance clarity.

783

784 **Figure 6:** The Raman spectral parameters of mature coals ( $R_o > 1\%$ ) plotted against the mean  
785 maximum vitrinite reflectance. The dotted blue lines are a guide to the eyes.

786

787 **Figure 7:** The Raman spectral parameters of immature coals ( $R_o < 1\%$ ) plotted against the  
788 mean maximum vitrinite reflectance. The dotted blue lines are a guide to the eyes.

789

790 **Figure 8:**  $FWHM_D$  vs.  $I_D/I_G$  and  $FWHM_G$  vs.  $\omega_D$  diagrams, for type II kerogens and immature  
791 coals ( $R_o < 1\%$ ).

792

793 **Figure 9:** 244 nm Raman spectra of Murchison as: raw matrix grains, Insoluble Organic  
794 Matter, and matrix grains treated with the micro-extraction device (see text).

795

796 **Figure 10:** 244 nm Raman spectra of primitive carbonaceous chondrites and IDP L2008x3.

797

798 **Figure 11:**  $FWHM_D$  vs.  $I_D/I_G$  (a),  $FWHM_G$  vs.  $\omega_G$  (b) and  $A_{DDG}$  vs.  $\omega_D$  (c) diagrams  
799 corresponding to coals, type II kerogen, chondritic IOM, IDP L2008x3 and analogs of [Kuga  
800 et al. \(2015\)](#). (d): comparison of corresponding Raman spectra, which clearly distinguishes  
801 sedimentary organic matter, chondritic IOM and IDP. Note that the data from Kuga et al.  
802 (2015) have been rescaled due to the use of different fit models.

803

804 **Figure 12:** Raman spectra of stratospheric IDPs L2008x3 and W7013I1. The blow up shows  
805 the  $1900\text{-}2500\text{ cm}^{-1}$  spectral range for two individual spectra (red) and smoothed spectra  
806 (blue). The weak features at  $2220$  and  $2320\text{ cm}^{-1}$  are assigned to the cyanide group  $-\text{CN}$  and  
807 adsorbed  $\text{N}_2$ , respectively.

808

809 **Figure 13:** The  $FWHM_G$  versus  $\omega_G$  diagram of 514 nm Raman data earlier published in  
810 [Quirico et al. \(2003\)](#). This diagram clearly distinguishes coals with  $R_o < 0.4\%$  and  $0.4 < R_o <$   
811  $1\%$ , in agreement with spectra collected with a 244 nm excitation ([Fig. 7](#)).

812 **Figure A1:** The spectrum of cellulose collected at 244 nm during 20 and 200 s, compared to  
813 the FT-Raman (1064 nm) of amorphous cellulose ([Agarwal, 2019](#)).

814

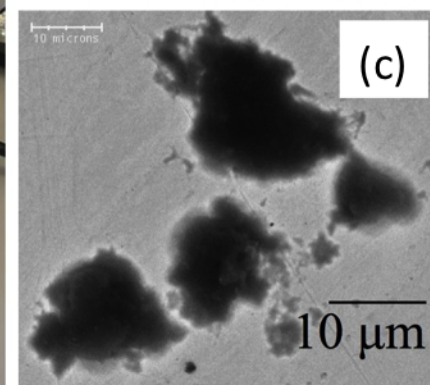
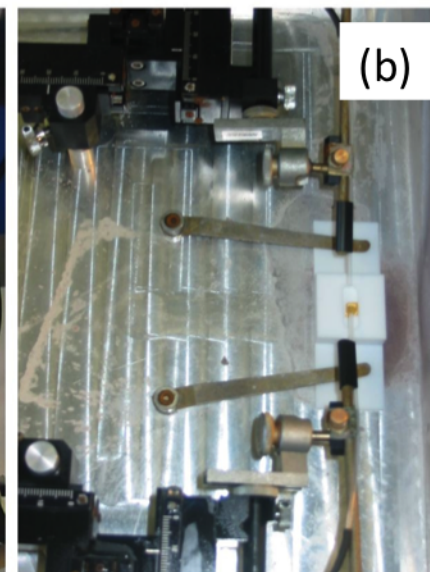
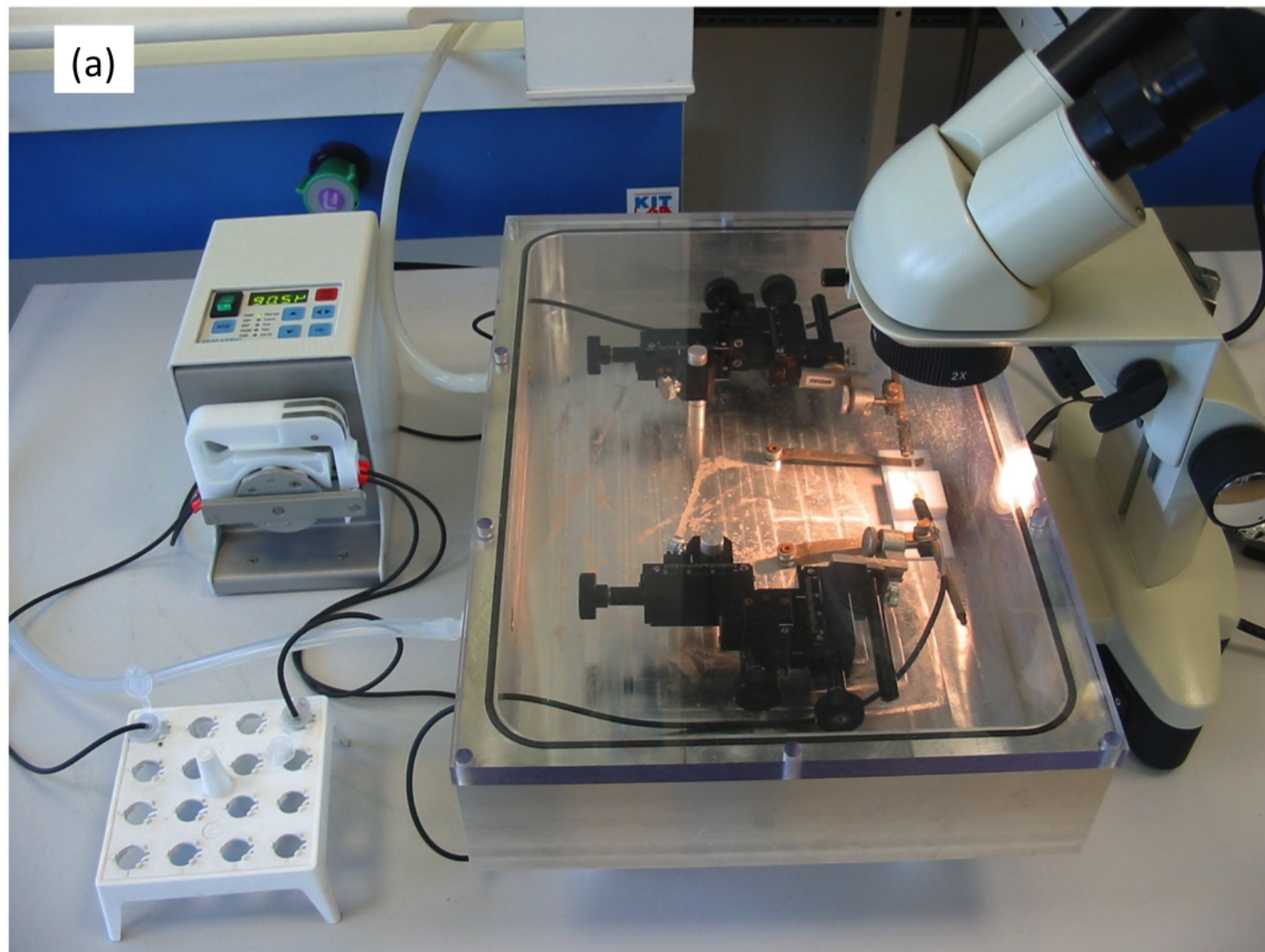
815 **Figure A2:** Automatic collection of 244 nm Raman spectra (acquisition duration 150 s;  
816 grating 600 gr/mm).

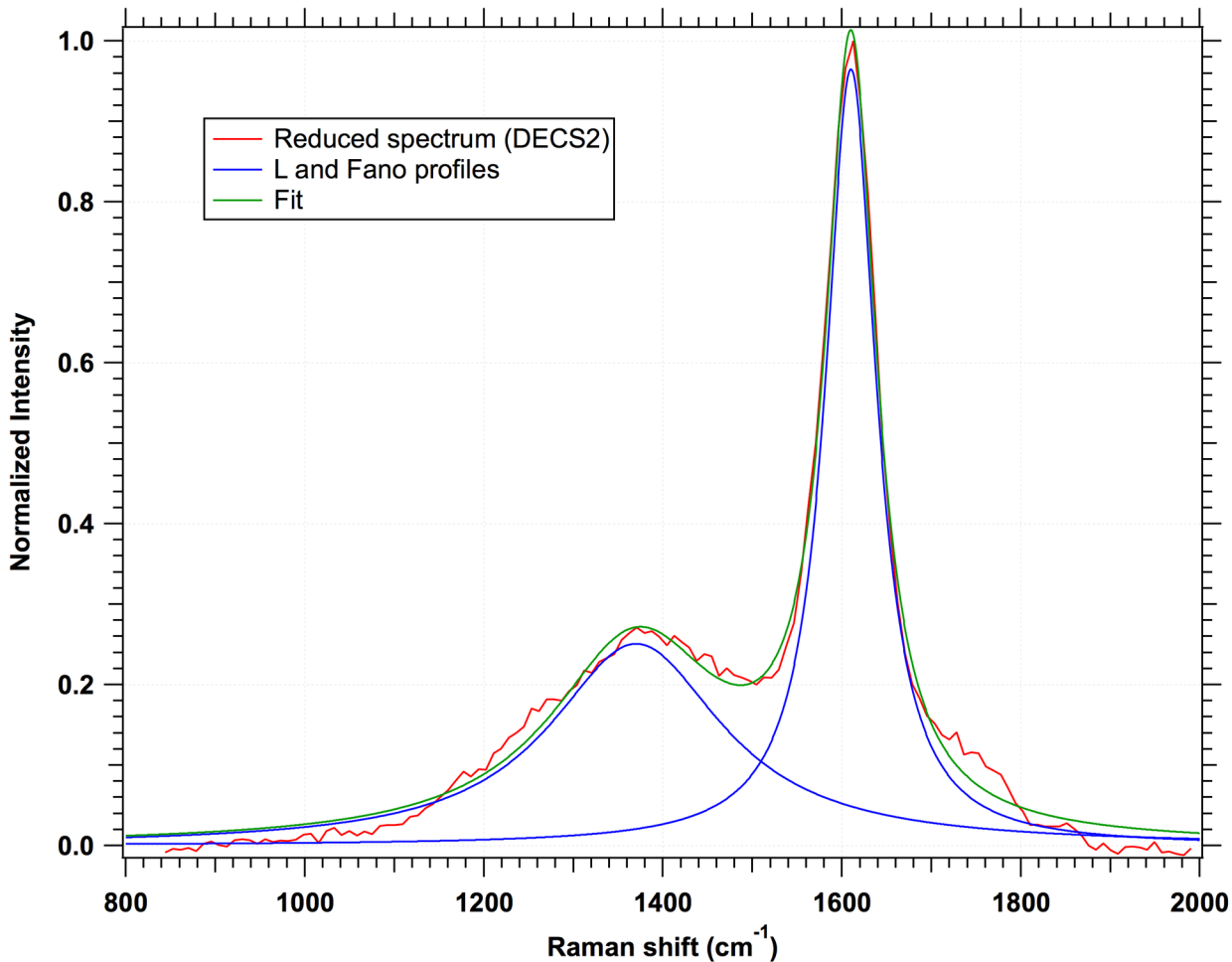
817

818 **Figure A3:** The Raman parameters derived from the spectra shown in [figure A2](#), with a  
819 LBWF fit. The error bars are the standard deviation calculated from the data collected at  
820 different locations of the Murchison IOM, under air and with a collection time of 2x150s  
821 ([Tab. 2](#)).

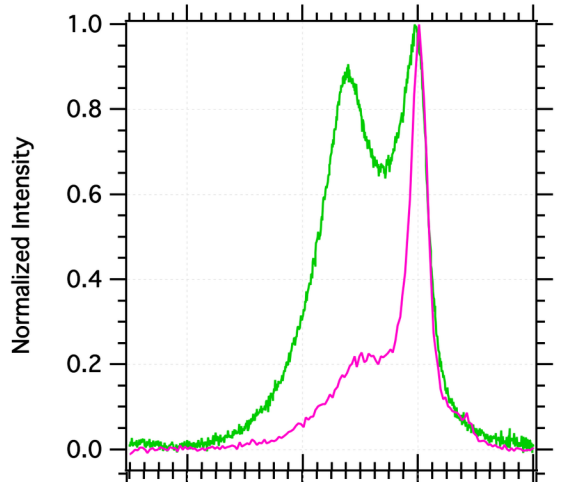
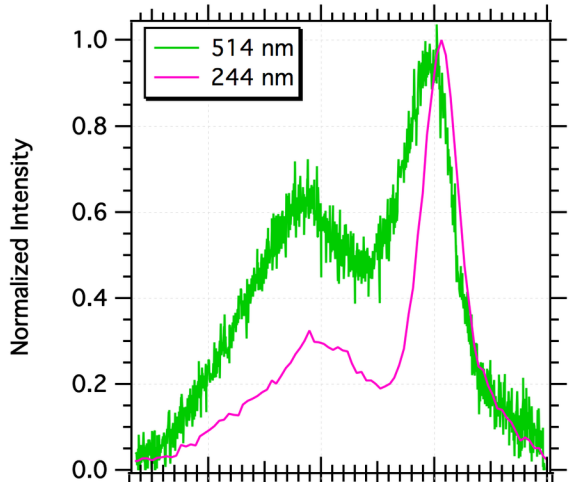
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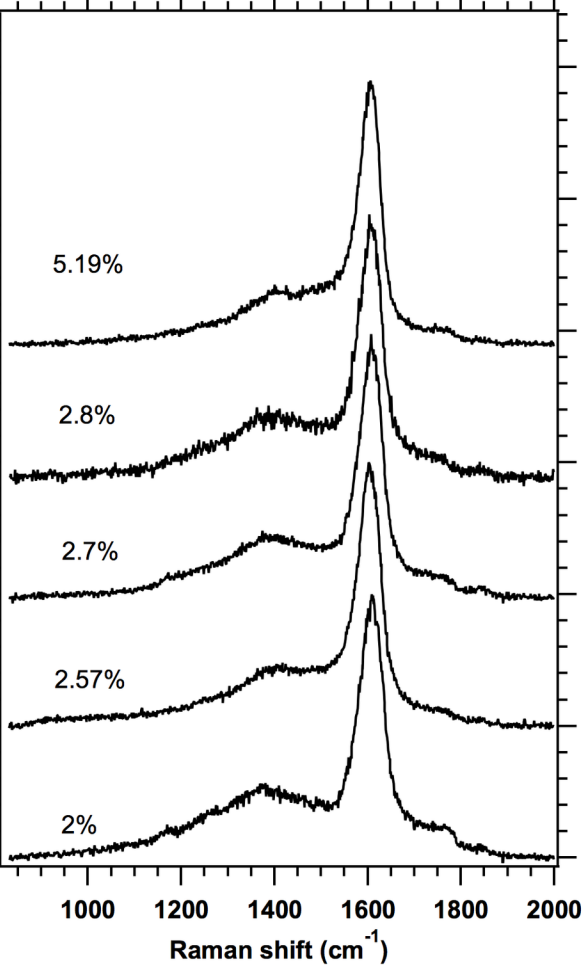
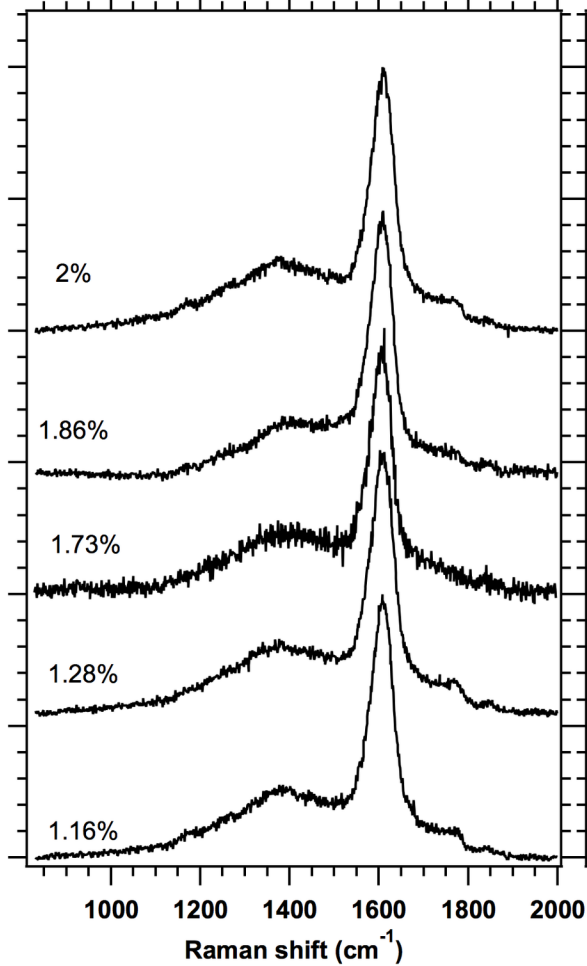


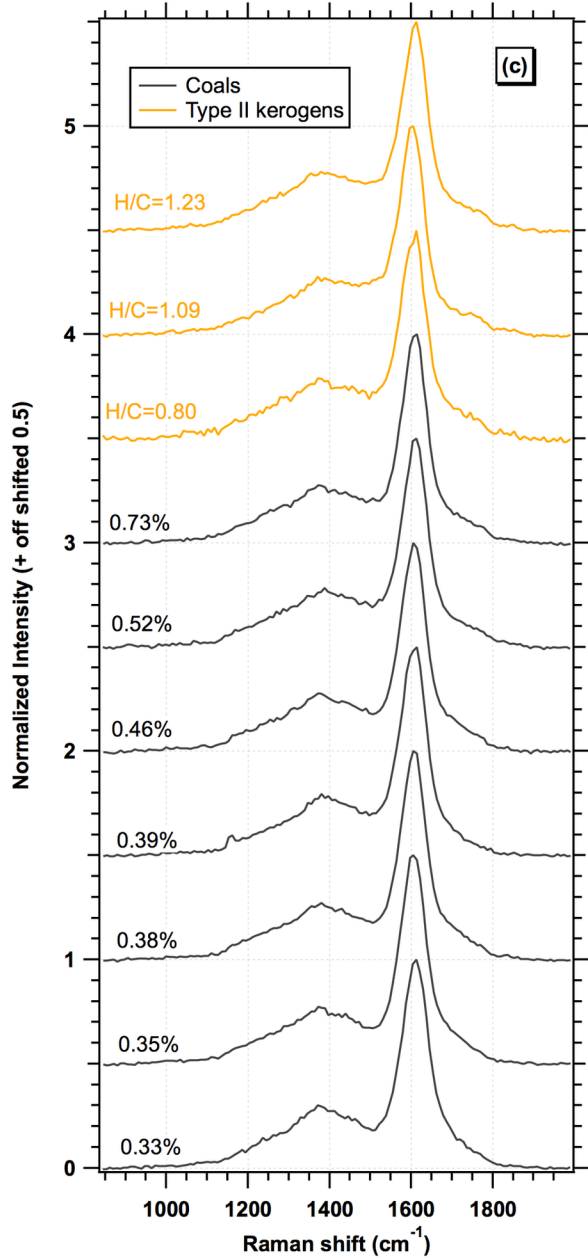
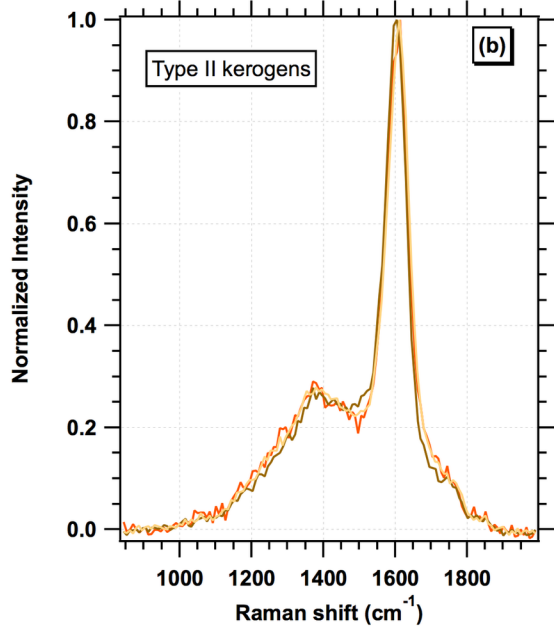
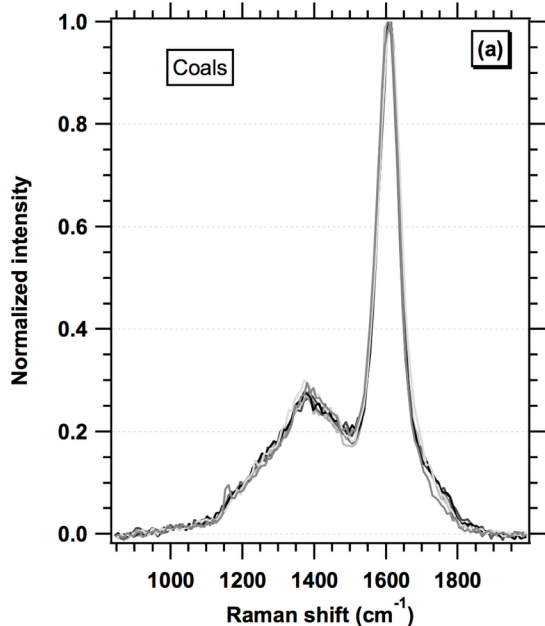


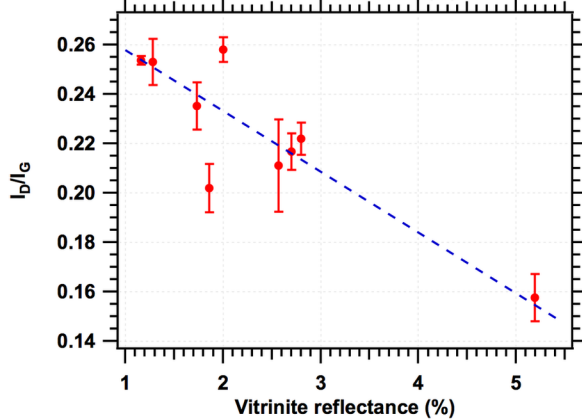
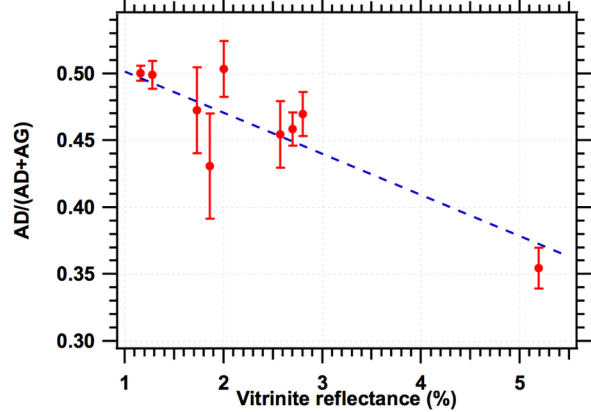
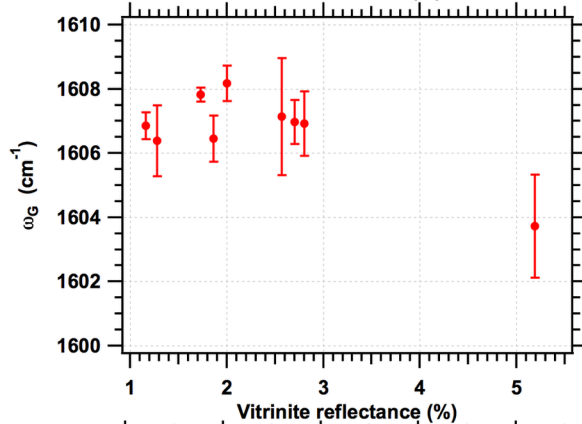
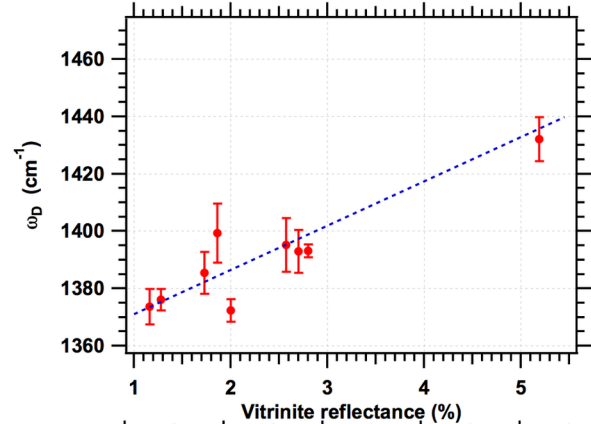
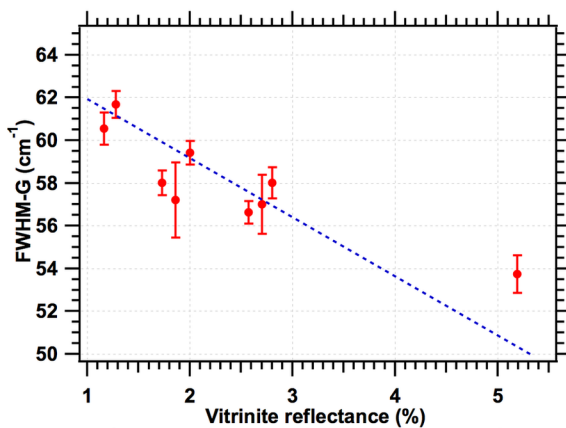
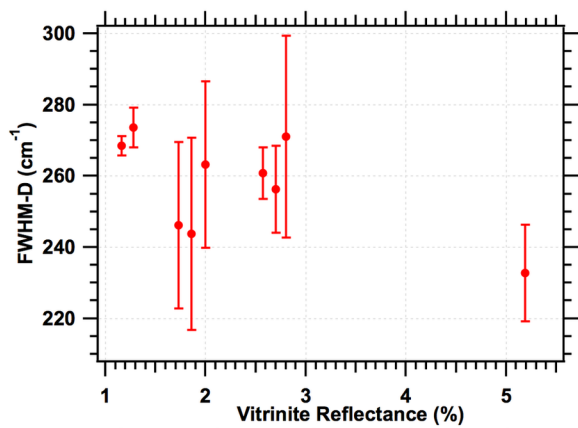


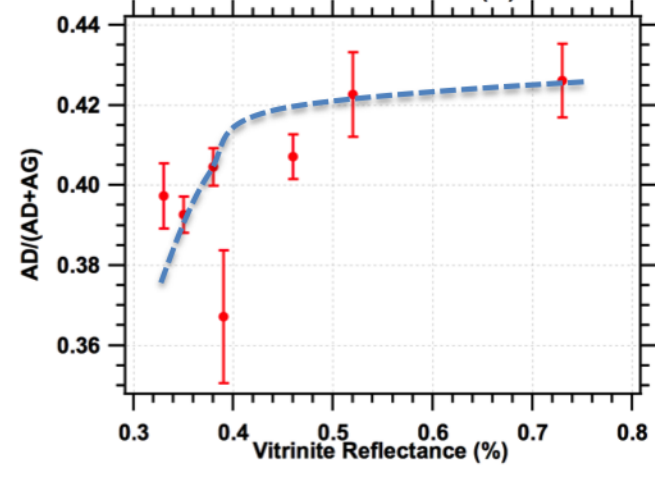
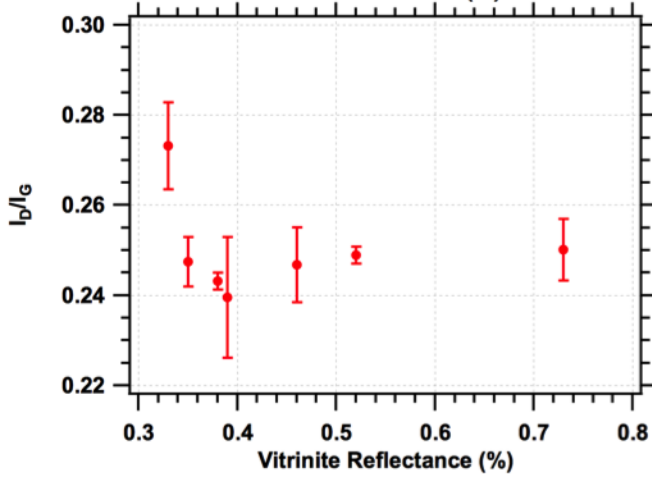
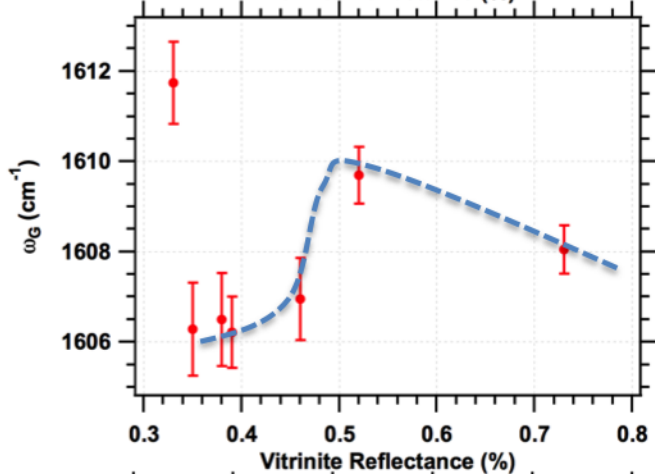
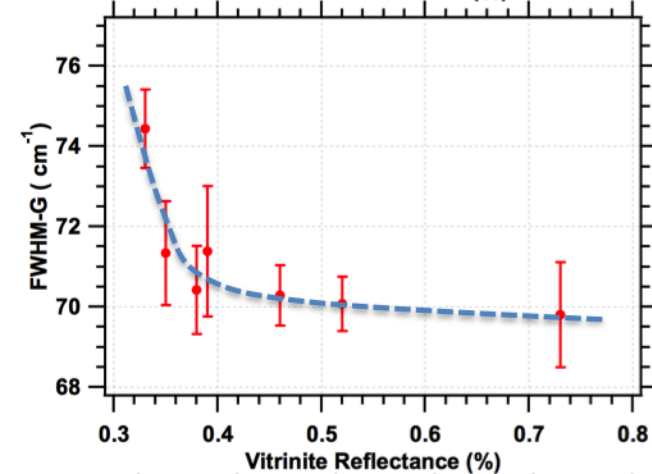
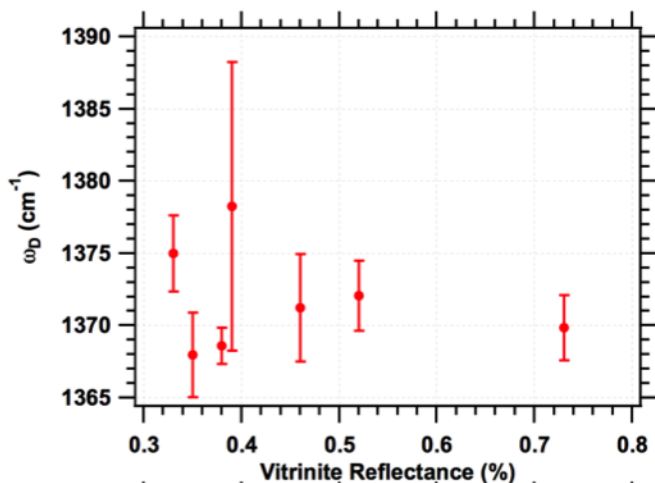
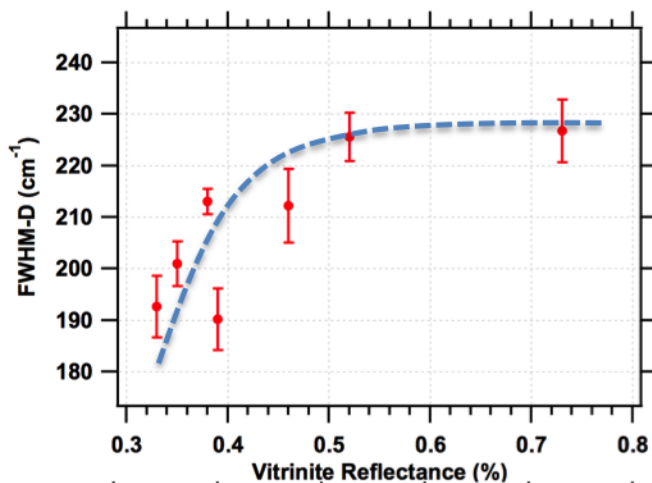


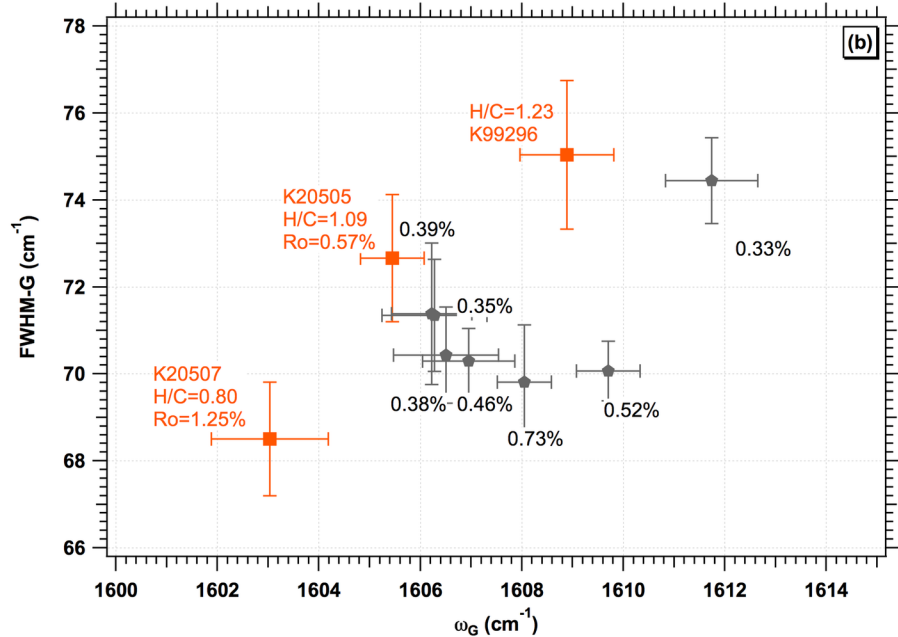
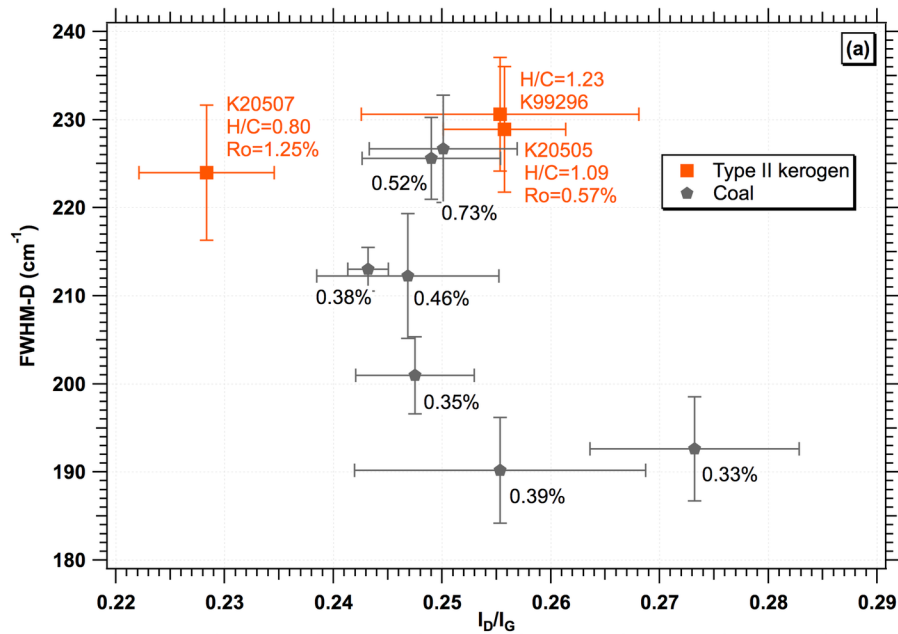
Normalized absorbance (+ off shifted)

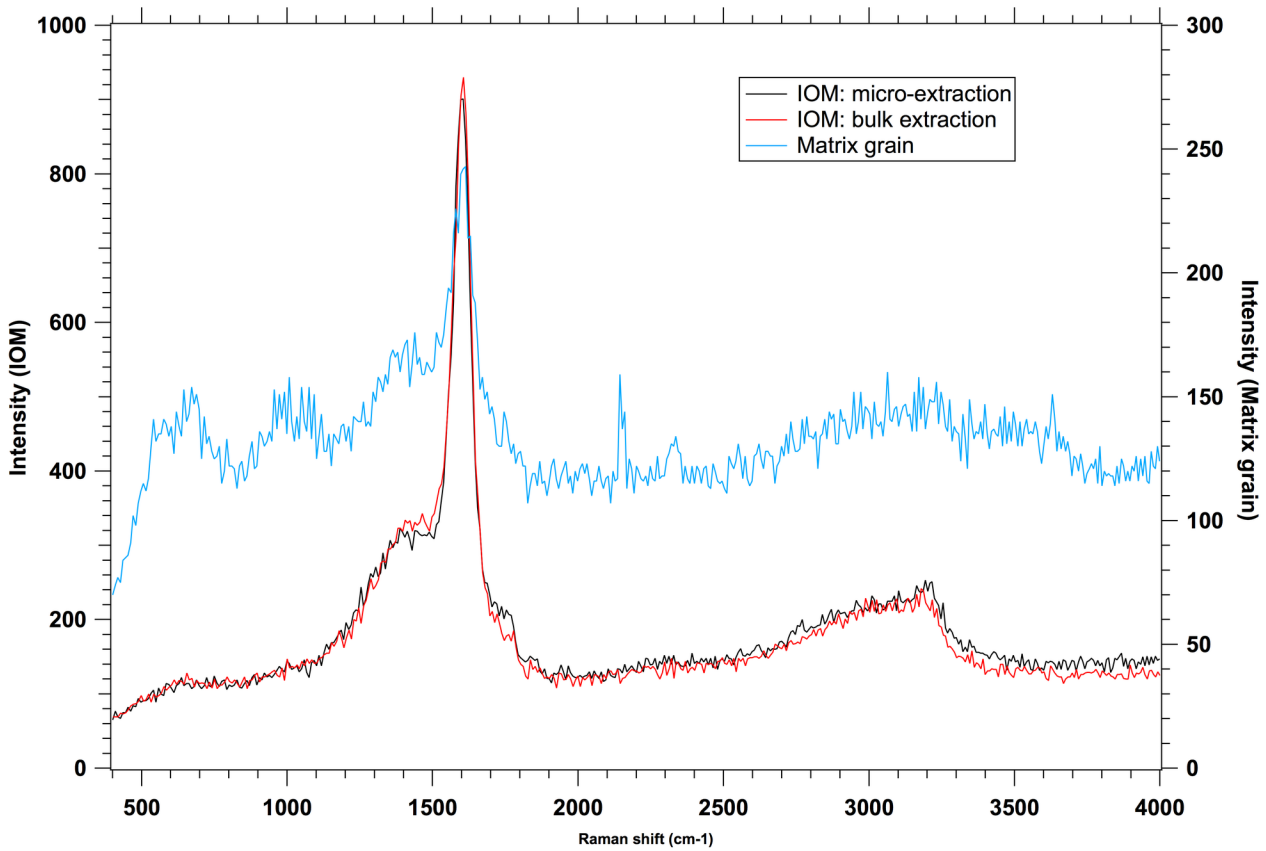


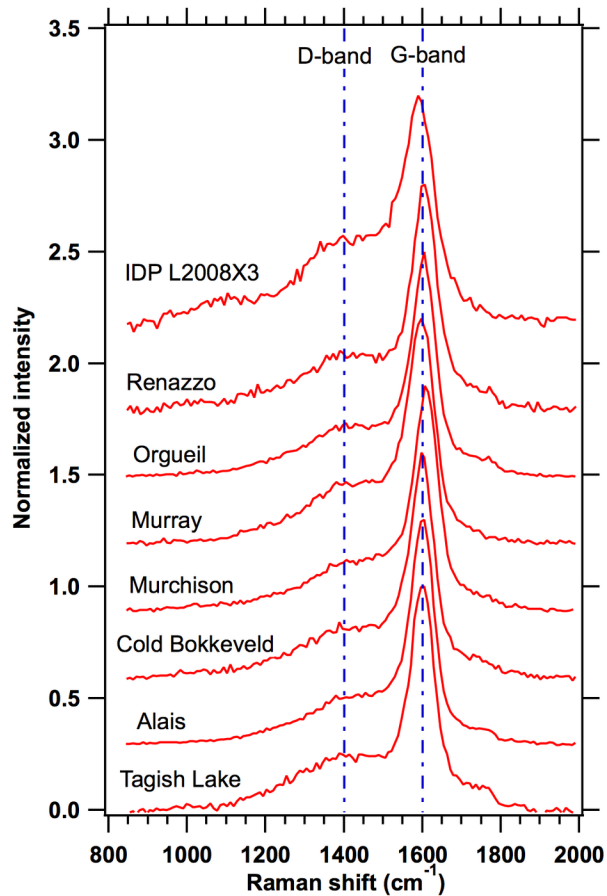
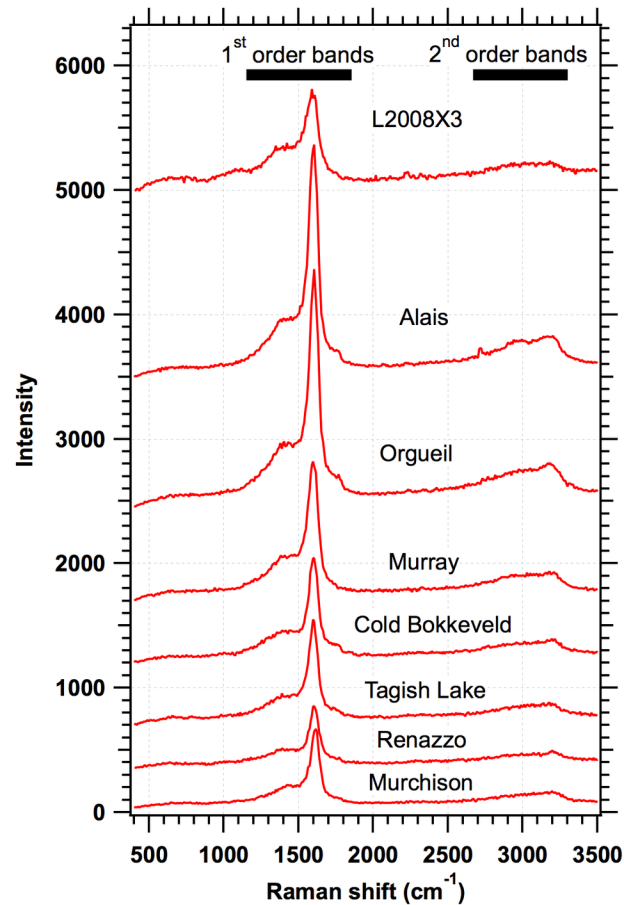




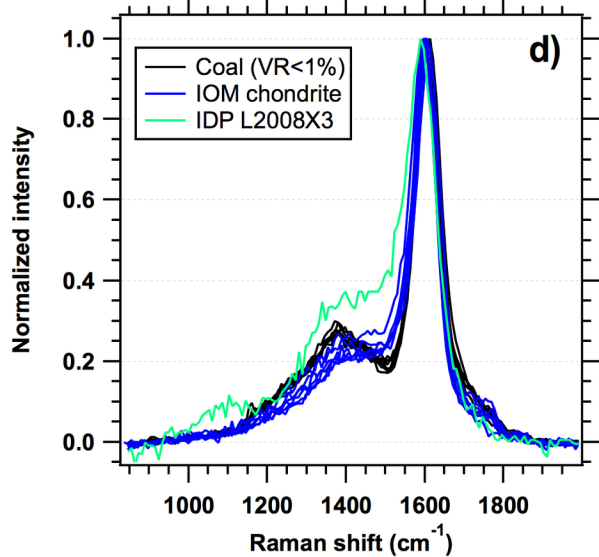
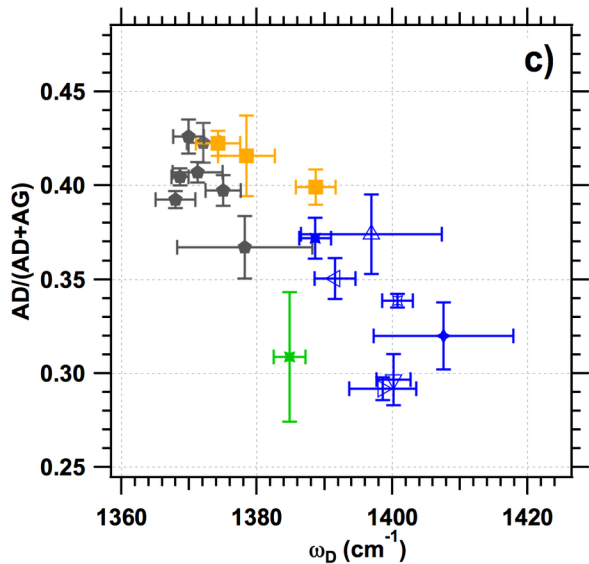
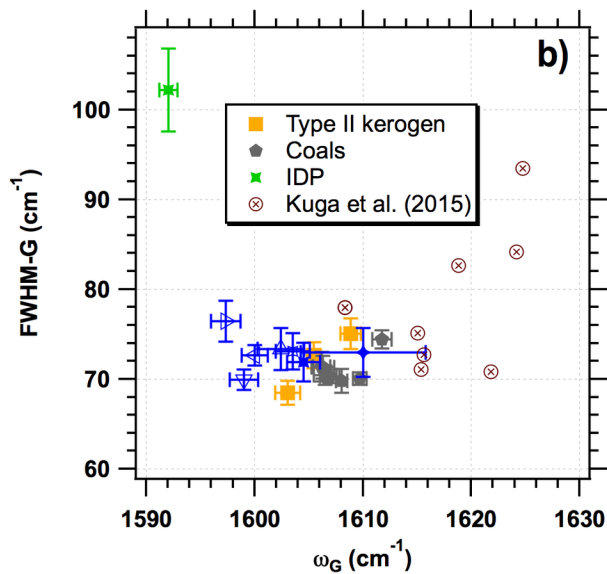
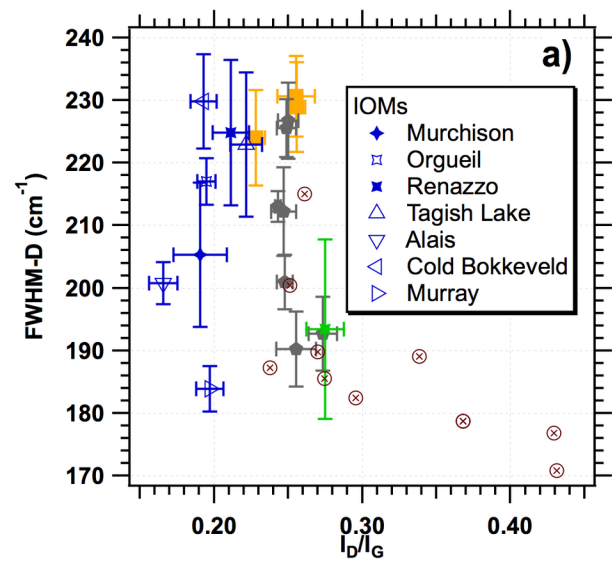


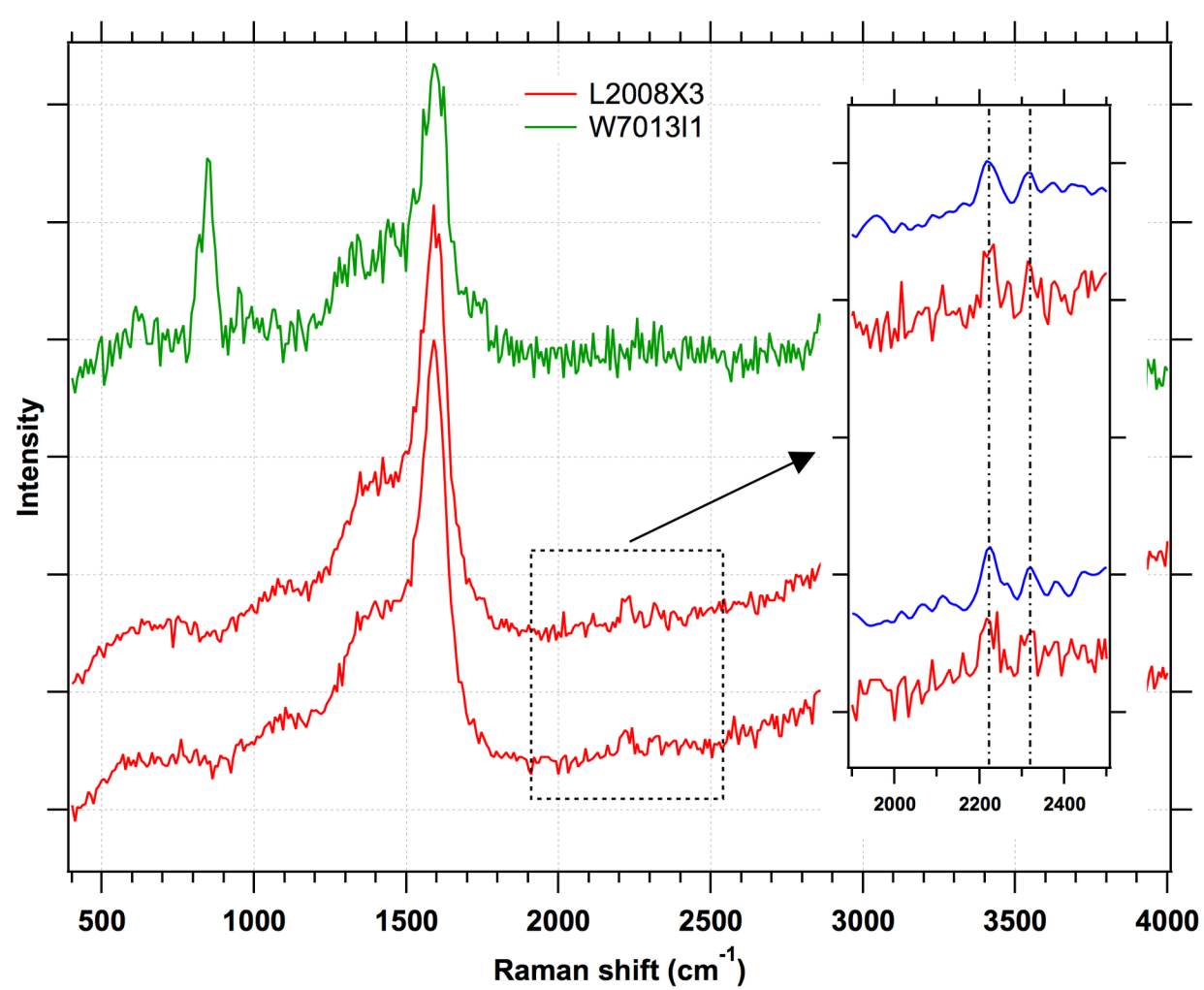


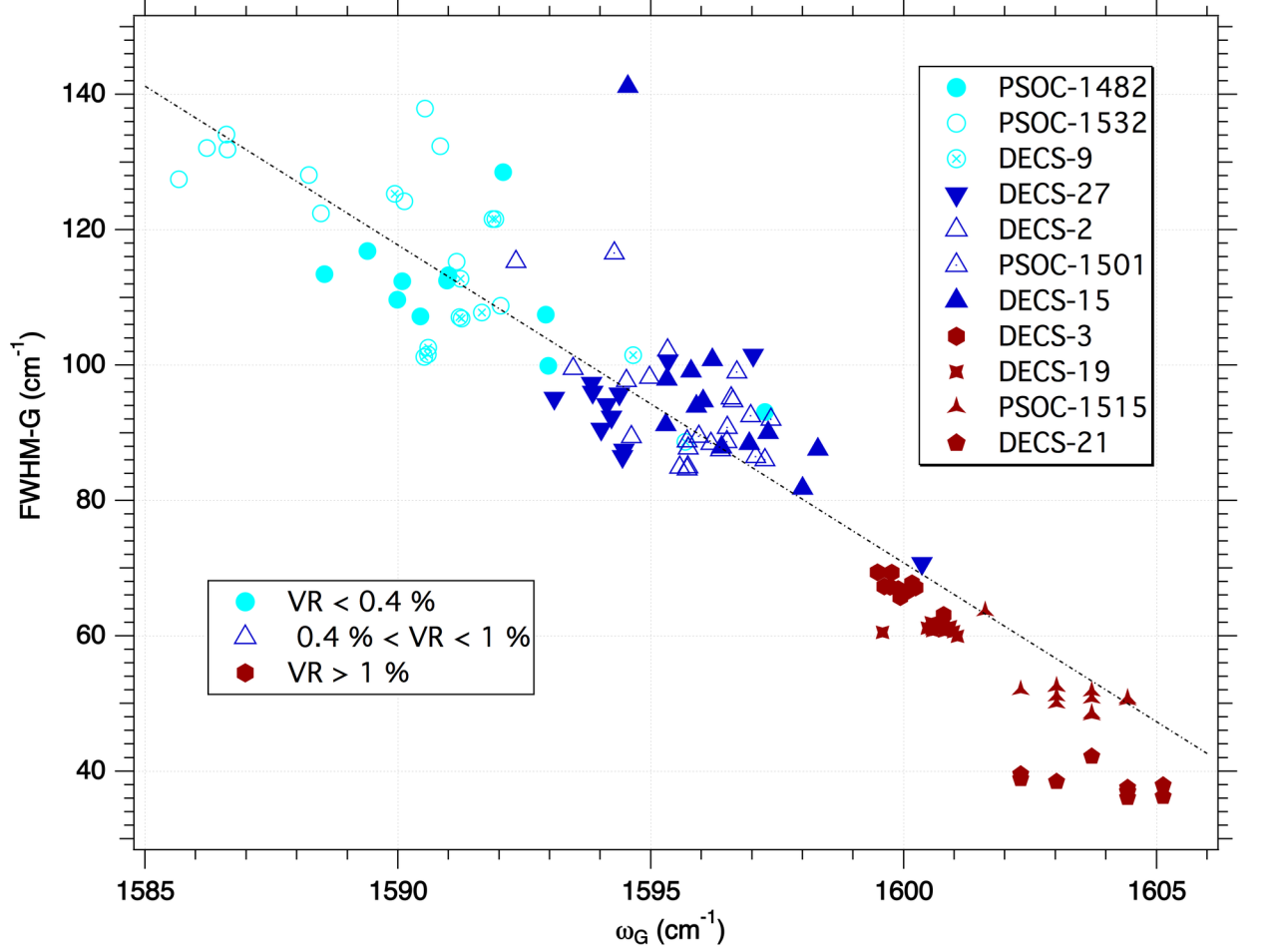












**Table 1**  
Samples investigated.

Name	Sample/Class	R <sub>O</sub> (%)	H/C	O/C
PSOC 1532	coal	0.33	0.90	0.25
DECS 11	coal	0.35	0.73	0.21
DECS 9	coal	0.38	0.82	0.17
PSOC 1482	coal	0.39	0.76	0.23
DECS 27	coal	0.46	0.82	0.13
DECS 2	coal	0.52	0.84	0.10
PSOC 1501	coal	0.73	0.79	0.11
DECS30	coal	1.16	0.73	0.038
PSOC 1540	coal	1.28	0.81	0.036
PSOC 1516	coal	1.73	0.63	0.026
PSOC 880	coal	1.86	0.66	0.020
PSOC 383	coal	2.57	0.54	0.023
PSOC 384	coal	2.7	0.50	0.012
PSOC 1515	coal	2.8	0.53	0.027
DECS 21	coal	5.19	0.53	0.029
K99296	Kerogen II		1.23	0.108
K20505	Kerogen II	0.57 <sup>a</sup>	1.09	0.037
K20507	Kerogen II	1.25 <sup>a</sup>	0.80	0.048
Orgueil <sup>b</sup>	CI		0.67	0.18
			0.72*	
Alais <sup>b</sup>	CI		0.72	0.15
Murchison <sup>b</sup>	CM		0.59	0.18
			0.70*	
Cold Bokkeveld <sup>b</sup>	CM (TII)		0.57	0.19
Murray <sup>c</sup>	CM (TII?)		0.68	0.17
Tagish Lake <sup>b</sup>	C2-ung (TII)			
Renazzo <sup>c</sup>	CR			
L2008x3 <sup>d</sup>	IDP			
W701311	IDP			

The coal samples were provided by the Penn State University data bank. Type II kerogen samples were provided by Institut Français du Pétrole (Rueil-Malmaison, France). TII: heating stage according to Nakamura (2005) classification, estimated by [Quirico et al. \(2018\)](#). R<sub>O</sub>: mean maximum reflectance of vitrinite, according to ADSTM classification (standard D-388). (a): allochthonous vitrinite. (b): spectra from [Quirico et al. \(2014\)](#), reanalyzed with a LBWF without constant (see text). (c): new IOM samples. (d): spectra from Dobrica et al. (2011), treated with a LBWF fit. H/C and O/C elemental ratio of Insoluble Organic Matter are from [Alexander et al. \(2007\)](#), except values tagged by a \* mark that are from [Gardiner et al. \(2000\)](#). IDP: stratospheric Interplanetary Dust Particle.

**Table 2**

Spectral parameters from 244 nm Raman spectra

	Type	FWHM-G (cm <sup>-1</sup> )	$\omega_G$ (cm <sup>-1</sup> )	I <sub>D</sub> /I <sub>G</sub>	A <sub>DDG</sub>	FWHM-D (cm <sup>-1</sup> )	$\omega_D$ (cm <sup>-1</sup> )
PSOC 1532*	coal	74.5 ± 1	1612 ± 1	0.27 ± 0.01	0.40 ± 0.01	193 ± 6	1375 ± 3
DECS 11		71 ± 2	1606 ± 1	0.25 ± 0.01	0.40 ± 0.01	201 ± 5	1368 ± 3
DECS 9		70.5 ± 1	1606.5 ± 1	0.24 ± 0.01	0.40 ± 0.01	213 ± 3	1369 ± 2
PSOC 1482		71.5 ± 2	1606 ± 1	0.24 ± 0.02	0.37 ± 0.02	190 ± 6	1378 ± 10
DECS27		70.5 ± 1	1607 ± 1	0.25 ± 0.01	0.41 ± 0.01	212 ± 7	1371 ± 4
DECS 2		70 ± 1	1610 ± 1	0.25 ± 0.01	0.43 ± 0.01	226 ± 5	1372 ± 3
PSOC 1501		70 ± 2	1608 ± 1	0.25 ± 0.01	0.43 ± 0.01	227 ± 6	1370 ± 3
<i>PSOC 1532#</i>		<i>68 ± 5</i>	<i>1605 ± 1</i>	<i>0.28 ± 0.02</i>	<i>0.48 ± 0.03</i>	<i>255 ± 37</i>	<i>1370 ± 1</i>
<i>DECS 30</i>		<i>61 ± 1</i>	<i>1607 ± 1</i>	<i>0.25 ± 0.01</i>	<i>0.50 ± 0.01</i>	<i>267 ± 3</i>	<i>1374 ± 6</i>
<i>PSOC 1540</i>		<i>62 ± 1</i>	<i>1606 ± 1</i>	<i>0.25 ± 0.01</i>	<i>0.50 ± 0.01</i>	<i>274 ± 6</i>	<i>1376 ± 4</i>
<i>PSOC 1516</i>		<i>58 ± 1</i>	<i>1608 ± 1</i>	<i>0.24 ± 0.01</i>	<i>0.47 ± 0.03</i>	<i>246 ± 23</i>	<i>1385 ± 7</i>
<i>PSOC 880</i>		<i>57 ± 2</i>	<i>1606 ± 1</i>	<i>0.20 ± 0.01</i>	<i>0.43 ± 0.04</i>	<i>244 ± 27</i>	<i>1399 ± 11</i>
<i>PSOC 383</i>		<i>57 ± 1</i>	<i>1607 ± 2</i>	<i>0.21 ± 0.02</i>	<i>0.45 ± 0.03</i>	<i>261 ± 8</i>	<i>1395 ± 9</i>
<i>PSOC 384</i>		<i>57 ± 2</i>	<i>1607 ± 1</i>	<i>0.22 ± 0.01</i>	<i>0.46 ± 0.02</i>	<i>256 ± 12</i>	<i>1393 ± 8</i>
<i>PSOC 1515</i>		<i>58 ± 1</i>	<i>1607 ± 1</i>	<i>0.22 ± 0.01</i>	<i>0.47 ± 0.02</i>	<i>271 ± 28</i>	<i>1393 ± 3</i>
<i>DECS 21</i>		<i>54 ± 1</i>	<i>1604 ± 2</i>	<i>0.16 ± 0.01</i>	<i>0.35 ± 0.02</i>	<i>233 ± 14</i>	<i>1432 ± 8</i>
K99296	kerogen II	75 ± 2	1609 ± 1	0.25 ± 0.01	0.42 ± 0.02	231 ± 7	1378 ± 4
K20505		73 ± 2	1605.5 ± 1	0.26 ± 0.01	0.43 ± 0.01	229 ± 7	1374 ± 4
K20507		68.5 ± 2	1603 ± 2	0.23 ± 0.01	0.40 ± 0.01	224 ± 8	1389 ± 3
Orgueil	CI1	73 ± 2	1604 ± 2	0.19 ± 0.01	0.34 ± 0.01	217 ± 4	1401 ± 3
Alais	CI1	70 ± 2	1599 ± 2	0.17 ± 0.01	0.30 ± 0.02	201 ± 8	1400 ± 3
Murchison	CM2	73 ± 3	1610 ± 6	0.19 ± 0.02	0.32 ± 0.02	205 ± 12	1408 ± 10
Cold Bokkeveld	CM2 [TII]	73 ± 1	1600 ± 2	0.19 ± 0.01	0.35 ± 0.01	230 ± 8	1391 ± 3
Murray	CM2 [TII ?]	76.5 ± 3	1597 ± 2	0.20 ± 0.01	0.29 ± 0.01	184 ± 4	1399 ± 5
Tagish Lake	C2-ung [TII]	73.5 ± 3	1602 ± 3	0.22 ± 0.01	0.37 ± 0.02	223 ± 12	1397 ± 10
Renazzo	CR2	72 ± 2	1604 ± 2	0.21 ± 0.01	0.37 ± 0.01	225 ± 12	1389 ± 3
L2008x3	IDP	102 ± 5	1592 ± 1	0.27 ± 0.01	0.31 ± 0.04	193 ± 15	1385 ± 3

# Immature coals (Ro<1%), collected with P=300 μW on the sample, 2x150 s and 600 gr/mm grating. \* Mature coals (Ro>1%), collected with P=500 μW, 2x300 s and 3600 gr/mm grating (in italic in the table). All samples fitted with a LBWF model without constant (see text).

**Table 3**

Spectral parameters from 514 nm Raman spectra (Bonal et al., 2011)

	<b>FWHM-G (cm<sup>-1</sup>)</b>	<b><math>\omega_G</math> (cm<sup>-1</sup>)</b>	<b>I<sub>D</sub>/I<sub>G</sub></b>	<b>FWHM-D (cm<sup>-1</sup>)</b>	<b><math>\omega_D</math> (cm<sup>-1</sup>)</b>
L2008x3	125.3 ± 3.8	1575.7 ± 2.7	1.03 ± 0.04	294.7 ± 17.2	1359.3 ± 2
W7013I1	108.5 ± 6.9	1686.5 ± 2.3	1.03 ± 0.04	235.2 ± 10.1	1359.6 ± 2.3