International Journal of Coal Geology 173 (2017) 1–8

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Maturity estimation of phytoclasts in strew mounts by micro-Raman spectroscopy

J.S. Schmidt [a,b,*], R. Hinrichs [a,c], C.V. Araujo [b]

[a] Programa de Pós-Graduação em Ciência dos Materiais, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Porto Alegre, RS, Brazil
[b] Division of Geochemistry, PETROBRAS R&D Center, Rua Horácio Macedo 950, Rio de Janeiro, RJ, Brazil
[c] Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form 28 January 2017
Accepted 3 February 2017
Available online 09 February 2017

Keywords:
Raman spectra
Vitrinite reflectance
Isolated kerogen
Source rock

ABSTRACT

In order to evaluate the potential for petroleum generation of a sedimentary rock, it is important to establish the thermal maturity of its organic matter. In rocks with low total organic carbon, the kerogen has to be isolated by acid maceration, and the traditional maturity assessment via vitrinite reflectance is sometimes hampered by the small amount of vitrinite exposed on polished plugs. This study presents an additional route of maturity estimation via Raman spectroscopy that is advantageous especially when only a small amount of vitrinite is available. Previous studies for maturation assessment based on Raman spectroscopy were mostly carried out on organic-rich rocks, prepared as whole-rock blocks. In this work we developed a maturity assessment based on Raman spectra obtained on isolated kerogen dispersed on strew mounts, as prepared for palynofacies analysis and spore coloration index, rendering additional information without further preparation. These strew mounts display a wider area for analysis per gram of isolated kerogen when compared to polished plugs, increasing the probability to find phytoclasts in scarce populations. The proposed method was developed regarding oil prospection, calibrating the Raman spectrometer with organic matter from rocks with vitrinite reflectance between 0.3 and 2.1%. A set of Raman parameters was combined using multilinear regression. Cross validation of the proposed regression showed that the spectral parameters of translucent phytoclasts resulted in a maturity estimate that correlated well with the vitrinite reflectance.

1. Introduction

Paleotemperature history is the main factor responsible for petroleum generation in potential source rocks containing sufficient and suitable organic matter (kerogen). Thermal maturity of the kerogen is a key information for various fields of research such as petroleum exploration, coalification, tectonics, stratigraphy, petrology, and lithospheric processes. The maturity assessment of sedimentary rocks is commonly carried out on its kerogen, using several techniques as vitrinite reflectance (VR), solid bitumen reflectance, spore coloration index (SCI), Rock-Eval pyrolysis, or spectral micro-fluorescence (Taylor et al., 1998; Tissot and Welte, 1984; Tyson, 1995). The application of multiple methods increases the reliability of the maturity estimate. However, in samples with scarce populations of vitrinite maceral and sporomorph groups, there might be insufficient individuals to perform quantitative petrologic analyses. When potential source rocks with low total organic carbon (TOC) need to have their maturity established based on vitrinite reflectance, acid maceration is performed to eliminate the minerals, leaving an isolated kerogen concentrate that can be prepared as polished resin plug (Mukhopadhyay et al., 1994) or as strew mount, dispersed on a glass slide (Taylor et al., 1998).

During thermal maturation, kerogen presents a progressive increase in aromaticity, depletion in hydrogen and oxygen, and loss of nitrogen and sulfur (Tissot and Welte, 1984). As a result of polymerization and aromatization reactions, the kerogen structure becomes more ordered, producing a well characterized color progression of the amorphous organic matter (AOM) and palynomorph groups (e.g. Tyson, 1995; Waples, 1981). Vitrinite reflectance is dependent upon refractive and absorption indices, both increase with the degree of aromatization, and are dependent on the concentration of delocalized electrons (Taylor et al., 1998; Waples, 1981).

The structural ordering of carbonaceous material (CM) can be assessed by Raman spectroscopy, as shown in many studies (Ammar et al., 2011, 2015; Chabalala et al., 2011; Ferrari and Robertson, 2000; Jehlicka et al., 2003; Keown et al., 2007; Kwiecinska et al., 2010; Reich and Thomsen, 2004; Sadezky et al., 2005; Thomsen and Reich, 2000; Zaida et al., 2007; Zeng and Wu, 2007). In highly ordered graphite the Raman spectra present a band around 1583 cm^{-1} that corresponds to symmetric vibrations E_{2g} of the carbon ring in the plane of the graphite sheet (G-band) (Reich and Thomsen, 2004; Tuinstra and Koenig, 1970).

---

[*] Corresponding author at: Division of Geochemistry, PETROBRAS R&D Center, Rua Horácio Macedo 950, Rio de Janeiro, RJ, Brazil.
E-mail address: jaquesschmidt@petrobras.com.br (J.S. Schmidt).

http://dx.doi.org/10.1016/j.coal.2017.02.003
0166-5162/

When the ordering of graphite crystallinity is lower, a second band around 1360 cm^{-1} appears, which is related to the A_{1g} breathing mode, allowed only at the broken borders of the graphene planes (Ferrari and Robertson, 2000; Tuinstra and Koenig, 1970). The position of this band, denominated D-band (disorder induced mode), systematically upshifts to higher wavenumbers with increasing laser frequency and its intensity increases with decreasing crystallinity (Ferrari, 2007; Guedes et al., 2010; Pimenta et al., 2007; Thomsen and Reich, 2000; Wang et al., 1990).

The Raman spectra of humic kerogen also present the G- and D-bands, and many attempts have been made to link the changes in spectral features to the thermal evolution of kerogen (Bonoldi et al., 2016; Du et al., 2014; Guedes et al., 2010; Hinrichs et al., 2014; Kelemen and Fang, 2001; Liu et al., 2013; Lünsdorf, 2016; Lünsdorf and Lünsdorf, 2016; Marques et al., 2009; Quirico et al., 2005; Spötl et al., 1998; Wilkins et al., 2014, 2015). Lasers of several wavelengths have been used in former Raman studies, however Lünsdorf (2016) recommended the use of low-wavelength lasers to obtain high signal-to-noise ratios, profiting from the enhancement in Raman intensity due to resonance (Rull, 2012). This occurs when the laser energy coincides with an electronic transition in the polycyclic aromatic hydrocarbon structures (PAHs) (Dabestani and Lvanov, 1999; Ruiz-Morales, 2002; Ruiz-Morales and Mullins, 2007), which are the constituents of basic structural units of humic kerogen (Bustin et al., 1995; Oberlin et al., 2012).

To extract the spectral parameters from the measured raw data, several fitting procedures have been proposed. In some studies, deconvolution of the Raman spectra was carried out with five to six spectral bands (e.g. Bonoldi et al., 2016; Chabalala et al., 2011; Morga et al., 2015; Sadezky et al., 2005; Ulyanova et al., 2014), while others employed nine to ten spectral bands (e.g. Keown et al., 2007; Li et al., 2006a,b; Mumm and İnan, 2016). Hinrichs et al. (2014) proposed a fitting with two Lorentzian bands and a linear background in the examined range between 0.2 and 4.7% VR. Recently, Lünsdorf and Lünsdorf (2016) developed a curve-fitting procedure with a variable number of pseudo-Voigt functions, without correlating them to the vibration modes that are convoluted in the G- and D-bands, differently from other authors that varied the intensities of specific modes in predetermined positions (e.g. Bonoldi et al., 2016; Chabalala et al., 2011; Keown et al., 2007; Li et al., 2006a,b; Morga et al., 2015; Sadezky et al., 2005; Ulyanova et al., 2014). The advantages of a multi-band fit to adjust only two prominent features are debatable (e.g. Hinrichs et al., 2014; Wilkins et al., 2014). The regressions proposed by Hinrichs et al. (2014) and Wilkins et al. (2014, 2015) show that simple two-band fitting procedures can estimate maturity based on Raman spectra obtained from vitrinite in coal blocks or dispersed kerogen plugs.

It has been shown that the acid treatment necessary to isolate the kerogen from the rock-forming minerals has no effect on the Raman spectra (McNeil et al., 2015; Kelemen and Fang, 2001; Roberts et al., 1995; Spötl et al., 1998). Considering that frequently only small amounts of rock are available for several analytical procedures, it is highly desirable to have a maturity estimation based on strew mounts, since this preparation consumes 5–10% of the kerogen mass needed for plugs and circumvents possible polishing artifacts in Raman spectra (Ammar and Rouzaud, 2012; Beyssac et al., 2003; Pasteris, 1989). When the sample preparation costs after the isolation process are compared between strew mounts and plugs, it becomes evident that the former are more profitable, demanding only glass slides, cover slips, resin, and a hot plate, while the latter require a resin mold/counter mold, a vacuum desiccator, grinding and polishing systems, specimen holders, and grinding disc and cloths. If an expedite analysis is needed, the strew mounts can be prepared by drying the isolated kerogen on top of a glass slide (e.g. Rantitsch et al., 2004; Spötl et al., 1998), however when samples have to be preserved for long term storage, cover slips will be attached with resin in order to pin the kerogen to the glass slide. Strew mounts can be used as well for palynofacies and SCI analyses, are easier to store and display a wider area for analysis when compared to plugs, thus increasing the chances of finding components of the phytoclast group in samples where they are scarce.

In this research we focused on the phytoclast group, extensively studied in reflected light (vitrinite and inertinite macerals), which renders well-defined Raman spectra (e.g. Bonoldi et al., 2016; Hinrichs et al., 2014; Liu et al., 2013; Lünsdorf, 2016; Wilkins et al., 2014, 2015).

The main objective of this paper is to evaluate Raman spectra from phytoclasts on strew mounts as a reliable estimate of the thermal maturity of potential source rocks.

2. Material and methods

The kerogen of twenty-eight sedimentary rock samples was analyzed. The total organic carbon (TOC) ranged from 0.3 to 12.2 wt.%, and their geological setting, stratigraphic age, maturation (VR), and palynofacies data are presented in Table 1. All samples were obtained either from drill cores or sidewall core sampling, or are collected in outcrops.

2.1. Phytoclasts categories

Phytoclasts located next to sporomorphs or AOM had their Raman spectra influenced by the strong fluorescence from the latter (Kelemen and Fang, 2001). We classified these spectra as outliers and rejected them. After outlier removal, the remaining spectra population derived from 577 translucent, 51 opaque and 110 degraded phytoclasts.

Phytoclasts are classified in three categories (Tyson, 1995), to analyse their Raman spectral parameters:

- Translucent phytoclasts - phytoclasts with defined biostructure (pitting) or with undefined biostructure but square, elongated, or lath-shaped (fibrous bundles and non-fibrous ‘solid’ with or without length-parallel strips or bands or fenestriform).
- Opaque phytoclasts - phytoclasts that are opaque up to the edge, non-fluorescent with or without biostructure.
- Degraded phytoclasts - phytoclasts without biostructure, with only residual trace of structure (pseudo-amorphous phytoclasts), and with irregular, degraded or embayed appearance.

2.2. Sample preparation

Kerogen was isolated using HCl and HF maceration without oxidation (Durand and Nicaise, 1980; Tyson, 1995). An aliquot of the isolated kerogen of each sample was embedded in a resin plug and polished, another aliquot was mounted with resin (Entellan®) on glass slides, sealed with cover slips, and cured at room temperature (Taylor et al., 1998). The cover slip is used to protect the kerogen from dust, weathering, and oxidation during long term storage. For Raman analysis, the laser was focused on the surface of the phytoclast below the cover slip, similarly to the procedure reported on successful Raman measurements of CM under transparent phases (e.g. Ammar et al., 2011). The Raman signal of the Entellan® resin did not hinder spectrum analysis (e.g. Yu and Sandercock, 2012).

2.3. Sample characterization

Vitrinite reflectance was determined according to ASTM D7708 (2014) on the isolated kerogen plugs in a reflected light microscope (Zeiss® Imager A2M) coupled with a photometer (J & M Analytische Mess- und Regeltechnik GmbH). The mean random reflectance (VR) was measured with light of 546 nm wavelength in immersion oil ($n_e = 1.518$ at 23 °C), and calibrated to reflectance standards (Klein & Beckers®). Maturity was established by vitrinite reflectance measurements on 26 samples. Two samples (samples: 19 and 28) lacked