Chemical properties of the graptolite periderm from the Holy Cross Mountains (Central Poland)

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Graptolite periderm in the Silurian shales from the Holy Cross Mountains of the Central Poland was examined by means of reflectance measurements and micro-FTIR spectroscopy. Mean graptolite reflectance (R<sub>r</sub>) reaches 0.70–0.77%, and the vitrinite reflectance equivalent (VRE) is 0.67–0.72%. Graptolite periderm is composed predominantly of aromatic groups and rings with lesser amount of aliphatic and carbonyl/carboxyl groups. Chemical composition 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. However, the samples from the Prągowiec ravine are characterized by higher hydrocarbon potential. It is found that many similarities occur in the chemical structure of the graptolite periderm and vitrinite within the reflectance range of R<sub>r</sub> ≈ 0.7–1.5%. With increasing reflectance the length of the aliphatic chains (as inferred from the CH<sub>2</sub>/CH<sub>3</sub> ratio) in the graptolite periderm decreases, and the relative content of the aromatic groups [as indicated by the CH<sub>ar</sub>/(CH<sub>2</sub> + CH<sub>3</sub>) ratio] begins to increase at R<sub>r</sub> ≈ 1.6%. This is accompanied by growth of the coherent domains and improvement in the structural order.

Key words: graptolites, chemical structure, infrared spectroscopy, Holy Cross Mountains.

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Graptolite reflectance (R<sub>r</sub>) is one of the most important indices of thermal maturity of pre-Upper Silurian rocks, in which vitrinite does not appear (e.g. Goodarzi 1984, 1985; Goodarzi & Norford 1985, 1987, 1989; Link et al. 1990; Cole 1994; Petersen et al. 2013; Luo et al. 2020). It is commonly employed in the recognition of the unconventional hydrocarbon deposits, which frequently occur in the Cambrian–Silurian organic-rich shales (e.g. Więcek et al. 2010, Schovsbo et al. 2011, Jarvie 2012, Petersen et al. 2013). However, the chemical structure of the graptolite periderm (or fusellum sensu Maletz et al. 2014) is still not fully resolved. Periderm of living graptolites was composed of collagen-like fibrils but their corresponding fossil counterparts lack protein and they underwent the coalification process similar to plant remains (Towe & Urbanek 1972, Link et al. 1990). Deep insight into graptolite paleobiology was given by Maletz et al. (2017). Research on the chemistry of the fossilized graptolite periderm (Bustin et al. 1989; Suchý et al. 2002, 2004; Caricchi et al. 2016; Morgá & Kamińska 2018; Luo et al. 2020) were mostly performed on graptolite specimens, reflectance (R<sub>r</sub>) of which exceeded values of 0.8–1%, and still little is known about chemistry of low reflectance graptolites. The purpose of this investigation is to determine, for the first time, chemical properties of the graptolite periders from the Holy Cross Mountains (R<sub>r</sub> < 0.8%), and compare them to those known from the previous studies. The research is a continuation of the microstructural examination performed on the same samples (Morgá 2019).

Geological setting

Four samples were collected from the outcrops of the Silurian rocks in Bardo Stawy and the Prągowiec ravine in the Holy Cross Mountains (HCM), Central Poland. Both localities are situated within the Bardo Syncline – in its southern and northern limb, respectively, ca 35 km SEE of the town of Kielce (Fig. 1). Due to outstanding geological and paleontological importance, they are very well-described (Tomeczykowa 1958, Modliński & Szymański 2001, Masiak et al. 2003, Trela & Salwa 2007, Smolarek et al. 2014, Mustafa et al. 2015, Schito et al. 2017). The Silurian rocks exhibited in Bardo Stawy belong to Llandovery series, while those in the Prągowiec ravine to Wenlock–Lower Ludlow. Two samples were taken in each locality, in the uppermost and lowermost parts of the Silurian strata, from a fresh rock to minimize the effects 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. They contain macroscopically visible graptolite remains. Geological setting and graptolite assemblages of Bardo Stawy were given in detail by Modliński & Szymański (2001), Masiak et al. (2003), and Trela & Salwa (2007), whereas broad description of the Prągowiec ravine geology and palaeontology one can find in Tomczykowa (1958) as well as Modliński & Szymański (2001).

**Methods**

Morphological and optical features of graptolites under reflected light were described in detail by Teichmüller (1978), Goodarzi (1984, 1985), Goodarzi & Norford (1985, 1987), and Link et al. (1990), among others.

Graptolite reflectance 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 $23 \, ^\circ C$) in 32 to 54 randomly chosen spots per sample. Only the well-preserved, homogenous areas were chosen. All other aspects of the measuring procedure followed the ISO 7404–5 (2009) standard. Based on that mean values ($R_\text{r}$) and standard deviations were calculated. All reflectance measurements were performed on non-granular graptolites (sensu Goodarzi 1984) to avoid possible scattering of the light beam on a granular tissue (Fig. 2).

Micro-FTIR analysis was carried out in reflectance mode, with the use of a Bio-Rad FTS-6000 spectrometer, equipped in the Bio-Rad UMA 500 microscope. Number of measurement points per sample varied between 10 and 12. Spectra were obtained within the range of $6000–750 \, \text{cm}^{-1}$, at a resolution of $4 \, \text{cm}^{-1}$. Interferograms were collected by co-adding of 512 scans, using a gold plate as a background. Fourier and Kramers-Krönig transformations of spectra were performed. Absorption bands were identified based on the works of Painter et al. (1981), Wang & Griffiths (1985), Sobkowiak & Painter (1992), Guo et al. (1996), Ibarra et al. (1996) as well as...
Table 1. Mean reflectance (Rr), Vitrinite Reflectance Equivalent (VRE) and the selected micro-FTIR spectral parameters of the graptolite periderm.

| Sample | Rr [%] | VRE [%] | CHar/(CH2 + CH3) | CH2/CH3 | C=O/C=CH | 'A1' | 'A2' | 'C1' | 'C2' |
|--------|--------|---------|-----------------|----------|-----------|------|------|------|------|
| P1     | 0.70   | 0.67    | 0.050           | 2.08     | 0.44      | 0.79 | 0.60 | 0.22 | 0.31 |
| n = 42 | 0.07   | 0.011   | 0.28            | 0.21     | 0.09      | 0.10 | 0.11 | 0.10 |
| P2     | 0.74   | 0.70    | 0.058           | 1.97     | 0.41      | 0.76 | 0.57 | 0.29 | 0.29 |
| n = 54 | 0.08   | 0.012   | 0.18            | 0.11     | 0.09      | 0.08 | 0.12 | 0.06 |
| B1     | 0.74   | 0.70    | 0.055           | 2.06     | 0.48      | 0.46 | 0.28 | 0.29 | 0.33 |
| n = 45 | 0.07   | 0.017   | 0.31            | 0.15     | 0.15      | 0.13 | 0.11 | 0.06 |
| B2     | 0.77   | 0.72    | 0.054           | 1.62     | 0.51      | 0.49 | 0.29 | 0.37 | 0.32 |
| n = 32 | 0.07   | 0.021   | 0.13            | 0.12     | 0.18      | 0.09 | 0.15 | 0.07 |

Abbreviations: Rr – mean reflectance of the graptolite periderm; VRE – Vitrinite Reflectance Equivalent; CHar/(CH2 + CH3) – relative content of the aromatic (3000–3100 cm⁻¹) and aliphatic (2800–3000 cm⁻¹) hydrogen functional groups; CH2/CH3 – relative intensity of the CH2 (2920–2940 cm⁻¹) and CH3 (2955–2975 cm⁻¹) bands; C=O/C=CH – relative content of the C=O groups (1650–1800 cm⁻¹) and C=C aromatic rings (1500–1650 cm⁻¹); ‘A1’ – the ‘A’ factor calculated as [CH2 + CH3 (3000–2800 cm⁻¹)] / [CH2 + CH3 (3000–2800 cm⁻¹) + C=C (1630 cm⁻¹)]; ‘A2’ – the ‘A’ factor calculated as [CH2 + CH3 (3000–2800 cm⁻¹) + C=C (1500–1650 cm⁻¹)] / [CH2 + CH3 (3000–2800 cm⁻¹) + C=C (1500–1650 cm⁻¹)]; ‘C1’ – the ‘C’ factor calculated as C=O (1710 cm⁻¹) / [C=O (1710 cm⁻¹) + C=C (1600 cm⁻¹)]; ‘C2’ – the ‘C’ factor calculated as C=O (1650–1800 cm⁻¹) / [C=O (1650–1800 cm⁻¹) + C=C (1500–1650 cm⁻¹)]; n – number of measurements; italics – the standard deviation is given.

Results and discussion

Graptolite particles under reflected light show two types of morphology: non-granular (Fig. 2A–C), which predominates, and granular – rarely observed (Fig. 2D). Non-granular fragments sometimes display, poorly visible, lamellar structure, typical for the fusellar tissue (Goodarzi 1984; Goodarzi & Norford 1985, 1987; Bustin et al. 1989), (Fig. 2A). Granular fragments (Fig. 2D) probably compose the common canal (Goodarzi 1984; Goodarzi & Norford 1985, 1987; Bustin et al. 1989), which is sometimes filled with fine-grained pyrite.

The mean values of graptolite reflectance (Rr) range between 0.70% and 0.77% (s = 0.07–0.08%) (Tab. 1), indicating maturity corresponding to the oil window.
zone. Relatively low number of measurements (32–54) is due to the limited amount of homogenous areas on the graptolite particles. The Vitrinite Reflectance Equivalent (VRE) values, calculated after Petersen et al. (2013), vary from 0.67% to 0.72% (Tab. 1). The results of R\textsubscript{t} measurements conform to the data presented by Smolarek et al. (2014). Similar or higher values were obtained by Schito et al. (2017). The results are also in line with the T\textsubscript{max} determinations (431–441 °C) made by Smolarek et al. (2014), Mustafa et al. (2015) and Schito et al. (2017). The oil window zone is also confirmed by the occurrence of scarce oil droplets, which reveal spherical shape and yellow colour under the fluorescent light.

Several bands of absorption are displayed in a typical micro-FTIR spectrum of the graptolite periderm (Fig. 3). They are assigned to OH groups (3400–3580 cm\textsuperscript{-1}), aromatic CH\textsubscript{ar} stretching vibrations (3000–3100 cm\textsuperscript{-1}), and aliphatic CH\textsubscript{3} + CH\textsubscript{2} stretching vibrations (2800–3000 cm\textsuperscript{-1}). Curve-fitting procedure revealed the occurrence of six or seven bands within the aliphatic region (Fig. 4): 2985–2990 cm\textsuperscript{-1} – symmetric stretching vibrations of CH groups (very weak, found only in some of the spectra); 2955–2960 cm\textsuperscript{-1} – asymmetric stretching vibrations of CH\textsubscript{3} groups; 2920–2930 cm\textsuperscript{-1} – asymmetric stretching vibrations of CH\textsubscript{2} groups; 2890–2905 cm\textsuperscript{-1} – stretching vibrations of CH groups; 2865–2875 cm\textsuperscript{-1} – symmetric stretching vibrations of CH\textsubscript{3} groups; 2845–2855 cm\textsuperscript{-1} – symmetric stretching vibrations of CH\textsubscript{2} groups; 2825–2830 cm\textsuperscript{-1} – a very weak band, not assigned (Ibarra et al. 1996).

Six bands of absorption were identified in the C=O + C=C region (1500–1800 cm\textsuperscript{-1}) (Fig. 5): 1760–1765 cm\textsuperscript{-1} – C=O stretching vibrations of esters; 1710–1715 cm\textsuperscript{-1} – C=O stretching vibrations of carboxylic acids; 1660–1670 cm\textsuperscript{-1} – conjugated C=O stretching vibrations (quinones and ketones) 1615–1620 cm\textsuperscript{-1}, 1570–1580 cm\textsuperscript{-1} and 1535–1545 cm\textsuperscript{-1} – C=C aromatic ring stretching vibrations.

In addition, bands assigned to aliphatic CH\textsubscript{2} + CH\textsubscript{3} deformation (~1350–1470 cm\textsuperscript{-1}), aromatic ether, ester or phenolic C–O stretching vibrations (~1100–1300 cm\textsuperscript{-1}), aliphatic ether C–O stretching vibrations (~1030–1080 cm\textsuperscript{-1}), and aromatic CH\textsubscript{ar} out-of-plane deformation (~750–900 cm\textsuperscript{-1}) are observed. Bands corresponding to clay minerals (illite, kaolinite) (~1000–1150 cm\textsuperscript{-1} and ~900 cm\textsuperscript{-1}), carbonates (mostly calcite) (~1430–1440 cm\textsuperscript{-1} and ~880 cm\textsuperscript{-1}), quartz (~1050–1100 cm\textsuperscript{-1} and ~780–800 cm\textsuperscript{-1}), as well as pyrite (~1000–1150 cm\textsuperscript{-1}) (Chen et al. 2014, 2015) are also detected.

The CH\textsubscript{ar}/(CH\textsubscript{2} + CH\textsubscript{3}) ratio reaches 0.050–0.058 (Tab. 1, Fig. 6), being higher than the values determined for the Silurian graptolites from the Baltic Basin of Northern Poland of similar (Caricchi et al. 2016) or even higher reflectance (Morga & Kamińska 2018). The CH\textsubscript{3}/CH\textsubscript{2} ratio decreases from 2.08 to 1.62 with the increasing reflectance, which demonstrates shortening of the aliphatic chains (Tab. 1, Fig. 7). These values correspond well with the ones determined for the Silurian graptolites.
(Suchý et al. 2002, 2004; Caricchi et al. 2016) as well as chitinozoans and scolecodonts (Dutta et al. 2013). Much lower values were observed in graptolites showing higher reflectance (Morga & Kamińska 2018). The $\text{C}=\text{O}/\text{C}=$C ratio is low (0.41–0.51) which reveals that weathering did not affect the chemical structure of the graptolite periderm (Tab. 1). In general, the ratio is lower in comparison to the graptolites having higher reflectance and examined from the core samples (Morga & Kamińska 2018). The ‘A₁’ factor varies between 0.46 and 0.79, while the ‘A₂’ factor between 0.28 and 0.60 (Tab. 1). Much higher values indicating higher hydrocarbon potential are observed regarding the samples from the Prągowiec ravine. Comparable results were gained for graptolites (Caricchi et al. 2016, Morga & Kamińska 2018), chitinozoans and scolecodonts (Dutta et al. 2013).

The ‘C₁’ factor changes from 0.22 to 0.37 and the ‘C₂’ factor from 0.29 to 0.33 (Tab. 1), falling within the ranges documented for the higher reflectance graptolites (Morga & Kamińska 2018), and being lower than those found by Caricchi et al. (2016). In general, these values are similar to those obtained for chitinozoans and scolecodonts (Dutta et al. 2013). Considering the ‘A₂’ and ‘C₂’ factors (Guo & Bustin 1998a, D’Angelo et al. 2010), the graptolite periderm represents kerogen type II or III (or can be treated as transitive type II/III) (Fig. 8), as was found in the previous studies (Bustin et al. 1989, Morga & Kamińska 2018).

The graptolite periderm in the studied samples is composed predominantly of aromatic groups and rings with lesser amount of aliphatic and carbonyl/carboxyl groups. The $\text{CH}_2/\text{CH}_3$ ratio indicates that aliphatic chains are relatively long in comparison to vitrinites and liptinites from coals (Guo & Bustin 1998a, Lin & Ritz 1993, Mastalerz & Bustin 1996, Komorek 2016, among others).
The results obtained for the two analysed localities (Prągowiec ravine, Bardo Stawy) are mostly consistent. The only distinct difference is in the ‘A1’ and ‘A2’ factors, higher values of which indicate much higher hydrocarbon potential of shales collected in the Prągowiec ravine, even though the reflectance values are similar. It should be mentioned, however, that the ‘A’ factor does not show close relationship with thermal maturity indices such as R_r or T_max, as was revealed from shale studies (Mroczkowska-Szerszeń et al. 2015, Caricchi et al. 2016). Besides, chemical features of the graptolite periderm may not fully reflect the hydrocarbon potential of the whole rock. Furthermore, TOC content in shales occurring in both localities is very varied. It ranges from 0.3% to 2.0% for Bardo Stawy and from 0.5% to 1.2% for the Prągowiec ravine (Mustafa et al. 2015, Schito et al. 2017). This means that the values of some geochemical parameters are dependent on the place of sampling in the rock profile of the two studied localities.

Many similarities between chemical structure of the graptolite periderm and vitrinite of the adequate rank (Vitrinite Reflectance Equivalent – VRE was used for comparison) are well-established. This regards principally the CH_ar/(CH_2 + CH_3) ratio (Machnikowska et al. 2002, Chen et al. 2012a) and the CH_2/CH_3 ratio (Lis et al. 2005, Petersen & Nytoft 2006, Chen et al. 2012a), the ‘A1’ factor (Chen et al. 2012a). Such relation was previously suggested by Bustin et al. (1989) and Morga & Kamińska (2018). To some extent it is also indicated by the kerogen type of the graptolite periderm, which is frequently detected as transitive – II/III, although typical marine kerogen is of type II, and type III (represented by vitrinite) represents a terrestrial origin.

It is observed that within the whole graptolite reflectance range (R_r = 0.70–1.83%) analysed in this and previous study (Morga & Kamińska 2018) the CH_ar/(CH_2 + CH_3) ratio stays stable and begins to increase only at higher reflectance (R_r > 1.6%), showing weak increase in aromaticity (Fig. 6). On the other hand, the CH_2/CH_3 ratio strongly decreases with increasing R_r, which reflects
shortening of the aliphatic chains (Fig. 7). Adequate relationship was found for vitrinite (Chen et al. 2012a).

The microstructural examination showed that the graptolite periderm from the Holy Cross Mountains is a poorly organized carbonaceous matter (Morga 2019). The study also proved that microstructure does not vary significantly between the samples from the two considered localities. The micro-FTIR derived spectral ratios can be compared to the micro-Raman spectral parameters obtained on the same sample set (Morga & Pawlyta 2018, Morga 2019). It is seen that aromaticity of the graptolite periderm, demonstrated by the CH$_2$/CH$_3$ ratio, tends to increase with the increasing I$_{1d}$/I$_{2d}$ ratio (Fig. 9), which is a measure of the diameter of the coherent domains (L$_c$) in the carbonaceous materials (Tuinstra & Koenig 1970, Ferrari & Robertson 2000 among others). The I$_{1d}$/I$_{2d}$ ratio increases with increasing L$_c$ when it is below 2 nm (which is the case here – see Morga & Pawlyta 2018), and decreases when L$_c$ exceeds 2 nm (Ferrari & Robertson 2000). At CH$_2$/CH$_3 = 1.3$, the full width at half maximum (FWHM) of the Raman G band, which arises from the E$_{2g}$ stretching vibrations in aromatic layers (Beyssac et al. 2003), begins to decrease with decreasing CH$_2$/CH$_3$ ratio (Fig. 10), which reflects improvement in the structural ordering (Kelemen & Fang 2001, Quirico (Fig. 10), which reflects improvement in the structural order of R that many similarities occur in the chemical structure of graptolite periderm from the Holy Cross Mountains is characterized by higher hydrocarbon potential. It is found that many similarities occur in the chemical structure of the graptolite periderm and vitrinite within the reflectance range of R$_v = 0.70$–0.77%; VRE = 0.67–0.72%).

Conclusions

Graptolite periderm in the Silurian shales from the Holy Cross Mountains of Poland (R$_v = 0.70$–0.77%; VRE = 0.67–0.72%) is composed predominantly of aromatic groups and rings with lesser amount of aliphatic and carbonyl/carboxyl groups. Chemical composition 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. However, the samples from the Prągowiec ravine are characterized by higher hydrocarbon potential. It is found that many similarities occur in the chemical structure of the graptolite periderm and vitrinite within the reflectance range of R$_v = 0.7$–1.5%. With increasing reflectance, the length of the aliphatic chains (as inferred from the CH$_2$/CH$_3$ ratio in the graptolite periderm decreases, and the relative content of the aromatic groups [as indicated by the CH$_2$/CH$_3$ ratio] begins to increase at R$_v = 1.6%$. This is accompanied by growth of the coherent domains and improvement in the structural order.

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