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Hydrous pyrolysis maturation of vitrinite-like and humic vitrinite macerals: Implications for thermal maturity analysis

Jaques S. Schmidt [a,*], Carla V. Araujo [a], Igor V.A.F. Souza [a], Renata B.A. Chagas [b]

[a] PETROBRAS S.A. – CENPES R&D Center – GEOQ, Rua Horácio Macedo 950, Rio de Janeiro, RJ, Brazil
[b] Fundação Gorceix, Rua Carlos Walter Marinho Campos 57, Ouro Preto, MG, Brazil

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ABSTRACT

The evaluation of thermal maturity of Lower Paleozoic sedimentary rocks is somewhat complex, mainly because of the absence of humic vitrinite maceral material. Various sedimentary basins of this age contain a syndepositional vitrinite-like maceral that resembles vitrinite but has a lower reflectance. Samples of shales from outcrops and boreholes from the Ponta Grossa Formation (Middle Devonian or older) in the Paraná Basin were studied for maturation assessment. Hydrous pyrolysis assays were conducted for 27 combinations of time and temperature to compare the reflectances of the vitrinite-like maceral and humic vitrinite in response to increasing temperature and time. This data confirmed that the maturation pathway of the vitrinite-like maceral is lower than that of humic vitrinite. The Spore Coloration Index for the outcrop samples was also evaluated for natural series studies. The combination of the natural and artificial series led to the development of two-stage linear regression equations that estimate the equivalent vitrinite reflectance values from measured vitrinite-like maceral reflectances. To validate the proposed equations, reported measurements of vitrinite-like maceral reflectances from sedimentary basins in China, North America and Europe were selected from the literature for comparison. The validations showed that the values obtained from the proposed equations correlated well with other maturity parameters.

1. Introduction

Vitrinite reflectance is the most widely used parameter in studies of thermal maturity in sedimentary rocks (Stach et al., 1982; Tissot and Welte, 1984), since its relationship with thermal history and the hydrocarbon generation path is well known (Robert, 1988; Stach et al., 1982; Teichmüler, 1986). Vitrinite maceral in coal is attributed to the humification process of vascular land plants, and it is assumed that the vitrinite found in sedimentary rocks has the same origin (Stach et al., 1982). Fossils of vascular land plants first appear in the Silurian (Gensel and Andrews, 1987); humic vitrinite is scarce or absent in pre-Silurian rocks (e.g., Bertrand and Héroux, 1987).

Early Paleozoic rocks with a reasonably large organic matter content of, and therefore hydrocarbon source potential, occur in basins around the world, including the Paraná, Parnaíba, Amazonas and Solimões Basins in Brazil (Milani et al., 2007a, b), the Tarim Basin in China (Xiao et al., 2000), the Williston Basin in USA and Canada (Ettensohn, 1998; Stasiuk, 1994; Webster, 1984) and the Appalachian Basin in USA (Araujo et al., 2014; Ryder et al., 2013).

Thermal maturity assessment of early Paleozoic basins based on organic petrology methods is hindered by many factors (Bertrand and Héroux, 1987; Xiao et al., 2000), notably the scarcity or absence of humic vitrinite precursor in early Paleozoic sedimentary rocks and the limited number of applicable maturity parameters due to the relatively high maturity of these rocks. The rare occurrence of zooclasts and the difficulty in distinguishing between them restrict their application for maturity assessment (e.g., Bertrand and Héroux, 1987; Goodarzi, 1984; 1985; Obermajer et al., 1996; Petersen et al., 2013; Tricker et al., 1992).

The occurrence of a "vitrinite-like" maceral that resembles vitrinite has been reported for early Paleozoic sedimentary rocks in several regions (Buchardt and Lewan, 1990; Buchardt et al., 1986; Fowler and Douglas, 1984; Glikson et al., 1992; Kisch, 1980; Thomsen et al., 1983; Van Gijzel, 1981; Xiao et al., 2000). Criteria for classifying vitrinite-like macerals have been well described by Buchardt and Lewan (1990), Stasiuk (1994) and Xiao et al. (2000). To summarize these, it is known that in reflected light microscopy the color of vitrinite-like macerals ranges from dark gray to grayish white, depending on maturity, and that they are present in a wide range of shapes – elongate, irregularly shaped lenses, angular or rounded – and are of syndepositional origin. For example, the predominant maceral particles in the Tarim Basin have been reported (Xiao et al., 2000) to be elongate and irregularly shaped lenses 20–150 μm long, parallel to the bedding plane. They generally have a smooth, homogeneous surface without internal structure, even at high maturation levels. Vitrinite-like macerals also have a dark brown fluorescence induced by blue light. The intensity of the

* Corresponding author.
E-mail address: jaquesschmidt@petrobras.com.br (J.S. Schmidt).

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fluorescence decreases with increasing maturity and is extinguished at reflectance values of 0.5–0.6% (Xiao et al., 2000). They widely occur in marine strata, notably in organic-rich argillaceous limestones and shales with type II kerogen. It has been suggested that vitrinite-like macerals in a source rock are derived from a single source material, although its exact nature is not clear (Buchardt and Lewan, 1990; Xiao et al., 2000).

The potential use of vitrinite-like maceral reflectance as a maturity parameter has been discussed in Buchardt and Lewan (1990) and Xiao et al. (2000). Initially Buchardt and Lewan (1990) investigated its response to thermal stress and found an inverse correlation between reflectance values and the atomic H/C ratios of the total kerogen in the Cambrian–Ordovician Alum Shale of southern Scandinavia. Xiao et al. (2000) subsequently proposed three linear correlations relating vitrinite-like reflectance to other organic petrological maturity parameters for an anhydrous pyrolysis artificial maturation series and a natural series.

2. Samples and methods

The Paraná Basin, located on the South American continent (Brazil, Paraguay, Uruguay and Argentina), is a wide intracratonic basin comprising Mesozoic and Paleozoic sedimentary and magmatic rocks. The Ponta Grossa Formation is a thick marine shale deposit representing the Devonian section in the Paraná Basin (Milani et al., 2007b), in which local layers of carbonaceous shale occur with up to 4% TOC weight (Milani et al., 2007a). The samples collected for the present study represent this facies; samples were collected from an outcrop, and one sample was selected from a borehole (Table 1).

Palynological studies have dated the outcrop samples to Late Pragian–Early Emsian (Lower Devonian), and the borehole sample to Eifelian–Givetian (Middle Devonian). The reflectance of the vitrinite-like maceral (VLR) was measured in polished resin-embedded isolated kerogen for the outcrop samples (VLR = 0.32–0.38%) and in polished resin-embedded whole rock for the borehole samples (VLR = 0.57%). In both cases the vitrinite-like particles were easily identified following the criteria established by Buchardt and Lewan (1990), Stasiuk (1994) and Xiao et al. (2000). The reflectance measurements were performed using a Zeiss® Imager A2M microscope coupled with a J&M Analytische Mess- und Regeltechnik GmbH photometer. Reflected light was used to measure the mean random reflectance percentage at 546 nm wavelength in immersion oil (n_e = 1.518 at 23 °C), calibrated to Klein & Beckers® reflectance standards. Due to the absence of humic vitrinite, the Spore Coloration Index (SCI) was evaluated as an additional maturity indicator. For comparison with other maturation data, an equivalent vitrinite reflectance based on SCI was obtained (VReq.SCI) (Barnard et al., 1981). The VReq.SCI was 0.5% for the outcrop samples and 0.7% for the borehole sample.

For comparison purposes, an aliquot of the borehole sample (VLR = 0.57%) was subjected to artificial maturation in 27 combinations of temperature (280–360 °C) and time (1–200 h) using programmed hydrous pyrolysis in a 250 ml-capacity stainless steel reactor. Both the manometer and heating system were regulated by a digital control unit. The aliquots consisted of 20 g of fragments from the rock samples (maximum fragment size 2 mm). The system was filled with distilled deionized water and the headspace was filled with argon. The maximum temperature attainable for this configuration was 360 °C and the highest pressure was 18.06 MPa.

For maturity control, Miocene-age humic lignite from an open pit mine was added in the proportion 1:9 (≈2 g). Vitrinite reflectance (VR) of the lignite was 0.31%. The reflectances of the vitrinite-like and humic vitrinite macerals were measured in polished resin-embedded whole rocks under the same conditions as described above.

3. Results

The vitrinite-like particles in the present study generally occurred as elongate, irregularly shaped lenses 20–150 μm long, parallel to the bedding plane, when observed in polished resin-embedded whole rock. In polished resin-embedded isolated kerogen, the morphology of the maceral was similar to that observed in the whole-rock samples (Fig. 1). The color ranged from dark gray to grayish white, depending on maturity, which in general is consistent with the colors of the vitrinite-like macerals described by Buchardt and Lewan (1990), Stasiuk (1994) and Xiao et al. (2000).

The natural series (A in Table 1) for the Ponta Grossa Formation enabled a lower range of maturation to be analyzed, this was possible using vitrinite-like reflectance and equivalent vitrinite reflectance of the Spore Coloration Index (Barnard et al., 1981). The hydrous pyrolysis experiments allowed the increase in vitrinite-like and humic vitrinite reflectance to be compared as artificial maturation progressed (B in Table 1). In the higher-temperature experiments, particle size shrinkage was observed when compared to the original sample (B, C in Fig. 1).

The vitrinite-like reflectance values for both the natural and artificial series were lower than for the humic vitrinite reflectance and for the equivalent vitrinite reflectance given by the Spore Coloration Index. To adjust the vitrinite-like reflectance to its equivalent vitrinite reflectance, two linear regression equations were fitted to the Paraná Basin data

Table 1
Reflectance data for all samples from Ponta Grossa Formation used in Eqs. (1) and (2), and comparison with the Xiao et al. (2000) equations.

Acronym	VReq.SCI (%)	VR (%)	1SD	n	VLR (%)	1SD	n	VReq.VLR 1–2 (%)	VReq.VLR* (%)
A	0.5				0.32	0.07	15	0.48	0.61
A	0.5				0.32	0.05	30	0.48	0.62
A	0.5				0.38	0.06	19	0.54	0.69
A	0.7				0.57	0.13	20	0.72	0.93
B		0.79	0.03	18	0.65	0.09	20	0.8	1.03
B		0.83	0.05	18	0.72	0.07	14	0.87	1.12
B		0.88	0.03	11	0.73	0.08	17	0.88	1.13
B		0.93	0.04	10	0.74	0.06	17	0.89	1.14
B		0.93	0.04	18	0.77	0.08	19	0.92	1.18
B		0.94	0.05	15	0.76	0.09	32	0.91	1.17
B		0.99	0.05	13	0.85	0.13	24	1.15	1.27
B		1	0.06	15	0.78	0.08	10	1.08	1.25
B		1.02	0.07	12	0.81	0.08	14	1.11	1.26
B		1.03	0.05	15	0.83	0.15	14	1.13	1.26
B		1.06	0.06	22	0.82	0.07	11	1.12	1.26
B		1.06	0.04	10	0.9	0.07	19	1.19	1.28
B		1.11	0.05	11	0.8	0.1	17	1.1	1.25
B		1.12	0.05	11	0.85	0.11	18	1.15	1.27
B		1.21	0.04	13	0.81	0.08	13	1.11	1.26
B		1.24	0.05	14	0.91	0.12	18	1.2	1.28
B		1.28	0.05	7	0.96	0.12	15	1.25	1.3
B		1.29	0.04	25	0.84	0.13	9	1.14	1.27
B		1.37	0.07	8	1.09	0.19	12	1.36	1.34
B		1.38	0.07	16	0.98	0.08	16	1.27	1.3
B		1.41	0.07	4	1.02	0.13	18	1.3	1.32
B		1.42	0.05	16	0.97	0.14	20	1.26	1.3
B		1.42	0.05	18	1.03	0.09	14	1.31	1.32
B		1.43	0.07	15	1.27	0.3	7	1.53	1.39
B		1.5	0.08	14	1.35	0.1	12	1.6	1.41
B		1.6	0.07	8	1.35	0.12	15	1.6	1.41
B		1.62	0.07	13	1.35	0.08	24	1.6	1.41

A — natural series from Ponta Grossa Formation (Middle Devonian or older).
B — hydrous pyrolysis assays.
VReq.SCI — equivalent vitrinite reflectance based on Spore Coloration Index (Barnard et al., 1981).
VR — vitrinite reflectance from humic coal.
VLR — vitrinite-like reflectance from Ponta Grossa Formation.
n — number of measured fields.
1SD — 1 standard deviation.
VReq.VLR 1–2 — equivalent vitrinite reflectance obtained from vitrinite-like reflectance using Eqs. (1) and (2).
VReq.VLR* — equivalent vitrinite reflectance obtained from vitrinite-like reflectance using (Xiao et al., 2000) equations.