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Raman microspectroscopy of funginite from the Upper Silesian Coal Basin (Poland)

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ABSTRACT

Raman spectral characteristics of funginite were compared with that of fusinite and semifusinite from the same coals. Inertinite concentrates prepared from four samples of coking coals from the Upper Silesian Coal Basin of Poland were examined.
The examination reveals that funginite spectral characteristics have common features with that of fusinite or, to smaller extent, to semifusinite. This suggests that the high reflectance of funginite might result from charring during wildfire activity.

1. Introduction

Funginite is a relatively rare coal maceral of the inertinite group, and its chemistry is weakly recognized. It consists of mainly high reflecting single or multi-celled fungal spores, sclerotia, hyphae and mycelia, and other fungal remains. Its reflectance may vary even within the same seam. Funginite is pale gray to white, sometimes yellowish white, and consists mainly of chitin (ICCP, 2001; Lyons, 2000). Its highly aromatic nature and relatively low degree of alkyl substitution in aromatic rings compared to vitrinite were confirmed by micro-FTIR measurements (Chen et al., 2013; Mastalerz and Bustin, 1993). Based on experimental work, Scott and Glasspool (2007) suggested that high reflectance of funginite might result from charring by wildfire. Variations in the temperature of charring led to varied reflectance of the maceral. In coal processing funginite is a non-reactive maceral.

Funginite was found in coals from all major coal-forming periods (O'Keefe et al., 2013), being more frequent in Cenozoic than in Paleozoic coals (Lyons, 2000). It is frequently found in association with vitrinite of slightly elevated reflectance or with degraded vitrinite (Hower et al., 2009), but also with resinite, cutinite, and suberinite (Hower et al., 2010, 2011a; Valentim et al., 2011). The presence of fungal material in coal and its association with huminite/vitrinite macerals provides important information about the depositional conditions and distinguishes coal dominated by oxic processes from coal dominated by anoxic processes (O'Keefe and Hower, 2011). The role of fungus in the formation of coal macerals was broadly discussed by Guo and Bustin (1998), Hower et al. (2009, 2011b), and O'Keefe et al. (2013), among others. Fungi colonize charcoal, as concluded from the lower reflectance of funginite in comparison with the surrounding fusinite and semifusinite (Hower et al., 2013a). Different forms of funginite in Late Cretaceous anthracites from New Mexico were presented by Hower et al. (2013b).

Though widely used in examination of carbonaceous materials, Raman spectroscopy recently has been found a useful and promising method of investigating the microstructure of individual coal macerals (Guedes et al., 2010, 2012; Morga, 2011a, 2011b). It is applied to evaluate the structural order, providing information both about the ordered ("crystalline") and amorphous phase. It has been used to determine the in-plane size (L_a) of polyaromatic layers, forming the Basic Structural Units (BSU).

The purpose of this study is to obtain, for the first time, Raman spectral characteristics of funginite, and to compare it with that of fusinite and semifusinite from the same coals.

2. Method

Examination was performed on funginite (Fig. 1) in inertinite concentrates (I content: 80–84%) prepared from four samples of Pennsylvanian coking coals from the Upper Silesian Coal Basin of Poland. Selected properties of the parent coals are summarized in Table 1. Obtaining the concentrates was described by Morga (2011a). Micro-Raman measurements were carried out on polished grain mounts, prepared from the concentrates, with the use of a Renishaw inVia spectrometer (excitation line $\lambda_0 = 514$ nm) on 6–10 funginite grains in each mount, in a spectral range of 1000–1800 cm^{-1}, with a spectral resolution of 2 cm^{-1}. The spectrometer was calibrated by an internal silicon standard (peak position—520 cm^{-1}). During each

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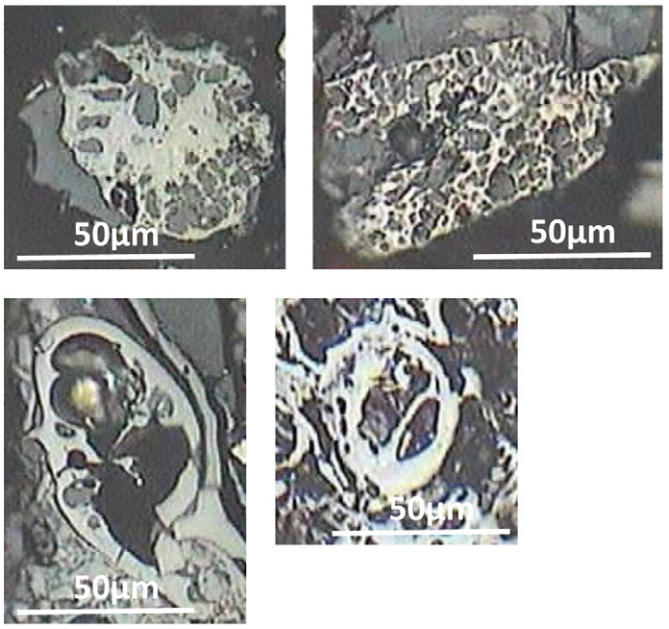

Fig. 1. Funginite in the examined coals.

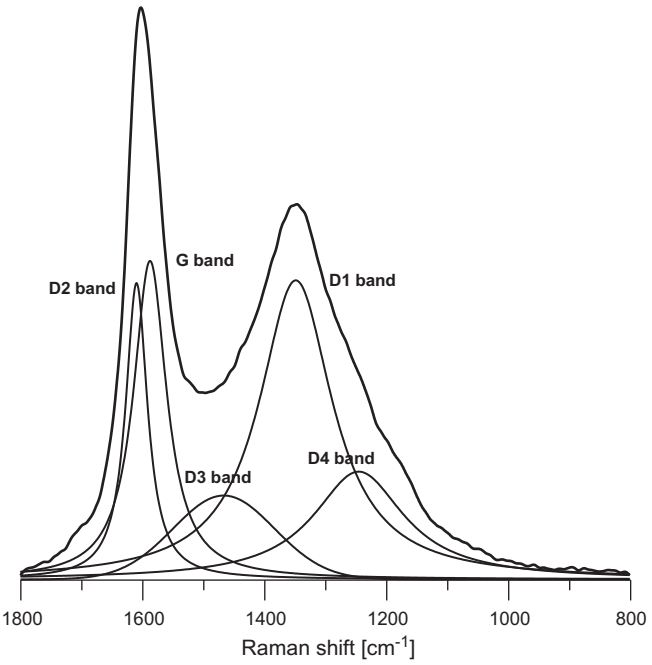

Fig. 2. Deconvolution of a micro-Raman spectrum of funginite.

measurement four acquisitions of 10 s were co-added. The measurement area was 2 × 2 μm. The spectra were deconvoluted with the use of GRAMS 32 software, following the Sadezky et al. (2005) method, which was previously used in studies of semifusinite and fusinite (Morga, 2011a, 2011b). Four Lorentzian (D2, G, D1, and D4 band) and one Gaussian (D3 band) lines were used (Fig. 2). Goodness of fit was checked by χ^2 test. Based on that, the position of the Raman bands and their width (FWHM) were found. The relative band intensities: A_{D2}/A_{ALL}, A_G/A_{ALL}, A_{D3}/A_{ALL}, A_{D1}/A_{ALL}, and A_{D4}/A_{ALL} (all calculated as the area ratios) as well as I_{D1}/I_G (calculated as the band height ratio) were determined. The spectral ratio RA1 (Lahfid et al., 2010):

$$RA1 = \frac{(A_{D1} + A_{D4})}{(A_{D2} + A_G + A_{D3} + A_{D1} + A_{D4})},$$

which correlates with the maximum metamorphic temperature was also calculated.

The attributions and interpretations of the Raman bands as well as the spectral ratios have been described by Tuinstra and Koenig (1970), Nemanich and Solin (1979), Rouzaud et al. (1983), Beny-Bassez and Rouzaud (1985), Jawhari et al. (1995), Schwan et al. (1996), Ferrari and Robertson (2000), Beyssac et al. (2003), Reich and Thomsen (2004), Sadezky et al. (2005), Zickler et al. (2006), and others. Their relevance in the study of coal macerals was also discussed in detail by Morga (2011a, 2011b). A review of Raman spectroscopy studies of coal was presented by Potgieter-Vermaak et al. (2011).

The results of funginite examination were compared with those of fusinite and semifusinite of the same mounts (Morga, 2011b) by the statistical robust Shapiro–Wilk test to assess normality of distribution. The Fisher–Snedecor test was applied to check the equality of variances and the Student's *t*-test was performed to compare the results with a significance level of $\alpha = 0.05$.

3. Results and discussion

The results of micro-Raman spectroscopy (Fig. 3) examination of funginite are reported in Table 2. When samples 1–3 are concerned, they vary within very narrow limits. These, obtained for sample 4, diverge from the rest. Despite these differences, the results are typical for poorly organized carbonaceous material ("crystallinity" level 1), which is indicated by the occurrence of the D3 and D4 bands (Fig. 2), and overlapping D2 and G bands (Beyssac et al., 2003; Lünsdorf et al., 2014). The G and D1 bands are relatively broad, and the I_{D1}/I_G ratio falls into the range typical for semifusinite and fusinite (Guedes et al., 2010, 2012; Morga, 2011a, 2011b). The G and D1 bands are about 10 cm^{-1} broader than detected in anthracite C spectra, and the $I_{D1}/_G$ ratio is about half of that, at the same method of deconvolution (Marques et al., 2009).

The fitting results of the Raman spectra of fusinite and semifusinite from the same samples are shown in Table 2. They are derived from the published study (Morga, 2011b), in which they were described in detail. Micro-Raman spectra of funginite, fusinite and semifusinite were set together for comparison in Fig. 3.

The Shapiro–Wilk test demonstrates that all sets of the results obtained for the Raman parameters determined in this study have normal or close to normal distribution, although the small number of data influences the validity of the test. The Fisher–Snedecor test shows that variances are equal in 120 from 128 analyzed pairs (the *p* value >0.05).

Table 1
Selected properties of the parent coals used in the study.

Sample	Seam	Age	R_r %	s_r %	V^{daf} %	RI	Vitrinite %	Liptinite %	Inertinite %	MM %
1	358/1	Westphalian A	0.92	0.05	33.81	71	73	6	19	2
2	703	Namurian A	0.94	0.06	33.70	75	70	8	20	2
3	358/1	Westphalian A	0.97	0.05	30.83	80	65	9	24	2
4	403/1	Westphalian A	1.11	0.06	26.25	64	66	3	29	2

Explanations: the samples were enumerated according to the increasing vitrinite reflectance value (R_r), s_r—standard deviation of R_r value, V^{daf}—volatile matter content, RI—Roga Index, MM—mineral matter content.