

LASER-INDUCED FLUORESCENCE: POTENTIAL INTERESTS FOR IMMATURE ORGANIC MATTER CHARACTERIZATION. L. Bonal¹, E. Quirico¹, G. Montagnac², B. Reynard², ¹Laboratoire de Planétologie de Grenoble (lydie.bonal@obs.ujf-grenoble.fr) Bât. D de Physique B.P. 53 38041 Grenoble Cedex 9, France; ²Laboratoire de Sciences de la Terre ENS-Lyon 46, allée d'Italie 69364 Lyon Cedex 7 France.

Introduction: Studying immature extraterrestrial Organic Matter (OM) is blemished of experimental constraints: the small quantity of matter necessitates to work, as far as possible, with non-destructive microscopic techniques. Raman spectroscopy has been successfully used for characterizing OM in slightly metamorphosed chondrites [1,2]. However, Raman spectra of immature OM are more difficult to interpret, partly because of a photoluminescence background induced by the laser excitation which perturbs the Raman features. This drawback of Raman spectroscopy is however interesting. The use of the fluorescence to characterize sedimentary OM has been proposed by several authors [e.g. 3,4]. In all of these studies, the main goal was to assess the maturity of the samples. In the actual state of knowledge, a consequent work is still needed for providing an analytical approach linking the fluorescence signal (spectral shape and absolute intensity) to compositional and structural information. Exploiting the information of the fluorescence signal and applying it to the study of immature extraterrestrial OM, such as Interplanetary Dust Particles (IDPs) and Carbonaceous Chondrites (CCs) is the goal of the present work.

The elaboration of a new analytical technique applied to very complex natural materials requires working on the widest possible variety of samples. In view of working on IDPs and CCs, we have chosen to work on Insoluble Organic Matter (IOM) of different classes of primitive CCs (CI1, CM2), on terrestrial sedimentary OM such as coals and kerogens, on Tholins which are analogs of Titan's aerosols and on various synthetic materials such as PAH or polymers.

In this paper, preliminary results are presented to underline the potentiality of the Laser Induced Fluorescence (LIF).

Samples and Experiments: Raw samples of CI chondrites (Alais, Ivuna, Orgueil) and of CM chondrites have been supplied by MNHN (Paris-France). IOM of Orgueil and Murchison were kindly provided by S. Derenne. Type II kerogens were provided by Institut Français du Pétrole (courtesy of Mrs Vandenbroucke): 99296 (VR=n.d.; H/C=1.229; O/C=0.1076); 20505 (VR=0.57%; H/C=1.093; O/C=0.0372); 20506 (VR=0.65%; H/C=1.035; O/C=0.0313). Thus, the 99296 kerogen is the less mature and the 20506 kerogen is the most one.

Kerogens, tholins and synthetic materials do not require particular preparation. Several grains of these various samples were selected under a binocular microscope and crushed between two glass slides, which were used as fluorescence substrates.

LIF measurements were performed in Laboratoire de Sciences de la Terre (ENS-Lyon, France) with a Raman spectrometer (Labram HR800, Jobin Yvon) coupled to argon ion or helium-neon lasers (457.9, 514.5 and 632.8 nm excitations). Using different wavelengths is essential to investigate complex mixtures, as selective population of chromophores can be excited. To record the luminescence signal a 150 l/mm grating was used. The covered spectral range was 400-1000 nm. Photo-instability of the materials due to chemical reactions with atmospheric oxygen induces large variations of the intensity of the fluorescence signal [6]. Therefore, experiments were carried out under an inert atmosphere (Ar) in a dedicated cell. In that manner, the signal was relatively stable and the individual subscans were stitched together without applying a gain factor. Laser Induced Fluorescence is a non-destructive technique, as long as the photon flow is sufficiently low. Thus, care was taken to irradiate the sample with low power fluxes (typically 100µW on the surface), to prevent modifications of the structure.

Results: a minimum of 30 spectra were acquired for each sample in blue and green excitation wavelengths. On Fig. 1, 2, 3 only representative spectra are presented.

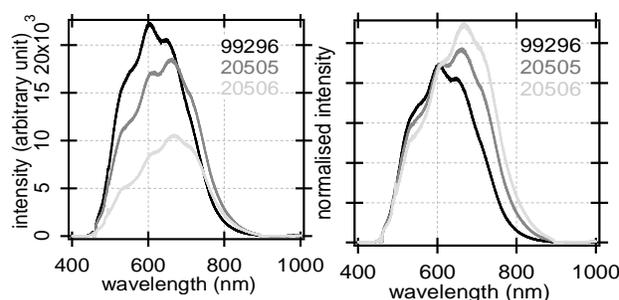


Figure 1: fluorescence spectra of 99296, 20505, 20506 type II kerogen using blue excitation wavelength. **a)** rough spectra **b)** spectra normalized at 605nm.

Type II kerogens: On Fig. 1a rough spectra of the type II kerogens are presented. 99296, the more

immature sample, is characterized by systematically higher fluorescence intensity, than respectively 20505 and 20506. On Fig. 1b, the spectra are normalized at 605 nm. The kerogens are distinguished by a different broadening and by different maximum emission wavelengths. Fluorescence emission of 99296 is maximum at 605 nm, of 20505 at 660 nm and of 20506 at 670 nm.

Fluorescence of kerogen is essentially due to its aromatic and polyaromatic content. The increase of the relative concentration of these fluorophores, as well as their condensation, with the aromatization leads to a progressive change of the fluorescence emission [3]: decrease of the fluorescence intensity (Fig. 1a) and red shift and broadening (Fig. 1b). Thus LIF signature allows to distinguish kerogens characterized by different H/C and O/C ratio.

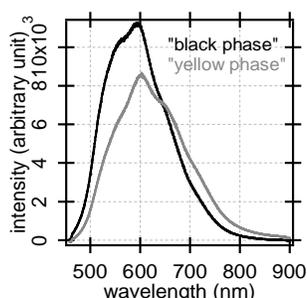


Figure 2: fluorescence spectra of both black and yellow distinguishable phases of a Tholin, using blue excitation .

Tholins: Recent studies have shown that Titan's Tholins synthesized from a $N_2:CH_4=98:2$ mixture in a cold plasma [7] are heterogeneous at the micrometric scale. Two phases were observed, as yellow and black grains with various morphologies. Fluorescence spectra (Fig. 2) show significant differences, concerning the intensity as well as the spectral shape and are correlated to the color (Fig. 2). The chemical characterisation of these Tholins is underway. Yellow phases are complex molecular mixtures soluble in water/ CH_2Cl_2 , whereas the black ones are refractory. The IR spectra are very closed, except the lack of CH_2/CH_3 functions in the black fraction. The UV Raman spectra of both reveals the presence of aromatic compounds. More work is necessary to disclose the chemical factor(s) which control the variations of the spectral shape of the fluorescence spectra.

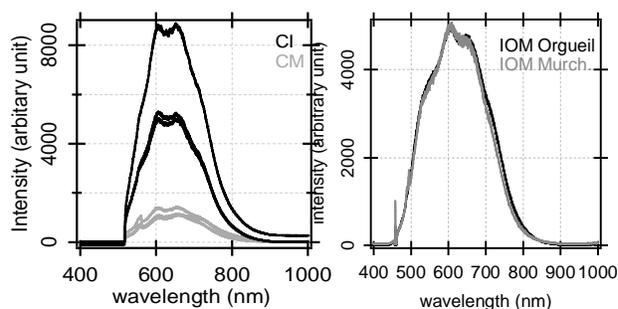


Figure 3: fluorescence spectra of CI and CM carbonaceous chondrites. a) rough spectra at green excitation, b) normalised spectra of IOM of Orgueil and Murchison using blue excitation

CC chondrites: Fluorescence spectra of CI and CM chondrites are very similar: bandwidth, structures and maximum emission wavelength are similar. In particular, spectra of IOM of Orgueil and Murchison are undistinguishable (Fig. 3b). Nevertheless, in raw samples under the same experimental conditions, the maximum intensity of the CI samples is systematically higher than of CM samples (Fig. 3a). The similar spectral shape is consistent with the fact that IOM of CI and CM are chemically and structurally similar [5]. The large variations of the fluorescence intensity are still unexplained.

Conclusion: Further work is still needed for the exploitation of the fluorescence signal. Nevertheless, the first results presented here show the sensitivity of the fluorescence signal to the composition and to the structure of the material. It augurs a subsequent potentiality of this technique for the characterization of immature organic matter in the planetary field of sciences.

References: [1] E. Quirico et al. (2003) *MPS*, 38, 795. [2] L. Bonal et al., *GCA, sub.* [3] B. Pradier et al. (1991) *Org. Geochem.*, 17(4), 511-524. [4] R.W.T. Wilkins et al. (1995) *Org. Geochem.*, 22(1), 191-209. [5] A. Gardinier et al. (2000) *EPSL*, 184, 9-21. [6] E. Quirico et al. (2005) *Spectrochimica Acta*, accepted. [7] J.M. Bernard et al. (2005) LPSC XXXVIth.

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