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# Microstructure of graptolite periderm in Silurian gas shales of Northern Poland

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ABSTRACT

Core samples of Silurian graptolite shales from an exploration borehole within the Baltic Basin were examined by optical microscopy, Raman spectroscopy and high resolution transmission electron microscopy. Graptolite periderm is composed of poorly ordered carbonaceous material of mainly aromatic structures. The dimension of the coherent domains is 1–2 nm. They are composed of two to three stacked layers. Raman spectral parameters of graptolite periderm are correlated with the mean random ($R_r$) and mean maximum ($R_{max}$) reflectance of graptolites. The spectral $I_{D1}/I_G$ ratio predicts thermal maturity in a mean reflectance of graptolites ($R_r$) range between 1.30% and 1.80% ($R_{max} \approx 1.40–2.00\%$; Vitrinite Reflectance Equivalent VRE ≈ 1.10–1.50%). It is possible to calculate $VRE_{Raman}$ from the $I_{D1}/I_G$ ratio.

## 1. Introduction

The optical properties of the graptolite periderm have been studied for many years. Graptolite reflectance is an indicator of thermal maturity of organic matter in pre-Upper Silurian rocks in which vitrinite is absent (Goodarzi, 1984, 1985; Goodarzi and Norford, 1985, 1987, 1989; Bustin et al., 1989; Riediger et al., 1989; Link et al., 1990; Goodarzi et al., 1992a, 1992b; Malinconico, 1993; Cole, 1994; Rantitsch, 1995; Williams et al., 1998; Petersen et al., 2013; İnan et al., 2016). Graptolite reflectance is correlated to vitrinite reflectance (Bertrand and Héroux, 1987; Bustin et al., 1989; Goodarzi and Norford, 1989; Bertrand, 1990; Link et al., 1990; Petersen et al., 2013; İnan et al., 2016). Due to the varied and often strong optical anisotropy of the graptolite periderm, maximum reflectance ($R_{max}$) measurements are taken on the slides parallel to bedding plane (Goodarzi and Norford, 1985, 1987, 1989; Link et al., 1990; Hoffknecht, 1991; Goodarzi et al., 1992a; Rantitsch, 1995). Investigation of thermal maturity is crucial in exploration for shale gas, which frequently occurs in the Cambrian–Silurian organic-rich shales (e.g. Schovsbo et al., 2011; Jarvie, 2012; Petersen et al., 2013).

Periderm of living graptolites was composed of collagen-like fibrils but their fossils lack protein (Towe and Urbanek, 1972; Link et al., 1990). Infrared spectroscopy demonstrates that the graptolite periderm is composed of aromatic molecules with aliphatic groups (Bustin et al., 1989; Suchy et al., 2002, 2004; Caricchi et al., 2016). However, the microstructural properties of the graptolite periderm are poorly known.

A common way to obtain microstructural characteristics of carbonaceous matter is micro-Raman spectroscopy, which evaluates the structural order. This method was frequently applied to examine coals, their individual macerals and dispersed organic matter (Kelemen and Fang, 2001; Beyssac et al., 2003; Jehlička et al., 2003; Rantitsch et al., 2004; Quirico et al., 2005; Zickler et al., 2006; Guedes et al., 2010; Lahfid et al., 2010; Liu et al., 2013; Hinrichs et al., 2014; Morga et al., 2014; Romero-Sarmiento et al., 2014; Ulyanova et al., 2014). Some Raman spectral parameters were suggested to be useful maturity indices.

Raman studies of the graptolite periderm were performed by Suchy et al. (2004), who observed a decrease of the G band width with a decreasing distance to a magmatic intrusion. That indicated improvement in the structural ordering of the graptolite periderm by temperature corresponding with the increase of the mean reflectance ($R_r$). Measurements were also carried out by Liu et al. (2013). Mumm and İnan (2016), as well as İnan et al. (2016) found the position of the G-peak and the distance between the D1 and G-peak in the graptolite periderm spectra as reliable maturity indicators. It is important to note, however, that only the G and D1 bands were considered in these studies.

Nanostructure of carbonaceous materials can be also investigated by means of high resolution transmission electron microscopy (HRTEM), imaging the size of the graphene layers ($L_a$), the number of stacked layers and the interlayer distance ($d_{002}$) (Oberlin and Oberlin, 1983; Rouzaud et al., 1983; Beny-Bassez and Rouzaud, 1985; Rouzaud and

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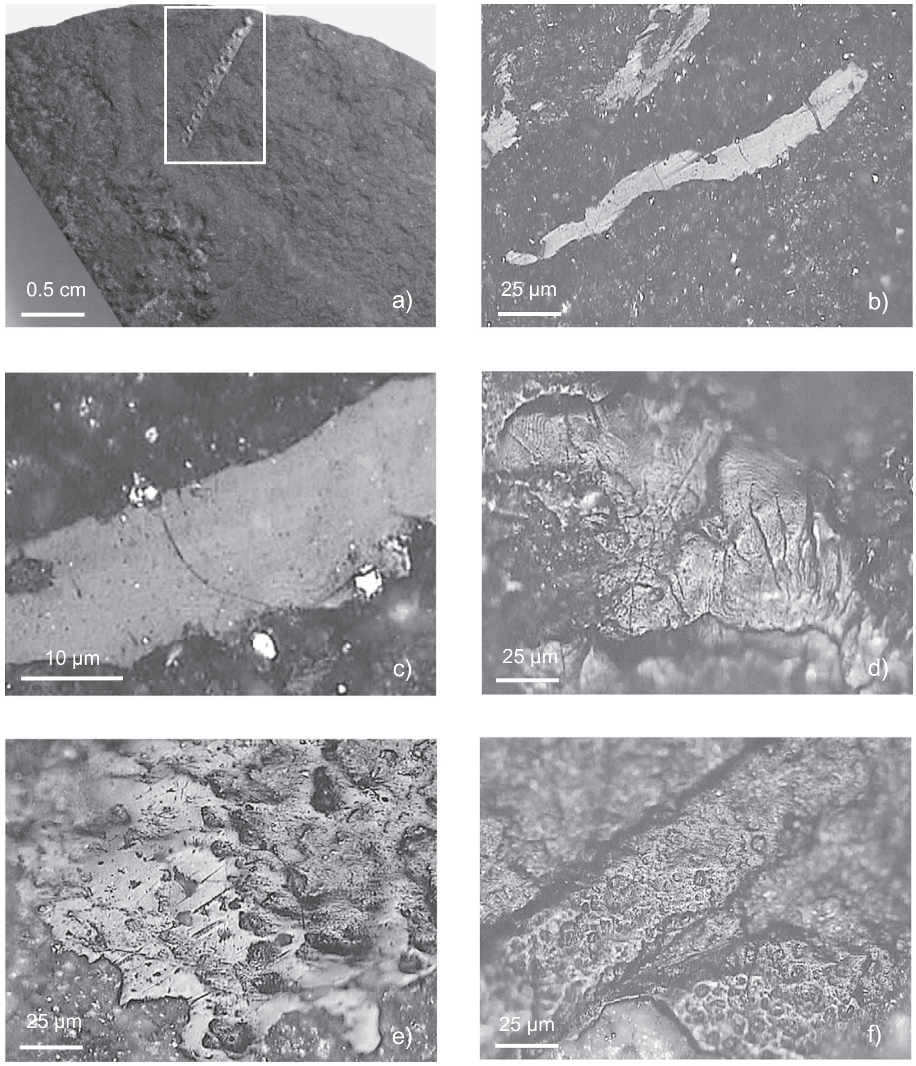


**Fig. 1.** A photograph and microphotographs of graptolites in the studied samples (section parallel to bedding): a) - sample 1; b) - sample 1, non-granular morphology; c) - an enlarged part of the same fragment as in b) with lamellar structure; d) - sample 3, non-granular morphology and lamellar structure; e) - sample 6, non-granular morphology; f) - sample 7, granular morphology.

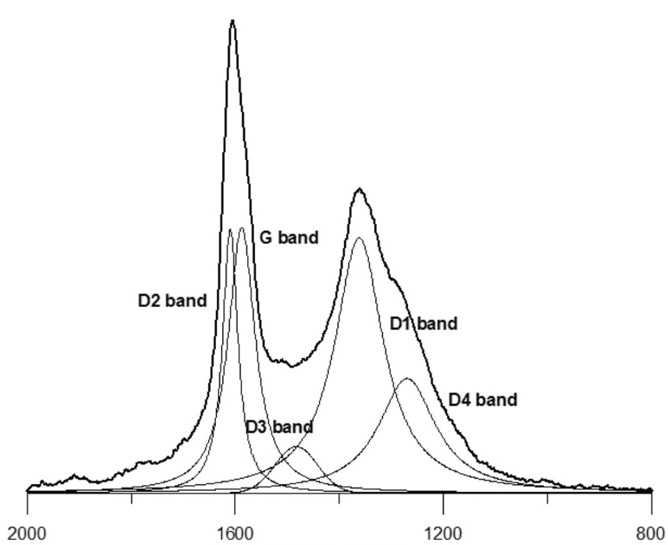


**Fig. 2.** Representative Raman spectrum of a graptolite periderm (sample 10).

Oberlin, 1989; Rouzaud, 1990; Bustin et al., 1995; Sharma et al., 2000, 2001; Beyssac et al., 2002a; Feng et al., 2002; Rouzaud and Clinard, 2002; Rantitsch et al., 2004; Duber, 2011; Pawlyta, 2013; Krzesińska et al., 2014; Romero-Sarmiento et al., 2014). HRTEM-derived microstructural data of the graptolite periderm are presented here for the first time.

The aims of this study are: (1) to characterize microstructure and optical properties of the graptolite periderm in Silurian shales of the Baltic Basin, (2) to correlate Raman spectral parameters with reflectance, (3) to evaluate Raman spectral parameters as alternative thermal maturity indices.

Raman spectroscopy can be used as an alternative method of maturity evaluation when optical microscopy is not available or when microstructural data is needed. Furthermore, the measurements can be carried out on smaller analytical spots than reflectance spots are (see also: Mumm and İnan, 2016).

## 2. Methods

18 core samples of Silurian graptolite shales were collected from the interval of 3690–3947 m of an exploration borehole within the Baltic Basin (N-Poland). The geological setting of this area was described in detail by Caricchi et al. (2016). The Ordovician and Silurian shales of