MATURATION GRADE OF ORGANIC MATTER IN METAMORPHOSED CARBONACEOUS CHONDRITES. N. Chaumard[1,*], E. Charon[2,†], J.-N. Rouzaud[2], and B. Devouard[1,§], [1]Laboratoire Magmas et Volcans, UMR 6524 Université Blaise Pascal – CNRS, 5 rue Kessler, 63038 Clermont-Ferrand, France (nchaumard@mnhn.fr); [2]Laboratoire de Géologie, ENS, UMR CNRS 8538, 24 rue Lhomond, 75231 Paris Cedex 5, France; [*]Present address: LMCM, MNHN, UMR 7202 – CNRS, 61 rue Buffon, 75005 Paris, France; [†]Present address: CEA-Saclay, DSM/IRAMIS/SPAM – Laboratoire Francis Perrin, Bat. 522, 91191 Gif-sur-Yvette Cedex, France; [§]Present address: CEREGE, Aix-Marseille Université, UMR CNRS 7330, Europôle de l'Arbois, BP 80, 13545 Aix-en-Provence Cedex 4, France.

Introduction: The determination by Raman spectroscopy of the maturation grade of meteoritical organic matter (OM) is used as a metamorphic tracer, since it is sensitive to the peak metamorphic temperature and independent of the mineralogy and aqueous alteration [1,2]. This method was used by [2,3] to determine the metamorphic grade of several CV3 and CO3 chondrites, but, up to now, was never extended to higher petrologic types. The goal of this study is the determination of the maturation grade of OM in metamorphosed CVs and CKs that are the only metamorphic group of carbonaceous chondrites (types 3–6) [4].

Samples: We studied Allende (CV3), NWA 779 (CV3), NWA 2900 (CV3), NWA 1559 (CK3), and TNZ 057 (CK4). Our measurements were performed on fresh and polished sections.

Methods: SEM-BSE imaging was performed using a JEOL JSM-5910LV electron microscope and quantitative analyses were measured on a CAMECA SX100 electron microprobe at Laboratoire Magmas et Volcans (Clermont-Ferrand, France). Raman spectroscopy was performed at Laboratoire de Géologie (ENS Paris, France) with a microspectrometer Renishaw InVia equipped with a Spectra Physics argon ion laser using 514.5 nm excitation. The laser beam was focused by a microscope equipped with a ×50 objective. The power at the sample surface was 2 mW and the acquisition time varied from 60 to 120 s. Spectra were acquired under atmospheric conditions, in the spectral region 800–2200 cm^{-1} (1800 l/mm grating) including the first order carbon bands. We used the method described by [2] to obtained the D- (~1350 cm^{-1}) and G-band (~1600 cm^{-1}) spectral parameters (peak position: $\omega_{D,G}$, full width at half maximum: FWHM-D,G, and peak intensity: $I_{D,G}$).

Results: *Petrography.* Texturally and petrologically, Allende is the least metamorphosed sample analyzed during this work (mean matrix olivine grain size: 6.1±0.2; mean olivine composition: $Fa_{50.0\pm5.0}$). NWA 779 displays a higher metamorphic grade. Matrix contains tabular olivine grains from 10 to 20 µm in size embedded in a fine-grained assemblage (2–5 µm), with a composition of $Fa_{45.4\pm4.1}$. Matrix in NWA 1559 is mainly composed of olivine grains ($Fa_{36.1\pm0.1}$) with a mean size of 16.7±0.6 µm. Matrices in TNZ 057 and NWA 2900 are chemically equilibrated ($Fa_{32.0\pm0.5}$ and $Fa_{35.0\pm0.8}$, respectively) and olivine grains have a mean size of 65.0±25.0 µm and 52.4±3.5 µm, respectively.

Maturation of organic matter. All spectra exhibit first order D- and G-bands (Fig. 1). The intensity of the fluorescence background in Raman spectra is weak for Allende and NWA 779, rises for NWA 1559 and NWA 2900, and is high for TNZ 057. The spectral parameters of the G- and D-bands are given in table 1.

For Allende and NWA 779, the peak intensity of the D-band is higher than that of the G-band, whereas $I_D/I_G < 1$ for NWA 2900, NWA 1559, and TNZ 057 (Fig. 1). In addition, Raman maps show a diminution of the carbon content from Allende, NWA 779, to NWA 1559.

Our results reveal a slight diminution of the FWHM-D parameter, a feature typical of OM maturation. However, this parameter seems correlated with a decrease of the I_D/I_G ratio for CKs and CVs which are more metamorphosed than Allende (Fig. 2). On the basis of the FWHM-D and I_D/I_G parameters, CVs and CKs studied can be classified as increasing in OM maturation grade, as follows: Allende < NWA 779 < TNZ 057 ≈ NWA 2900 < NWA 1559.

Discussion: Spectral parameters obtained for Allende are slightly different than those of [2]. Since FWHM-D parameters are almost the same (70±3 cm^{-1} in this work, 65±4 cm^{-1} calculated by [2]), the spectral parameter differences appear to be the consequence of the manual fitting procedure. The baseline correction could explain the differences of I_D/I_G ratio measured in this work and by [2], 1.37±0.05 and 1.54±0.06, respectively.

The full widths at half maximum of the D and G-bands are reliable parameters of carbonization and graphitization, respectively [5, 6], and NWA 1559 should be more metamorphosed than TNZ 057. However, textural, petrologic, and chemical observations indicate that TNZ 057 is the most metamorphic sample studied. These observations, associated with the de-

crease of the carbon content in CK matrices and the presence of intense fluorescence backgrounds, suggest that the maturation grade of the OM is independent of the textural and chemical reequilibration of CV-CK. However, our Raman analyses of the OM in NWA 2900 confirm the textural and chemical observations realized in matrix. In terms of metamorphic grade, NWA 2900 and TNZ 057 are comparable.

OM present in the CK samples analyzed is much more mature than in primitive chondrites [2] and appears to enter the graphitization domain (Fig. 2). Indeed, the study of [7] shows two evolution trends for carbons submitted to the temperature effect. The first, where I_D/I_G increases, corresponds to the carbonization domain, i.e. a chemical process (obtention of a pure sp^2 carbon), without crystalline growth. The second, corresponds to the graphitization domain (crystal growth within already pure sp^2 carbons) [6–8]. The pioneer results of [8] showed that the I_D/I_G decrease is a signature of a graphitization process. The evolution of the structural maturity of OM in CVs characterized by HRTEM by [2] falls within the left part of the figure 2 and corresponds to coherent domain sizes (L_a) inferior to 2 nm; no crystalline growth occurred and all these OM suffered a carbonization process only. Our results, which show a diminution of the I_D/I_G ratio as the FWHM-D decreases, fall within the right part of the figure 2 (L_a > 2 nm), i.e. in the true graphitization range [6]. The maximal I_D/I_G ratio seems reached for Allende, in agreement with the L_a measured by HRTEM, approximately 2 nm [9].

Conclusions: In NWA 779, NWA 2900, and the two CKs analyzed, the maturation grade of OM indicates an entry in the graphitization domain, whereas CO and CV chondrites less metamorphosed than Allende define an evolution trend within the carbonization domain. By comparison with the data of [2], this work seems to demonstrate the existence of a possible evolution of the OM maturation grade from a carbonization domain (CVs) to a graphitization domain (CKs). Thus, this study supplies a new argument in favour of a continuous CV-CK metamorphic series, where the OM is first carbonized, then graphitized for the highest petrologic types (> 3). However, the study of OM in COs by Raman spectroscopy [3] cannot exclude the existence of a genetic link between COs and CKs.

References: [1] Quirico E. et al. (2003) *MAPS, 38,* 795–811. [2] Bonal L. et al. (2006) *GCA, 70,* 1849–1863. [3] Bonal L. et al. (2007) *GCA, 71,* 1605–1623. [4] Kallemeyn G. W. et al. (1991) *GCA, 55,* 881–892. [5] Ammar M. R. et al. (2011) *Spectr. Lett., 44,* 535–538. [6] Charon E. et al. (submitted) *Carbon*. [7] Ferrari A. C. and Robertson J. (2000) *Phys. Rev., B61*, 14095–14107. [8] Tuinstra F. and Koenig J. L. (1970) *J. Chem. Phy., 53,* 1126–1130. [9] Le Guillou C. et al. (2012) *MAPS, 47,* 345–362.

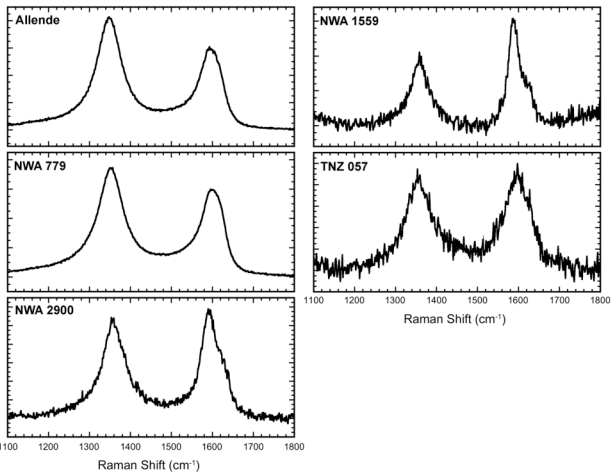

Figure 1: Selected representative raw spectra of the OM in the CVs and CKs analyzed. Vertical axis: intensity in arbitrary unit.

	Allende		NWA 779		NWA 2900		NWA 1559		TNZ 057	
	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ
ω_D	1350	2	1353	1	1358	4	1359	1	1357	0
$FWHM_D$	70	3	67	16	70	13	33	15	71	18
I_D	10686	4053	6536	5072	614	283	1101	533	515	413
ω_G	1605	2	1607	9	1597	5	1592	7	1608	12
$FWHM_G$	64	3	72	27	55	4	37	17	71	5
I_G	7804	2957	5150	4060	721	329	1958	1002	535	391
I_D/I_G	1.37	0.05	1.25	0.08	0.86	0.11	0.57	0.02	0.93	0.10

Table 1: Raman parameters for the studied CV and CK chondrites.

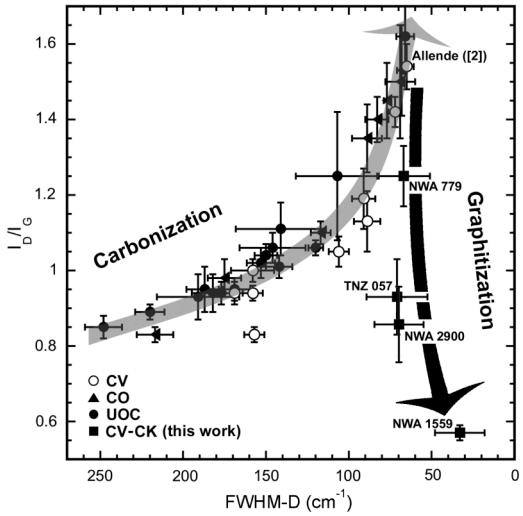

Figure 2 : Diagram I_D/I_G vs. FWHM-D showing the metamorphic evolution of three metamorphic series of primitive chondrites (CV, CO, and unequilibrated ordinary chondrites (UOC); after [2, 3]) and containing CVs and CKs analyzed during this work. The grey and black arrows indicate an increase of the metamorphic grade (carbonization and graphitization processes, respectively).