About the Microstructure of the Graptolite Periderm - Examples from the Holy Cross Mountains (Poland)

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Abstract. Graptolite reflectance is one of the main parameters for assessing thermal maturity of pre-Devonian rocks in which vitrinite does not occur. However, microstructure of the graptolite periderm has been known only recently, and still little is known about low-reflectance graptolites. The purpose of the work was to determine microstructural features of the graptolite periderm in the oil window shales and compare them to those known from the previous studies, in which more matured organic matter was investigated. Four samples were collected in the Holy Cross Mountains (Central Poland), in two localities (Bardo Stawy and Prągowiec ravine). Reflectance (R_r) measurements as well as micro-Raman analysis were carried out on the sections parallel to the bedding. Micro-Raman analysis was performed on unpolished surfaces to exclude influence of polishing on microstructure. The obtained spectra were curve-fitted using four Lorentzian (G, D1, D2 and D4 band) and one (D3 band) Gaussian lines. Graptolites (R_r=0.70–0.77%; Vitrinite Reflectance Equivalent VRE=0.67–0.72%) occur in the Silurian dark grey clay shales of the Llandovery (Bardo Stawy) and Wenlock - Lower Ludlow (the Prągowiec ravine) age. Graptolite periderm represents poorly organized carbonaceous material, which is inferred from the occurrence of the D3 and D4 bands, and overlapping D2 and G bands. Microstructure does not vary significantly between the samples from the two considered localities (the exception being the D1 band FWHM), which corresponds to the narrow range of graptolite reflectance. Compared to the Raman spectra obtained from graptolites with higher reflectance, the G peak is significantly moved to the lower and the D1 peak to the higher wavenumbers. The FWHM of the G band is higher, while the I_D1/I_G ratio usually smaller. Taking into account the results from the previous study, it can be concluded that in the reflectance range of 0.7–1.8% the G band position first moves to the higher, and at R_r≥1.2% to the lower wavenumbers, while the D1 peak gradually shifts to the lower wavenumbers. The G band FWHM decreases with increasing graptolite reflectance, which reflects improvement in structural ordering, while the I_D1/I_G ratio starts to increase at R_r≈1.5%, indicating the growth of the coherent domains within the graptolite periderm.

1. Introduction

Graptolite reflectance (R_r) is one of the main parameters for assessing thermal maturity of pre-Devonian rocks in which vitrinite does not occur [1-7]. It is widely used especially in recognition of the unconventional hydrocarbon deposits, which are frequently found in the Cambrian–Silurian organic-rich shales [7-10]. However, microstructure of the graptolite periderm has been known only
recently [11-13]. Graptolite reflectance (R_r) of the samples examined in these studies [11-13] usually exceeded 0.8-1%, and still little is known about microstructure of low reflectance graptolites. The purpose of this work is to determine microstructural features of the graptolite periderm in the oil window shales (R_r=0.5-1.0%) and compare them to those known from the previous studies.

2. Methods
Four samples were collected from the outcrops of the Silurian rocks in the Holy Cross Mountains (Central Poland). They come from two localities: Bardo Stawy and Prągowiec ravine, situated within a geological structure named the Bardo Syncline - in its northern and southern limb, respectively, ca. 35 km SEE of the town of Kielce (figure 1).

![Figure 1. Geological sketch of the Holy Cross Mountains with location of the sampling points (after Kremer [14], changed).](image)

Both are very well known and described in literature, due to their geological significance. The part of the Silurian section exhibited in Bardo Stawy represents Llandovery, while that in the Prągowiec ravine belongs to Wenlock - Lower Ludlow [15-21]. Two samples were taken in each locality, in the uppermost and lowermost points of the Silurian rock profiles, from a solid rock to minimize the effect of weathering. Silurian rocks in Bardo Stawy are mainly graptolitic dark grey shales with intercalations of radiolarian shales, while those at the Prągowiec ravine are mainly calcareous clay shales and siltstones, passing into graptolite-rich dark grey clay shales. Description of the geological setting and graptolite assemblages of the Bardo Stawy outcrop one can find in [16-18], whereas detailed characterization of the Prągowiec ravine geology and paleontology was given by Tomczykowa [15] as well as Modliński and Szymański [16].

Reflectance (R_r) was measured on polished sections parallel to the bedding by the use of a Zeiss Axioskop microscope in immersion oil (n_o=1.518 at 23°C) in 32 to 54 spots per sample.

Micro-Raman measurements were performed on visible graptolite remains (figure 2). They were carried out on the unpolished surface (to exclude influence of polishing on microstructure), parallel to the bedding on 16-25 randomly chosen points per sample (1-4 points per graptolite particle, depending on its size). A Renishaw inVia spectrometer (excitation line \( \lambda_e=514 \) nm) calibrated against a silicon standard was used. The spectra were collected in the range of 800–2000 cm\(^{-1}\), with a spectral resolution of 2 cm\(^{-1}\). For each measurement ten acquisitions of 10 s were accumulated. After the
baseline correction curve-fitting was performed in the range of 1000–1800 cm$^{-1}$ by the use of GRAMS32 software, following the method of Sadezky et al. [22]. Four Lorentzian curves (G, D1, D2 and D4 band) and one Gaussian (D3 band) curve were used. The goodness of fit was checked by the χ$^2$ test. The position of the Raman bands and their FWHMs were found, and the $I_{D1}/I_G$ and $I_{D2}/I_G$ ratios were calculated from the D1 and G band intensities. The distance between the G and D1 peak ($\Delta G_{-D1}$) was determined as well.

![Figure 2. Graptolite specimens in samples from the Prągowiec ravine (P1) and Bardo Stawy (B2)](image)

3. Results and discussions
Graptolite reflectance ($R_r$) ranges between 0.70% and 0.77%, increasing with the stratigraphic position. The Vitrinite Reflectance Equivalent (VRE) value calculated from $R_r$ with the use of the Petersen's formula [7] varies from 0.67% to 0.72% (table 1). Representative Raman spectra of the graptolite periderm obtained from samples P1 and B2 are given in figure 3, and an example of the curve-fitted Raman spectrum is shown in figure 4. The G band at ~1580 cm$^{-1}$ is assigned to the stretching vibration mode with $E_{2g}$ symmetry in the graphite aromatic layers [23, 24]. The D2 band (~1610 cm$^{-1}$) being a shoulder on the G band corresponds to a disordered graphitic lattice vibration mode ($E_{2g}$ symmetry) [25, 26].

![Figure 3. Representative Raman spectra of the graptolite periderm (samples P1 and B2)](image)
Figure 4. A curve fitted spectrum of the graptolite periderm (sample B2).

The D3 band (~1460 cm⁻¹) originates from interstitial defects outside the aromatic layers [27, 28]. It is related to the occurrence of organic molecules, fragments or functional groups forming "amorphous" carbon phase [22, 26, 29]. The D1 band (~1365 cm⁻¹) is attributed to graphitic lattice vibration mode A₁g, and assigned to in-plane defects between the Basic Structural Units (BSUs) or to the occurrence of heteroatoms [23, 25, 27, 28]. The D4 band (~1280 cm⁻¹) corresponds to mixed sp²-sp³ or sp³-rich carbon structures such as alkyl-aryl C-C structures [22, 30].

The selected spectral parameters are given in Table 1. The graptolite periderm spectra acquired in this study are typical for poorly organized carbonaceous material [30, 31], which is inferred from the occurrence of the D3 and D4 bands, and overlapping D2 and G bands (figure 4). The G band position (ω G) is about 1578 cm⁻¹, and the FWHM rises with increasing reflectance (Rₐ) from 69.71 cm⁻¹ to 73.68 cm⁻¹. The D1 band is centered at 1366-1368 cm⁻¹, while its FWHM differs significantly between the two locations, being much smaller (92-95 cm⁻¹) in the spectra obtained from the Prągowiec ravine samples (P1 and P2) than those from Bardo Stawy (B1 and B2; 130-132 cm⁻¹).

Table 1. Mean reflectance (Rₐ), Vitrinite Reflectance Equivalent (VRE) and the selected Raman spectral parameters of the graptolite periderm.

|     | Rₐ [%] | VRE [%] | ω G [cm⁻¹] | FWHM G [cm⁻¹] | ω D1 [cm⁻¹] | FWHM D1 [cm⁻¹] | I_D1/I_G | I_D2/I_G |
|-----|--------|---------|------------|---------------|-------------|----------------|----------|---------|
| P1  | 0.70   | 0.67    | 1577.38    | 69.71         | 1366.20     | 92.04          | 0.89     | 0.92    |
|     | 0.07   | 1.60    | 2.48       | 1.82          | 4.65        | 0.05           | 0.15     |         |
| P2  | 0.74   | 0.70    | 1577.51    | 73.48         | 1366.05     | 94.63          | 0.92     | 0.90    |
|     | 0.08   | 1.25    | 5.80       | 0.84          | 9.81        | 0.05           | 0.12     |         |
| B1  | 0.74   | 0.70    | 1577.90    | 70.30         | 1368.35     | 130.40         | 0.91     | 0.84    |
|     | 0.07   | 0.95    | 2.74       | 0.68          | 4.41        | 0.06           | 0.11     |         |
| B2  | 0.77   | 0.72    | 1578.11    | 73.68         | 1367.11     | 131.59         | 0.92     | 0.80    |
|     | 0.07   | 1.36    | 5.31       | 1.35          | 4.84        | 0.06           | 0.12     |         |

Explanation: in italics the standard deviation values are given.
The $I_{D2}/I_G$ ratio varies from 0.89 to 0.92, while the $I_{D3}/I_G$ ratio decreases from 0.92 to 0.80. The distance between the G and D1 peak ($\Delta G_{D1}$) is about 211 cm$^{-1}$. Thus, except of the D1 band FWHM, the spectral parameters determined for the graptolite periderm from both locations are very consistent which reflects narrow range of graptolite periderm revealed in this study ($R_e=0.70-0.77\%$). The differences observed between the samples usually fall within the standard deviation values.

In comparison to the earlier research performed by Morga and Pawlyta [13] on graptolites of higher reflectance ($R_e=1.30-1.83\%$), the G peak is significantly moved to the lower wavenumbers and the D1 peak to the higher wavenumbers (figures 5a and 5b). This also means that the G-D distance is also smaller. The FWHM of the G band is higher (figure 6a), while the $I_{D1}/I_G$ and $I_{D2}/I_G$ ratio are usually smaller (figure 6b and 7). It is observed that within the graptolite reflectance range ($R_e=0.70-1.83\%$) analysed in this and previous study [13] the G peak position first moves to the higher, and then (starting at $R_e=1.2\%$) to the lower wavenumbers with the increasing graptolite reflectance (figure 5a). This is accompanied by the gradual decrease in the G band FWHM (figure 6a), which indicates improvement in structural ordering, as previously found for coals, coal macerals, kerogen and chitinozoans [32-39]. The D1 band moves to the lower wavenumbers (figure 5b). The $I_{D1}/I_G$ ratio increases with reflectance when $R_e$ exceeds $R_e\approx1.5\%$, which reflects increasing diameter of the coherent domains ($L_d$), if $L_d<2$ nm [40]. Similar trends were also found for coals and their macerals [35, 37, 39]. When reflectance is lower than 1.5%, the value of the $I_{D1}/I_G$ ratio seems to be stable, as the differences between the samples vary within the standard deviation value (figure 6b). To confirm this, further examination is needed on graptolites with reflectance varying between 0.9% and 1.2%. The $I_{D2}/I_G$ ratio follows the trend observed for the $I_{D1}/I_G$ ratio (figure 7).

![Figure 5](image_url)

**Figure 5.** Relationship between the G (a) and D1 (b) band position and the mean reflectance of the graptolite periderm ($R_e$) (data referring to $R_e=1.30-1.83\%$ after Morga and Pawlyta [13]).

4. Conclusions

Graptolite periderm in the Silurian shales collected in the Holy Cross Mountains of Poland ($R_e=0.70-0.77\%$; VRE=0.67-0.72\%) represents poorly organized carbonaceous material. Microstructure does not vary significantly between the samples from the two considered localities (the Prągowiec ravine and Bardo Stawy), which corresponds to the narrow range of graptolite reflectance. Compared to the Raman spectra obtained by Morga and Pawlyta [13] from graptolites with higher reflectance, the G peak is significantly moved to the lower and the D1 peak to the higher wavenumbers. The FWHM of
the G band is higher, while the I_D1/I_G ratio usually smaller. In the graptolite reflectance range of ≈0.7-1.8% the G peak position first moves to the higher, and at R_r≥1.2% to the lower wavenumbers, while the D1 peak gradually shifts to the lower wavenumbers. The G band FWHM decreases with increasing graptolite reflectance, which reflects improvement in structural ordering, while the I_D1/I_G ratio starts to increase at R_r≈1.5%, indicating the growth of the coherent domains within the graptolite periderm.

**Figure 6.** Relationship between the G band FWHM (a) and the I_D1/I_G ratio (b) and the mean reflectance of the graptolite periderm (R_r) (data referring to R_r=1.30-1.83% after Morga and Pawlyta [13]).

**Figure 7.** Relationship between the I_D2/I_G ratio and the mean reflectance of the graptolite periderm (R_r) (data referring to R_r=1.30-1.83% after Morga and Pawlyta [13]).
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