

**CARBON THERMOMETRY APPLIED TO CHONDRITES AND TERRESTRIAL ROCKS: EFFECT OF ORGANIC PRECURSOR.** E. Quirico<sup>1</sup>, G. Montagnac<sup>2</sup>, J-N Rouzaud<sup>3</sup> and B. Reynard<sup>2</sup> <sup>1</sup>Laboratoire de Planétologie de Grenoble Université Joseph Fourier / CNRS France [eric.quirico@obs.ujf-grenoble.fr](mailto:eric.quirico@obs.ujf-grenoble.fr), <sup>2</sup> Laboratoire de Sciences de la Terre, Ecole Normale Supérieure de Lyon France, <sup>3</sup>Laboratoire de Géologie Ecole Normale Supérieure de Paris France

**Introduction:** The time-temperature history of unequilibrated chondrites is poorly known. Their poor mineralogy and the lack of thermodynamic equilibrium prevents from properly applying thermometric techniques. This leads to a state of confusion, as a wide range of peak temperatures have been proposed in literature. A paththrough to investigate such geological contexts may be thermometric approaches based on the degree of structural order of the kerogen trapped in the rocks. They have been widely developed since 2001, either for terrestrial geological context [1,2] and chondrites [3,4].

The geothermometer proposed by [1] for temperature > 300 °C appears efficient, fairly independant from organic precursor, barometric history and possibly fluids circulation. Ranges of temperature below 300°C may be more tricky. It is not clear, whether or not, they could be explored using a single geothermometer [5].

In this study, we report series of Raman measurements on both terrestrial carbonaceous rocks (20 coal, 4 type II kerogens) and ~40 ordinary and carbonaceous chondrites covering a wide range of metamorphism. These measurements definitely evidence the control of the Raman spectra by the chemical structure of the organic precursor. They demonstrate that a universal cosmotheometer, suited to every kind of carbonaceous rocks, does not exist. However, it is demonstrated that systematic measurements provide information both on the type of precursor and the maturity. We also report the first 244 nm Raman measurements on extraterrestrial organic matter.

**Raman measurements:** Raman measurements were obtained using 514 and 244 nm wavelength excitations. JOBIN-YVON Raman micro-spectrometers using Ar<sup>+</sup> laser were used. Spot size was around 2-3 µm (514 nm) and 4-5 µm (244 nm). Power onto sample ranged between 100-500 µW, and acquisition time between 30-90 s (514 nm) and 300s-15 minutes (244 nm). Sample stability is a critical issues, in particular using 244 nm. Peculiar care was devoted to check the lack of sample alteration. Series of spectra at the same spot location were systematically recorded, and a rotating sample-holder was used to investigate damages induced by the 244 nm micro-beam. All spectra do contain the first-order carbon bands (G and D), in the region 700-2000 cm<sup>-1</sup>.

The interpretation of Raman spectra has been the object of numerous studies. No theoretical background is definitely available. In the case of weakly mature kerogens, no empirical relationship like the Tuinstra-König's connect the Raman spectra and some physical parameters.

Raman spectra have been treated by Principal Component Analysis (PCA). This kind of analysis is powerful to point out similarity and systematic variations in a large set of data. As whole variations in the spectra are considered, the chemical control of the spectral distribution in the first-order carbon bands can be studied.

We present 3 sets of data. The first contains metamorphic series of coals and unequilibrated ordinary and carbonaceous chondrites (514 nm excitation). PCA analysis reveals clearly two metamorphic pathways (Fig. 1). The Raman spectra thus do contain information on the maturity and on the chemical structure of the initial organic precursor.

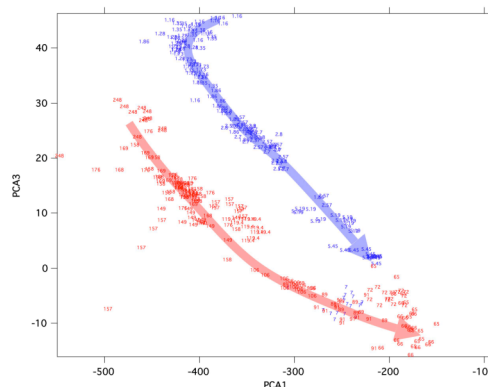


Fig. 1 : Blue : coal series. Red : chondrites series. Two distinct metamorphic pathways are observed. This diagram evidences two distinct groups of organic precursors.

The second set of data consists of UV 244 nm spectra acquired on weakly matured coals (diagenesis), type II kerogens, and kerogens extracted from unmetamorphosed carbonaceous chondrites. PCA analysis shows that samples plot along three distinct groups (Fig. 2). Raman spectroscopy is thus able to decipher between type II and type III kerogens.

The third group contains spectra acquired with a 514 nm excitation, from immature carbonaceous chondrites and coal samples. Though less clear than the 244

nm data set, consistent results are obtained regarding the discrimination between coals and carbonaceous chondrites (Fig. 3). The presence of a fluorescence background in the 514 nm spectra may partly explain the less clear discrimination.

**Discussion:** PCA analysis evidence the ability of Raman spectroscopy to decipher distinct organic precursors in metamorphic series. Distinct organic precursors between coals and chondrites are evidenced thanks to 514 nm measurements. In both series, the organic precursors appear fairly similar, though they are not strictly (e.g. coals were collected in different deposits). Looking in details data within each series reveal overlaps for less mature samples, and more or less poor correlations, which may reflect variations of structure and composition among initial precursors.

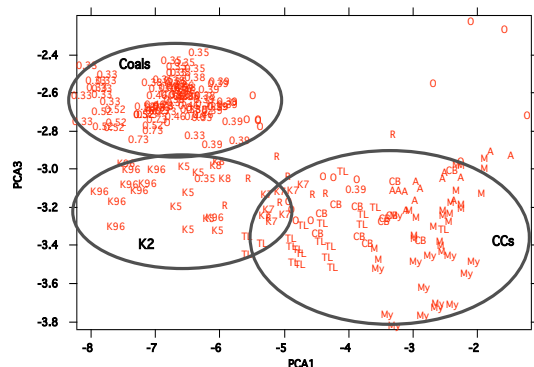


Fig. 2 : PCA analysis of 244 nm spectra of coals, type II kerogens and IOM of carbonaceous chondrites.

244 nm Raman spectra of immature samples allow to decipher immature coals, type II kerogens and IOMs from unmetamorphosed carbonaceous chondrites. The use of a 244 nm excitation prevents from the huge fluorescence of type II kerogen. These measurements suggest that, in a range of low metamorphism (e.g.  $T < 300$  °C), no geothermometer can be used for all series of kerogens (I, II and III). Earlier and recent attempt of carbon thermometry in this temperature range should thus be considered with care [2, 6]. Furthermore, geothermometers derived from compilation of large set of data from sedimentary basins containing the same family of kerogen lack sensitivity (the correlation between a peak temperature and any maturity tracer does not exceed 0.7) [6]. They are consistent with our observations on coals, where data are rather scattered for samples of low maturity. In such a temperature range, catalytic effects from minerals, and possibly hydrous alteration, may play a key role in the maturation process along with temperature. Slight chemical variations of the organic precursors may also explain these fluctuations.

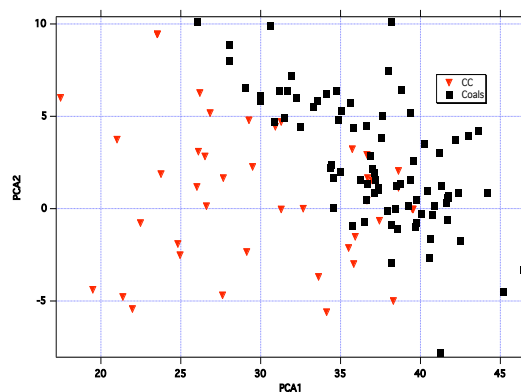


Fig. 3 : PCA analysis of 514 nm Raman spectra of coals and unmetamorphosed carbonaceous chondrites.

Last, both 514 and 244 nm measurements on immature samples demonstrate that carbon thermometry based on Raman spectrometry is insensitive to very low metamorphism grades : roughly, for a coal series, vitrinite reflectance  $< 1$  %.

**Conclusion:** Carbon thermometry for low metamorphism grades appear more tricky than for higher ones. Raman spectra are controlled by both the composition of the initial organic precursor and by the maturation grade. Co-factors as mineral catalysis or hydrous alteration may also play a role in the maturation process. In any case, a cosmotheometer suitable for chondrites cannot be calibrated with terrestrial rocks.

**References:** [1] Beyssac O. et al. (2002) JMG 20, 859–871 [2] Rahl et al. (2005) EPSL 240, 339–354 [3] Bonal et al. (2006) GCA 70, 1849 [4] Bonal et al. (2007) GCA 71, 1605 [5] Barker and Goldstein (1990) Geol. 18, 1003–1006 [6] Buntbarth G. (1986) Paleogeothermics, 79–93