International Journal of Coal Geology 121 (2014) 19–25

Contents lists available at ScienceDirect

International Journal of Coal Geology

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

The relationship between micro-Raman spectral parameters and reflectance of solid bitumen

Qin Zhou [a,b], Xianming Xiao [a,*], Lei Pan [a,b], Hui Tian [a]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form 25 October 2013
Accepted 29 October 2013
Available online 6 November 2013

Keywords:
Solid bitumen
Raman spectral parameter
Bitumen reflectance
Maturity indicator

ABSTRACT

Solid bitumen occurs widely in the Early Paleozoic and Precambrian strata and its reflectance is a generally-accepted indicator for thermal maturity. Even though some recent papers have been published concerning the Raman characteristics and spectral parameters of solid bitumen, a systematic investigation on the relationship between the Raman spectral parameters and thermal maturity of solid bitumen is still lacking. In this study, a low maturity solid bitumen sample was pyrolysed under laboratory-controlled conditions to obtain a suite of artificial bitumen samples with different maturities (BRo = 1.1–4.81%), which are used to investigate the relationships between Raman spectral parameters and reflectance of solid bitumen. The Raman spectral parameters of the artificial bitumens, including band position (W_D and W_G), band separation (RBS), full width at half maximum (FWHM-D and FWHM-G), and band intensity ratio (I_D/I_G) are all related to the bitumen reflectance, but with considerably different correlations, constrained apparently by thermal maturity. Linear regressions were performed between these parameters and bitumen reflectance, and two parameters with higher correlation were selected. They are RBS (within 1.5–3.5% of BRo) and I_D/I_G (within 3.0–5.0% of BRo), with a correlation coefficient as high as 0.97. It is believed that the two Raman spectral parameters of solid bitumen will be of significant practical use for the maturity assessment of the Early Paleozoic and Precambrian strata when standard measurement and curve fitting procedures are utilized.

1. Introduction

In recent decades, numerous papers have reported that the Raman spectral characteristics and related parameters of geological solid organic matter, including coals, carboniferous fossils and carbonaceous materials, can be used as indicators for thermal maturity (i.e., Beyssac et al., 2002; Ferrari and Robertson, 2000; Guedes et al., 2010; Kelemen and Fang, 2001; Kwiecinska et al., 2010; Muirhead et al., 2012; Quirico et al., 2005, 2009; Rahl et al., 2005; Roberts et al., 1995; Schopf et al., 2005; Schopf and Kudryavtsev, 2009; Zeng and Wu, 2007). Detailed studies have focused on coals with different rank (Green et al., 1983; Guedes et al., 2010; Kelemen and Fang, 2001; Marques et al., 2009; Quirico et al., 2005; Sonibare et al., 2010). The first-order characteristic bands of the Raman spectrum of carbon in coals have been found to generally occur at approximately 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band) (Guedes et al., 2010; Kwiecinska et al., 2010; Wopenka and Pasteris, 1993). The D band is also called D1 band (Marques et al., 2009; Wopenka and Pasteris, 1993) or A band (Kelemen and Fang, 2001), and it originates in vibrations of the disordered structure of carbonaceous material (Beyssac et al., 2002, 2003). The G band is assigned to vibrations of the ordered (graphitic) structure (Beyssac et al., 2002, 2003). With increasing thermal maturity, these two bands show regular changes in their position, FWHM (full width at half maximum) and intensity, which have been shown to be clearly correlated with maturity (Guedes et al., 2010; Kelemen and Fang, 2001; Kostova et al., 2012; Quirico et al., 2005).

Solid bitumen is a type of organic matter extensively occurring in petroleum-bearing basins and also in Precambrian shale-rich strata (Jacob, 1989; Lomando, 1992; Schoenherr et al., 2007). Available data indicate that despite the fact that solid bitumen is different from coal in their precursors, their Raman spectral characteristics and related changes in the process of thermal maturation are very similar (Court et al., 2007; Jehlicka et al., 2003). However, as yet few studies have been focused on the Raman spectral characteristics of solid bitumen, a systematic study is lacking on changes to the Raman spectral parameters in the process of thermal maturation. In the present study, a solid bitumen sample with a low maturity was pyrolysed to obtain a suite of artificial bitumen samples with different maturities, then their Raman spectra were investigated, and the changes of the parameters with the maturity were revealed. Combined with data from natural samples, the use of Raman spectral parameters of natural and synthetic bitumen as maturity indicators was explored.

* Corresponding author. Tel.: +86 20 85290176.
E-mail address: xmxiao@gig.ac.cn (X. Xiao).

0166-5162/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.coal.2013.10.013

2. Sample and experiment

The original solid bitumen sample was collected from a bitumen vein in the Permian strata of the Changjianggou area, western Sichuan Basin of southwestern China. As the outcrop resulted from the cutting of a new road, the sample is fresh and has not been or very little subjected to weathering and oxidation. The bitumen is of low maturity, with a bitumen reflectance (BRo) of 0.43%. Since the Permian organic rich mudstone in this area is in a lower mature stage, it is believed that the bitumen was derived from the Early Paleozoic marine shales, which are widely distributed over the whole Sichuan Basin (Zhou et al., 2013). The bitumen was powdered to 80-mesh, and heated in a vacuumed autoclave to 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C and 750 °C, respectively, remaining for 24 h at each preset temperature point. In this way artificial bitumen samples with different maturities were obtained. These samples were prepared as polished blocks for bitumen reflectance measurements and Raman spectral analyses.

Bitumen reflectance was measured using a 3Y-Leica DMR XP microphotometer, according to the usual method of coal petrology as described by Dai et al. (2012). Depending on the maturity of the bitumen sample to be measured, a matching standard sample was selected for use from the three available standard samples of YAG-08-57 ($R_o = 0.904\%$), NR1149 ($R_o = 1.24\%$) and cubic zirconia ($R_o = 3.11\%$). An oil immersion objective 50/0.85 was used. For each sample, 50 individual bitumen particles were measured and their mean value was taken as the bitumen reflectance.

A HORIBA-JY LabRAM spectrometer equipped with a He–Ne laser (source power 30 mV) was applied for Raman spectral analysis of the

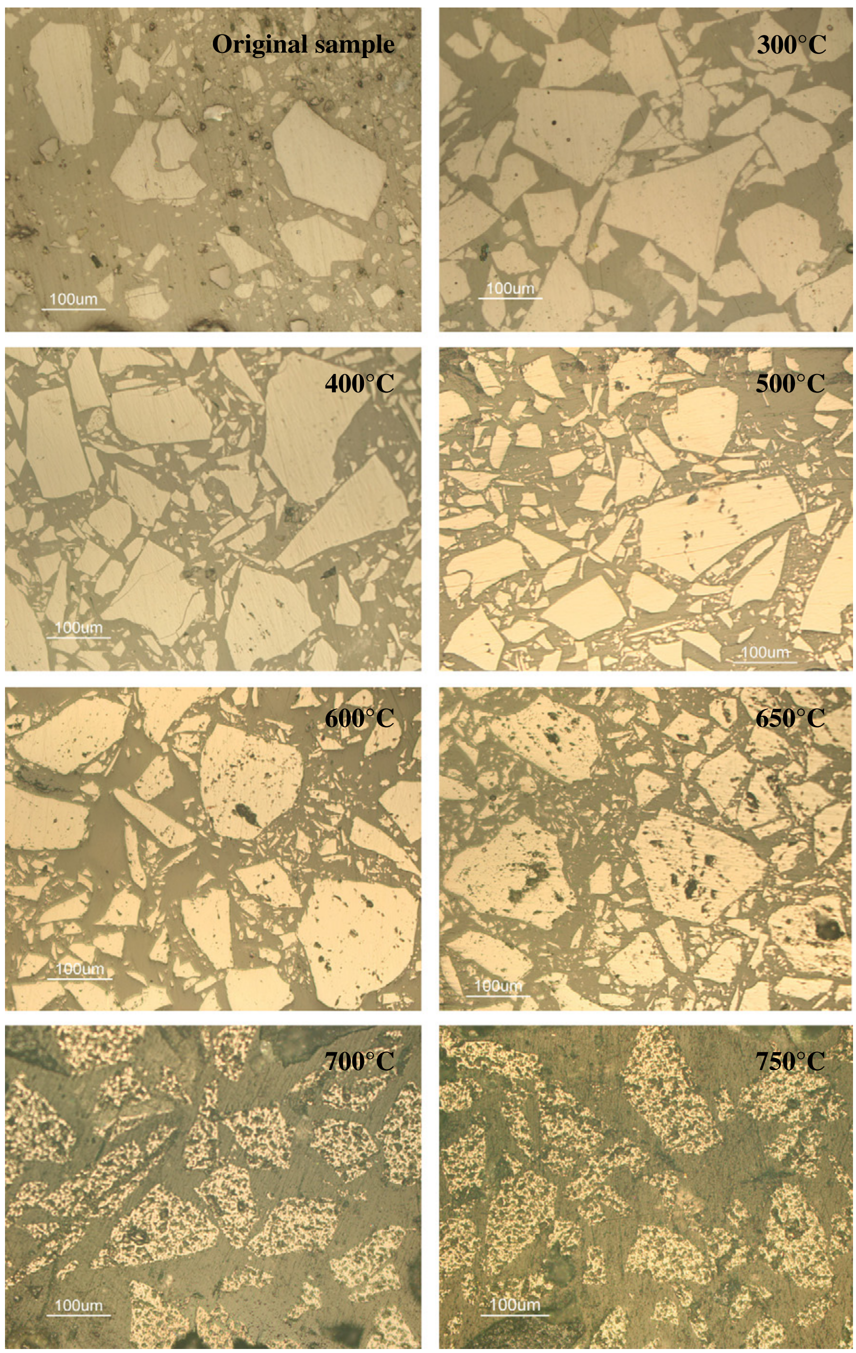

Fig. 1. The solid bitumen at different heated temperatures. Reflect light and oil immersion of optical microscope.