



The effect of bacterial degradation on bituminite reflectance



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ABSTRACT

Within bituminite particles, high reflectance oxidation rims (HROR) were observed in close proximity to framboidal pyrites. Through examining a maceral with the framboidal pyrite physically removed, a high number of reflectance measurements were made covering the entire surface of the maceral. Additional measurements were taken in the form of transects across the maceral, allowing an examination of the relationship between reflectance and distance from the bacterial sulfate reduction (BSR) zone. A baseline reflectance value of approximately 0.50%R_o was measured, with peak values of approximately 0.75%R_o measured adjacent to the pyrite. This large variability in bituminite reflectance (BR_o) was not induced via thermal catagenesis; however, it could be accounted for by a diagenetic process. This process involves labile organic matter (OM) entering a BSR zone. In this zone, anaerobic bacteria reduces dissolved sulfate to oxidize OM. This process results in the formation of bacterially-derived framboidal pyrite in close proximity to HROR in bituminite macerals. Although there has been a previous report of elevated BR_o associated with biogenic gas in the regional scale, there was no microscopic evidence of such occurrence reported. This study examines low reflectance bituminite particles with embedded framboidal pyrite and associated HROR.

Examination of the measured transects yielded a very rapid drop in reflectance a few micrometers away from the BSR zone. This study demonstrates a bacterial process that causes elevation of BR_o on a micrometer scale and leads to a positively skewed, highly variable BR_o population. We also demonstrate the magnitude of variation that can be expected when measuring BR_o which could result in significant overestimation of thermal maturity.

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1. Introduction

Thermal maturity is the measurement index of the transformation of organic matter (OM) when subjected to higher temperature and pressure over geologic time. This heating results in liberation of hydrogen and oxygen-rich molecules within the maceral, gradual loss of functional groups, and increasing aromaticity (Tissot and Welte, 1984; Seewald, 2003). In labile OM this results in an atomic restructuring of OM (Taylor et al., 1998). This can be measured by an increase in Rock-Eval residual carbon, a decrease in hydrogen index, and an increase in Rock-Eval T_{max}. Optically, oxidation processes cause an increase in reflectance of light and loss of fluorescing properties of OM (Taylor et al., 1998). Reflectance (R_o) of vitrinite, solid bitumen, and zooclasts (e.g. graptolites) is widely used to evaluate thermal maturity of sedimentary rocks and is an important technique for the characterization of OM (Hartkopf-Fröder et al., 2015).

Thermal maturity is known to increase R_o of macerals. However other factors affecting R_o, including variation in hydrogen content,

sub-aerial oxidation or oxidation within the water column, rapid thermal degradation due to igneous intrusion, or bacterial degradation (anaerobic or aerobic) are less well understood and are rarely documented (Hartkopf-Fröder et al., 2015 and references therein). Anomalous increases in reflectance are generally attributed to rapid thermal degradation or variation in initial conditions (Fang and Chen, 1992; Wegner and Baker, 1987). These authors ascribed reflectance enhancement to variations in initial hydrogen content of the maceral or deposition in an oxic environment (aerial oxidation within the water column). Suppression of reflectance within organic particles has been documented frequently (e.g., Carr, 2000 and references therein) and is well understood.

Amorphous organic matter (AOM) is generally abundant in oil-prone source rocks deposited under oxygen-deficient bottom water conditions (Hartkopf-Fröder et al., 2015). This unstructured organic matter is classified under the term bituminite and exhibits low reflectance and reddish to dark brown fluorescence (Taylor et al., 1998; Teichmüller and Ottenjann, 1977). Bituminite commonly occurs in lenses of irregular shapes and within the mineral matrix merged with non-organic matter (Littke et al., 1988). The study of bituminite is important for the quantification of thermal maturity and the assessment of kerogen in source rocks under reflected white light as well as

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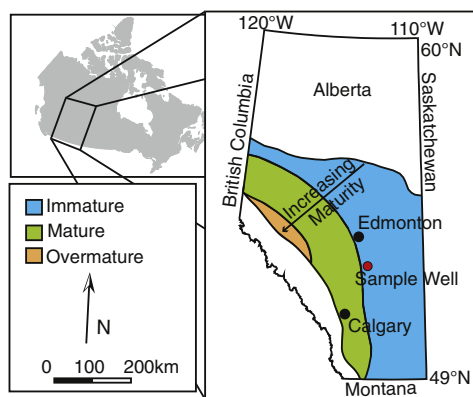


Fig. 1. Sample location map: location of sampled well (102/07-12-042-21W4) in relation to Second White Specks Formation regional thermal maturity zones. Modified after Creaney and Allan (1990), Kwan and Mooney (2010), and Furmann et al. (2014).

fluorescent light using the classification schemes of Tyson (1995) and Thompson and Dembicki (1986).

This study aims to explain why the reflectance (BR_o) of a single bituminite maceral in close proximity to framboidal pyrite varies widely, from 0.5% up to 0.8%, and why the distribution of BR_o values is right skewed towards higher values. It is hypothesized that the elevated BR_o is related to bacterial sulfate reduction (BSR). Although there has been a previous report of elevated BR_o associated with biogenic gas (Stasiuk and Goodarzi, 1988), no microscopic evidence was reported. OM with a reflectance value below ~0.6% would be considered thermally immature. A reflectance value between ~0.6% to ~1.2% would be considered mature (in the oil window) and therefore a prime candidate as a petroleum source rock (Tissot and Welte, 1984) if sufficient organic matter of the right type is present. This study aims to present evidence of BSR resulting in the elevation of BR_o that could result in erroneous interpretation of OM being in the peak oil-generation window.

2. Geological setting

Samples were taken from a core in the Cenomanian-Turonian Second White Specks Formation of the Upper Colorado Group in south-central Alberta (Fig. 1). This formation is primarily composed of calcareous, organic rich mudstone/shale deposited during an overall transgression from the Albian to the Turonian (the Greenhorn Cycle) (Slingerland et al., 1996; Schröder-Adams et al., 1996). During this transgression, oceanic productivity was high and the organic matter was deposited into predominantly anoxic bottom waters (Caldwell et al., 1978; Schröder-Adams et al., 1996; Bloch et al., 1999). Stasiuk and Goodarzi (1988) interpreted a majority of the macerals to the east, in Saskatchewan, to be from the liptinite group with well-preserved algal bodies. Thermal maturity in the formation trends from immature in Saskatchewan up to the oil window in west-central Alberta and the gas window in western Alberta and eastern British Columbia (Creaney and Allan, 1990) (Fig. 1).

3. Methodology

Eighteen samples from a core in well 102/07-12-042-21W4/00 (52.60°N, 112.89°W) (Fig. 1) located in south-central Alberta were sampled at approximately 1 m intervals between depths of 1008.0 m to 1020.5 m. The core is stored at the Alberta Energy Regulator Core Research Centre in Calgary, Alberta. This study will focus on observations taken at a depth of 1010.0 m.

Samples were finely ground and analyzed using the standard cycle of a Vinci Technologies Rock-Eval 6® analyzer (Lafargue et al., 1998). This pyrolysis method involves a constant temperature of 300 °C for 3 min followed by increasing temperature at a rate of 25 °C per minute to a final temperature of 650 °C. The amount of hydrocarbons released during each heating stage is then measured under the S1 and S2 peaks (mg HC/g rock). Simultaneously, the amounts of CO₂ and CO released are measured under the S3 and S4 peaks (mg CO₂/g rock) (Lafargue et al., 1998). The residual carbon and inorganic carbon content is obtained through oxidation in air from up to 850 °C and added to the pyrolyzed organic carbon in order to calculate the total organic carbon (TOC) of the sample (Lafargue et al., 1998).

Four samples (from depths 1008 m, 1009 m, and 1010 m) containing pyrite crystals were analyzed for sulfur isotope ratio in order to confirm that the framboidal pyrite was derived from bacterial processes. Chromium reduction was used to convert S from pyrite to H₂S for S isotope measurement (Canfield et al., 1986; Mayer and Krouse, 2004). Approximately 100 mg of sample with 10 mL ethanol was placed in the reaction vessel. 40–60 mL of 1 M CrCl₂ solution was obtained by reduction of CrCl₃ and 20 mL 6 M HCl was introduced to the sample via a rubber septum under a stream of N₂ (Canfield et al., 1986). The sample and solution was boiled for 1 to 2 h and released H₂S was trapped, precipitated as ZnS, and converted to Ag₂S for S isotope analysis (Canfield et al., 1986; Mayer and Krouse, 2004). The $\delta^{34}\text{S}$ value of pure Ag₂S was measured by thermal decomposition in an elemental analyzer coupled to an isotope ratio mass spectrometry (EA-IRMS) at the University of Calgary. The ³⁴S/³²S ratios measured on the produced SO₂ are expressed relative to the internationally accepted standard Canyon Diablo Troilite (V-CDT) using the standard δ notation. For sulfur isotope measurements, IAEA S1 (−0.3‰), S2 (+22.7 ± 0.2‰), and S3 (−32.6 ± 0.2‰) were repeatedly analyzed for calibration and normalization purposes. Precision and accuracy as 1 sigma of ($n = 10$) lab standards for $\delta^{34}\text{S}$ is equal to 0.3‰.

Eight samples were also prepared into a polished block for organic petrology analysis. These blocks were prepared using a cold-setting epoxy-resin mixture. The resulting sample pellets were then polished and ground in final preparation for petrographic analysis. Petrographic analysis was carried out using a Zeiss Axioimager II microscope system equipped with white light sources and the Diskus-Fossil system for reflectance measurements. Reflectance measurements were carried out under oil immersion using an ultra-fine measurement probe (0.3 μm² spot size). The standard reference used for reflectance measurements was yttrium-aluminum-garnet with a standard reflectance of 0.906% under oil immersion. High density measurements were taken from the observed maceral with the goal of measuring its entire surface. Three transects of 13, 11, and 6 measurements respectively labeled transects 1, 2, and 3, were taken moving outward perpendicularly from the BSR zone, away from the visible HROR.

Table 1

Bituminite reflectance data summary statistics. Summary of reflectance data taken at sample depth 1010 m in well 102/07-12-042-21W4.

Sample depth (m)	Sample set	Number of measurements	Minimum	Maximum	Median	Mean
1010.00	Whole sample	243.00	0.18	1.02	0.43	0.47
1010.00	Whole maceral	300.00	0.46	0.78	0.55	0.56
1010.00	Transect 1	13.00	0.50	0.76	0.57	0.59
1010.00	Transect 2	11.00	0.50	0.70	0.51	0.57
1010.00	Transect 3	6.00	0.55	0.71	0.58	0.61

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