Comparing vitrinite reflectance and micro-Raman spectroscopy indexes to assess thermal maturity of organic matter dispersed in sediments: a case history from the South Atlantic passive margin

Andrea Schito[1], Sveva Corrado[1], Claudia Romano[1] and Domenico Grigo[2]
[1] Università degli Studi di Roma Tre, Dipartimento di Scienze, Largo San Leonardo Murialdo 1, 00146 Rome, Italy
[2] ENI S.p.A. - Milan, Italy.

Introduction

The reliable assessment of thermal maturity of sedimentary successions is a key topic for the quantitative evaluation of hydrocarbons generation/expulsion. Nevertheless uncertainties in thermal maturity assessment can frequently occur when using traditionally adopted thermal indicators derived from optical characterization of organic matter dispersed in sediments, especially when exploring targets that are devoid of vitrinite and/or are poor in organic matter. The level of uncertainty, linked to input data to calibrate thermal modelling, can negatively influence decisions on the development of prospects. In order to reduce this problem, we propose the use of Raman micro-spectroscopy as a reliable support to the traditional organic petrographic approach. To achieve this aim we compared the application of both methods to an about two kilometers thick Miocene section drilled offshore Angola, in one of the most productive petroleum provinces in the world.

Vitrinite reflectance is by far the most popular indicator of thermal maximum exposure adopted since the '50 as a measure of thermal maturity for organic matter dispersed in sediments. Whereas Raman spectroscopy application to organic matter is much less widespread. In detail Raman spectroscopy has already been used for the characterization of the thermal maturity of organic matter(Jehlička et al., 2003; Kelemen and Fang, 2001). Two bands on the Raman spectra, called G (graphitic) and D (disordered), are related to the growth of the ordered in respect to the amorphous organic matter. Parameters linked - either directly or indirectly - to D and G bands have been used to describe the temperature paths of metamorphic rocks (Beyssac et al., 2003; Endo et al., 2012; Lahfid et al., 2010). Furthermore few studies focused on the relations between these parameters and vitrinite reflectance during coal maturation stages. Kelemen and Fang (2001), Guedes et al. (2010) and Liu et al. (2012) found correlations between Raman parameters, related to D and G bands, and vitrinite reflectance of kerogen at different maturity levels. Nevertheless reliable correlations between Raman indexes and maximum experienced paleo-temperatures are available only above 200-220°C (Lafhid et al. 2010). This work shows the preliminary results obtained at lower thermal maturity levels (from immature to early mature stages of HC generation).

Methods

Mean random reflectance on vitrinite fragments (R_o%) and Micro-Raman analyses were carried out on concentrated kerogen.

For micro-Raman spectroscopic analyses we used a Jobin Yvon micro-Raman LabRam system in a backscattering geometry, in the range of 700-2300 cm^{-1} using a 600 grooves/mm spectrometer gratings and CCD detector under a maximum of 100X optical power.

A laser source Neodimium-Yag at 532 nm (green laser) was used as the light source and optical filters adjusted the power of the laser (<6mW). The Raman backscattering was recorded after an integration time of 20s for 6 repetitions for each measure. This, together with the use of green laser and filters, allowed to reduce the fluorescence that could entirely cover the spectrum in samples at low levels of thermal maturity. For each sample between ten and fifteen measurement on different grains have been performed. Each organic grain was analysed focusing an illuminated spot of about 2 µm with a 50× objective lens.

Spectra were deconvoluted using LabSpec software in order to determine frequencies, bandwidths and the relative intensities of bands. Each spectrum was deconvoluted into six bands following Li et al. (2007), using a Lorentzian curve-fitting.

The parameters adopted as thermal tool are:
- position of D and G bands;
- width at half height of D and G bands (FWHM);
- D/G intensity ratio (D/G) (according to Guedes et al., 2010);
- the area ratio between the first three and the last three peaks that in the deconvoluted spectra form the D and G bands. RA2 ratio, modified after Lahfid et al. (2010).

Results

The analysed succession was sampled at depths comprised between about 1.3 and 3.3 km. It is made up of organic-rich shales, interbedded with near shore to deep water sandstones.

The organic matter dispersed in the sediments is composed by amorphous organic matter (AOM), marine phytoplancton (MPH), and continental plants fragments (CHF and CWF). Vitrinite reflectance distribution shows an increase from 0.33% at the top, to 0.52% at the bottom (Fig. 1).

Calculated Raman parameters do not always show a regular trend with depth and/or with vitrinite reflectance. A good correlation was recognised with: the width at half height of G peak (FWHM-G), the position of D peak, D/G and RA2 ratio. In detail: FWHM-G values decrease from the top (92 cm^{-1}), to the bottom (80 cm^{-1}); the position of D peak shifts from 1380 cm^{-1} at the top to 1360 cm^{-1} at the bottom. D/G ratio is about 0.39 at the top and 0.47 at the bottom (Fig.1). Finally the RA2 ratio values range between about 0.6 at the top to about 0.73 at the bottom of the well (Fig.1).

Comparing these parameters with vitrinite reflectance, the best correlations are recorded for FWHM-G, D/G ratio and RA2 ratio that show respectively a R^2 values of 0.78, 0.76 and 0.84.

Final remarks

The preliminary results in the first three kilometers of depth of the analysed well in the offshore of Angola show that thermal maturity of the Miocene succession is comprised from the immature to the early mature stages of HC generation.

Micro-Raman spectroscopic investigation allow to define a series of parameters that show a regular trend with depth. In detail, three indexes (RA2, D/G and FWHM-G) are the most sensitive to temperature changes even at low thermal maturity stages and can satisfactorily be correlated with vitrinite reflectance.

Thus this work provides new insights on the application of micro –Raman analyses on the organic matter even at low maturity levels. The development of such a methodology could be a useful tool either as a support or as a substitute to the organic petrography when traditional optical analyses cannot provide reliable thermal maturity assessment.

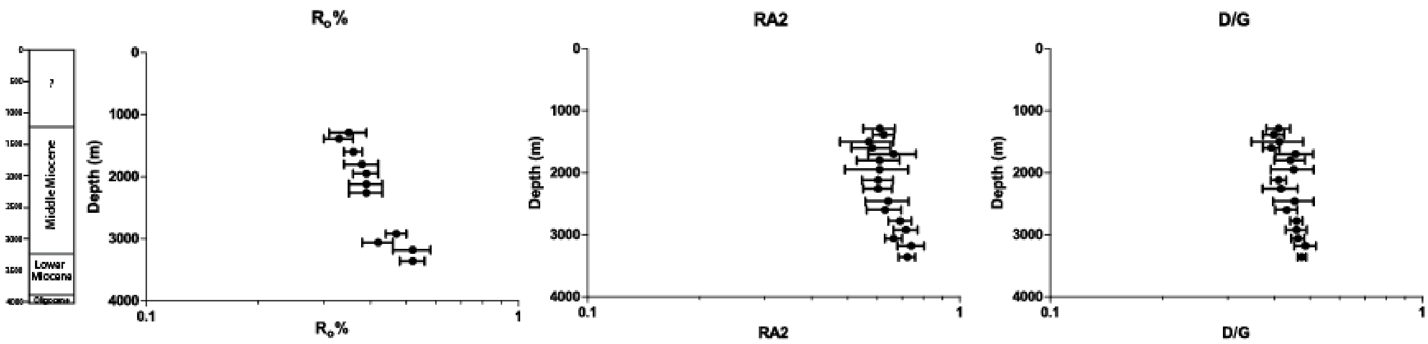

Figure 1 Distribution of vitrinite reflectance and selected Raman spectroscopy parameters (RA2 and D/G) with depth

Bibliography

Beyssac, O., Goffé, B., Petitet, J.-P., Froigneux, E., Moreau, M., and Rouzaud, J.-N., 2003, On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy: Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, v. 59, no. 10, p. 2267-2276.

Endo, S., Wallis, S. R., Tsuboi, M., Torres De LeÓN, R., and Solari, L. A., 2012, Metamorphic evolution of lawsonite eclogites from the southern Motagua fault zone, Guatemala: insights from phase equilibria and Raman spectroscopy: Journal of Metamorphic Geology, v. 30, no. 2, p. 143-164.

Guedes, A., Valentim, B., Prieto, A., Rodrigues, S., and Noronha, F., 2010, Micro-Raman spectroscopy of collotelinite, fusinite and macrinite: International Journal of Coal Geology, v. 83, no. 4, p. 415-422.

Jehlička, J., Urban, O., and Pokorný, J., 2003, Raman spectroscopy of carbon and solid bitumens in sedimentary and metamorphic rocks: Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, v. 59, no. 10, p. 2341-2352.

Kelemen, S. R., and Fang, H. L., 2001, Maturity Trends in Raman Spectra from Kerogen and Coal: Energy & Fuels, v. 20, no. 15, p. 653-658.

Lahfid, A., Beyssac, O., Deville, E., Negro, F., Chopin, C., and Goffé, B., 2010, Evolution of the Raman spectrum of carbonaceous material in low-grade metasediments of the Glarus Alps (Switzerland): Terra Nova, v. 22, no. 5, p. 354-360.

Liu, D., Xiao, X., Tian, H., Min, Y., Zhou, Q., Cheng, P., and Shen, J., 2012, Sample maturation calculated using Raman spectroscopic parameters for solid organics: Methodology and geological applications: Chinese Science Bulletin, v. 58, no. 11, p. 1285-1298.