



## Precursor and metamorphic condition effects on Raman spectra of poorly ordered carbonaceous matter in chondrites and coals

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### ABSTRACT

Geothermometers based on Raman spectrometry of carbonaceous matter and covering a wide range of temperatures (100–650 °C) have been developed over recent years. While Raman data have been largely interpreted in terms of temperature, they are also the fingerprint of certain metamorphic conditions, especially in the low temperature range relevant to poorly ordered carbonaceous matter. This study investigates the Raman spectra of two series of chondritic carbonaceous matter and coal samples formed from different precursors and under different metamorphic conditions.

The Raman spectra of Polyaromatic Carbonaceous Matter (PCM) from 42 chondrites and 27 coal samples, measured with visible (514 nm) and ultra-violet (244 nm) excitation wavelengths, are analyzed. The Raman spectra of low rank coals and chondrites of petrologic types 1 and 2, which contain the more disordered PCM, reflect the distinct carbon structures of their precursors. The 514 nm Raman spectra of high rank coals and chondrites of petrologic type 3 exhibit continuous and systematic spectral differences reflecting different carbon structures present during the metamorphism event. They result from differences in the chemical structures of the precursors concerning for instance the reticulation of polyaromatic units or an abundance of ether functional groups, or possibly from a lack of carbonization processes to efficiently expel oxygen heteroatoms, due to weak lithostatic pressure and confinement. These results suggest that the use of low temperature carbon thermometers should be restricted to a given geological context. At the same time, the sensitivity of Raman spectra to precursors and certain metamorphic conditions could be used to obtain information other than temperature.

The analysis also provides evidence of the accretion of *relatively* homogeneous PCM precursors among ordinary CO and CV carbonaceous chondrite parent bodies, given that the 514 nm Raman spectra of PCM efficiently trace the metamorphism grades. Looking closer, however, the 514 nm Raman data are more scattered in chondrites than in coals and the maturity tracers are less sensitive and miscorrelate with the atomic H/C ratio, suggesting slight compositional and structural differences among the PCM precursors accreted.

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### 1. Introduction

Polyaromatic Carbonaceous Matter (PCM) found in pristine chondrites has been structurally and chemically transformed during thermal metamorphism in the parent asteroid. The degree of advancement of this transformation (termed *maturity* in this study) reflects the degree of thermal metamorphism and its use for determining thermodynamic (maximum temperature) and/or kinetic (duration) parameters driving asteroidal metamorphism has become a challenging issue (Quirico et al.,

2003; Bonal et al., 2006, 2007; Busemann et al., 2007; Cody et al., 2008). The degree of structural order of chondritic PCM has been unambiguously related to the degree of thermal metamorphism in all classes of chondrites and has been used to determine petrologic types (Bonal et al., 2006, 2007; Rochette et al., 2008; Robin et al., 2008). However, several questions remain regarding the maturation conditions, such as the role of the weak pressure, extent of oxidation processes and possible chemical heterogeneity of the carbonaceous precursors (Yabuta et al., 2005; Alexander et al., 2007; Bonal et al., 2007).

For terrestrial geological contexts, carbon thermometry based on micro-Raman spectroscopy has been successfully developed in the 300–650 °C temperature range (Beyssac et al., 2002). Under these conditions, carbonaceous matter graphitizes and its Raman spectrum

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is controlled by the maximum temperature. A minimum pressure is required to promote graphitization, but above this threshold, pressure does not control the Raman spectra. The Raman spectra also seem to be insensitive to the nature of the organic precursor (Beysac et al., 2002, 2003). This thermometer has been tentatively extended to temperatures <300 °C (Rahl et al., 2005). However, in this range of metamorphism, precursor effects are expected and Raman spectra could also be the fingerprint of parameters other than temperature (e.g. tectonic constraints, duration, mineral catalysis).

The goal of this study is to question the interpretation of poorly ordered PCM Raman spectra by studying two series of different carbon materials: chondritic PCM and coals. PCMs in chondrites of petrologic types 1 and 2 have H/C and O/C elemental ratios similar to low rank coals, but exhibit a different chemical structure and geochemical signatures (Bandurski and Nagy, 1976; Gardinier et al., 2000; Binet et al., 2004). Interestingly, their Raman spectra exhibit spectral differences with those of chondrites (Quirico et al., 2003). We have performed an analysis of Raman spectra of PCM in 42 chondrites (petrologic types from 1 to 3) and 27 coal samples, which were collected using visible (514 nm) and ultra-violet (244 nm) excitation wavelengths. These data include those published earlier by Raynal (2003), Bonal et al. (2006, 2007). The decisive advantage of using these two excitation wavelengths concerns the highly disordered PCM in unmetamorphosed chondrites (petrologic types 1 and 2) and low rank coals, which are difficult to investigate using a single visible excitation (Ferrari and Robertson, 2001). The Raman spectra were analyzed by fitting the first-order carbon bands and by Principal Component Analysis (PCA) which made it possible to take into account the whole spectral variation.

## 2. Samples and analytical conditions

### 2.1. Samples and samples preparation

Two series of coals were used. The first is composed of coal powders provided by the Penn State University Data Bank. They were previously accurately characterized in this institute, providing the elemental compositions H/C and O/C, and the mean maximum vitrinite reflectance ( $R_m$ ) [see <http://www.energy.psu.edu/copl/doesb.html>]. This series covers a broad range of ranks, ranging from lignite to metaanthracite (Table 1). These samples were earlier studied by Raman spectroscopy using a 514 nm excitation (Raynal, 2003; Quirico et al., 2003, 2005). The second is the anthracite series presented in Duber et al. (2000), with ranks in the range  $2 < R_m < 7\%$ . For Raman analysis, grains were picked from coal powders and crushed onto a glass slide. The anthracite series of Duber et al. (2000) was measured on the polished sections used to characterize vitrinite reflectance. The effect of polishing was a particular concern, because this stage of sample preparation is known to induce structural defects in graphitic compounds (Pasteris, 1989). Raman spectra were measured on polished sections and raw powders of two coals of high ranks. They demonstrated that, for these compounds much less organized than graphite, polishing has no significant effect on the structure.

Chondrites were provided by several institutes, except for the Tagish Lake samples purchased from a private seller (Table 1). Chondrites of petrologic type 3 were analyzed as matrix fragments separated from whole rock under a binocular by hand or with a micromanipulator, and crushed onto a glass slide for Raman analysis. The Raman data for some of these objects have already been published (Raynal, 2003; Bonal et al., 2006, 2007). The scattering yield of PCM is lower in UV Raman spectroscopy than in visible Raman spectroscopy. Consequently, chondrites of petrologic types 1 or 2 could not be studied as raw matrix fragments because of their low carbon concentration (<4 wt.%). Their Insoluble Organic Matter (IOM) was chemically extracted by mineral dissolution. The standard procedure in organic geochemistry using HF/HCl acids was adapted to small

quantities by performing all the operations in the same polypropylene microtube (2 ml) in order to minimize matter loss. Shaking was achieved by argon bubbling and/or an ultrasound bath. Samples were first washed with water and a methanol/chloroform mixture [Me-OH/CHCl<sub>3</sub>, 1/2, v/v] to remove the soluble fraction. Carbonates were removed by washing with a 6N HCl solution (1 h), followed by neutralisation with distilled water. Silicates were dissolved using a [28N HF/6N HCl solution, 2/1, v/v] with 3 cycles of 8 h, each followed by neutralisation with distilled water. Hot HCl was then used to remove neoformed fluor bearing minerals. Lastly, the sample was washed again with water and the methanol/chloroform mixture to remove engaged soluble molecules and the final IOM was dried in an argon atmosphere.

Highly precious samples available in minute quantities (e.g. the CR2 Renazzo chondrite) were demineralized using an improved protocol. Micrometric matrix grains were deposited onto gold foils or a teflon grid at the bottom of a home made Teflon sample holder. The sample holder was located in an argon purged box in order to avoid oxidation by oxygen and atmospheric water. The sequence and products used for extraction were the same as in the protocol described above, but the liquids were delivered and expelled using a peristaltic pump. This avoided time-consuming neutralisation/centrifugation sequences. Complete extraction required 24 h, compared to one week with the standard protocol, and an initial mass lower by a factor of 1000–100,000. The protocol was adjusted using well known chondrites (Orgueil and Murchison). The IOM produced was compared with other IOM produced at LPG and Ecole de Chimie de Paris (courtesy of Dr S. Derenne). It was analyzed by Electron Dispersive Spectrometry with a scanning electron microscope and by micro-infrared and micro-Raman spectroscopy.

### 2.2. Raman spectrometers and measurement procedure

Raman measurements were performed at Laboratoire de Sciences de la Terre (ENS-Lyon, France). Unpolarized Raman spectra were excited with the 514.5 nm wavelength of an argon-ion laser (Spectra Physics) and collected in back scattering geometry at room temperature by two different micro spectrometers. The first was a DILOR XY with a double monochromator used in subtractive mode and equipped with an LN<sub>2</sub> cooled CCD (liquid nitrogen cooled charge-coupled device) detector. An Olympus X50 objective lens allowed a spot size of 2–3 μm across. The second micro spectrometer was a LabRam HR800 (Horiba Jobin-Yvon) implemented with a single dispersive grating. Olympus X50 and X100 objectives were employed providing spot size diameters of 2–3 μm and ~1 μm across, respectively. Unpolarized UV Raman spectra were excited by the 244 nm wavelength of a frequency doubled argon-ion laser (Spectra Physics) and collected with a LabRam HR800 (Horiba Jobin-Yvon) designed for UV radiation. An OFR X40 objective lens was used providing a spot size of 4–5 μm across.

The reproducibility of Raman micro-measurements on poorly ordered CM is a very complex issue. Sample heating and photostability (annealing, photooxidation, and photolysis) appear to be critical problems which cannot be fully resolved. Bonal et al. (2006) showed that their set of measurements correlate well with those of Quirico et al. (2003), but the slope of the regression line was not equal to one. Consequently, only Raman spectra acquired under similar experimental conditions were compared. Four runs of measurements were considered in this study (Table 1): (a) 514 nm excitation, ×50 objective, power onto sample  $P=400\text{--}800\ \mu\text{W}$ , irradiation time  $t=300\ \text{s}$  and spectrometer grating of 1800 g/mm (b) 244 nm excitation, ×40,  $P=100\text{--}300\ \mu\text{W}$ ,  $t=360\ \text{s}$  and 600 g/mm (c) 514 nm, ×50,  $P=515\ \mu\text{W}$ ,  $t=540\ \text{s}$  and 1800 g/mm and (d) 514 nm, ×100,  $P=500\ \mu\text{W}$ ,  $t=90\ \text{s}$  and 600 g/mm.

Sample photostability appears to be a very difficult issue in 244 nm Raman measurements, requiring care and a dedicated analytical strategy. They are addressed in detail in Quirico et al. (2008). In the

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