International Journal of Coal Geology 137 (2015) 165–171

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Dolomite fluorescence Red/Green quotient: A potential new thermal maturity indicator

Omid Haeri-Ardakani [a,*], Hamed Sanei [a,b,c]

[a] Geological Survey of Canada, Calgary Division, AB, Canada
[b] Department of Geosciences, University of Calgary, Calgary, AB, Canada
[c] Center for Energy Technologies (CET), AU-Herning, Aarhus University, Denmark

ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form 6 December 2014
Accepted 7 December 2014
Available online 13 December 2014

Keywords:
Dolomite fluorescence color
Red/Green Quotient
Thermal maturity
Utica Shale
Montney Formation

ABSTRACT

Geochemical and petrographic effects of burial temperature on sedimentary organic matter have long been recognized and used as various thermal maturity indicators (i.e., pyrolysis T_{max}, conodont and spore coloration, vitrinite/bitumen/zooclast reflectance), and fluorescent spectrometry (i.e., λ_{max} and Red/Green quotient). This study investigates variations in the fluorescence color spectra (in the visible light spectrum) of authigenic dolomite over a wide range of thermal maturities. Two sample sets of calcareous shales/siltstones from Eastern and Western Canada, with sparse dolomite crystals in the rock matrix were selected to examine the relationship between thermal maturity and fluorescent properties of dolomite. Results from a range of thermal maturities, from the oil window to the dry gas window, reveal a strong positive correlation between the Red/Green quotient (Q) of dolomite crystals and equivalent vitrinite reflectance ($VRo_{eqv.}$) values. This can be optically described as the color shift in fluorescent properties of dolomite with increasing maturity. This strong positive correlation between Q and thermal maturity can potentially be used as an alternative thermal maturity indicator in calcareous shales with low organic content. Compilation of worldwide data is required to understand the relationship trend and conversion equations among dolomite Q and other established thermal maturity indicators.

1. Introduction

A variety of thermal maturity indicators have been developed and implemented since the 1970s. Some of the most common maturity indicators include the Conodont Alteration Index (CAI), Thermal Alteration Index (TAI), and Spore Coloration Index (SCI), all utilizing transmitted light microscopy. Other methods using reflected light microscopy focus on the measurement of light reflectance from the surface of various types of macerals (i.e., vitrinite, bitumen) and zooclasts (i.e., graptolites, chitinozoans, and scolecodonts) (see Suárez-Ruiz et al., 2012 and references therein; Petersen et al., 2013).

Of these methods, vitrinite reflectance is a widely used and robust thermal maturity indicator (e.g., Hunt, 1996). Vitrinite is derived from ligno-cellulosic tissues of higher land plants, which appeared after the Late Silurian (Hunt, 1996). In the absence of vitrinite in Lower Paleozoic rocks, reflectance measurements may be carried out on zooclasts (graptolites, chitinozoans, and scolecodonts; Goodarzi and Norford, 1985; Goodarzi, 1985; Bertrand and Héroux, 1987) and solid bitumen (Bertrand, 1993; Jacob, 1985; Suárez-Ruiz et al., 2012 and references therein).

Fluorescence spectrometry is an important tool in the evaluation of thermal maturity trends (Jacob, 1964; Ottenjann et al., 1974; Suárez-Ruiz et al., 2012; Teichmüller and Wolf, 1977). Quantitative measurement of fluorescence color is possible through measurement of maximum peak (λ_{max}) and the Red/Green Quotient (Q), which is the ratio of relative intensity at 650 nm to relative intensity at 500 nm (Teichmüller and Wolf, 1977). Spectral fluorescence parameters such as Q and λ_{max} show positive correlation with degree of thermal maturity (Obermajer et al., 1999; Thompson-Rizer and Woods, 1987). With increasing maturity the fluorescent intensity of liptinite decreases, and fluorescent color shifts to longer wavelengths ("red shift"). This effect diminishes when the lower oil window is reached, at about 1.5% Ro (vitrinite reflectance). This degree of shift in spectral wavelength is commonly quantified as Red/Green quotient (Q). In measured liptinites found in the oil window the relationship between thermal maturity and Q is positive (Gentzis et al., 1993; Goodarzi et al., 1987; Obermajer et al., 1999; Taylor et al., 1998; Thompson-Rizer and Woods, 1987). The increase in λ_{max} and Q is related to the formation and expulsion of hydrocarbons (Teichmüller and Teichmüller, 1982).

Dolomite fluorescence petrography is a complementary method in dolomitization and carbonate diagenesis studies and is mainly used

* Corresponding author. Tel.: +1 403 383 8288; fax: +1 403 292 5377.
E-mail addresses: Omid.HaeriArdakani@NRCan-RNCan.gc.ca (O. Haeri-Ardakani), Hamed.Sanei@NRCan-RNCan.gc.ca (H. Sanei).

http://dx.doi.org/10.1016/j.coal.2014.12.005
0166-5162/

for cement stratigraphy. Fluorescence and cathodoluminescence (CL) microscopy proved to be a useful method in discerning growth zones in dolomite crystals (Dravis, 1991; Dravis and Yurewicz, 1985; Durocher and Al-Aasm, 1997; Lonnee and Al-Aasm, 2000; Wendte et al., 1998; Wierzbicki et al., 2006). In some cases it is evident that there is a tendency towards decreasing fluorescence color wavelength from the core to the rim of crystal (red to green shift). However, no systematic study looks at the relationship between dolomite fluorescence color and thermal maturity in siliciclastic rock with dispersed dolomite crystals in the rock matrix.

This paper presents analytical evidence of relationships between thermal maturity and shift in fluorescence spectrometry of dolomite in the Upper Ordovician, Utica Shale (southern Quebec) and Lower Triassic, Montney Formation, Western Canadian Sedimentary Basin (WCSB). Furthermore, the possibility of utilizing dolomite fluorescence as an alternative maturity index is discussed.

2. Methodology

Well locations and sampling depths for studied samples are provided in Table 1. A wide range of thermal maturities, from the oil window to the dry gas zone, as well as the presence of scattered dolomite in these sample sets were the major criteria for sample selection. The wide range of thermal maturities facilitated investigation of correlation between thermal maturity index (i.e., $VRo_{eqv.}$) and Q. Organic petrology was carried out on selected samples using polished blocks made with a cold-setting epoxy–resin mixture. The resulting sample pellets were ground and polished, in final preparation for microscopy using an incident light Zeiss Axio Imager II microscope system equipped with fluorescent light sources and the Diskus-Fossil system for reflectance measurements. Random reflectance (%Ro) measurements were conducted using an ultra-fine pixel size (0.3 μm^2) measuring probe in the Diskus-Fossil system. The goal was to conduct more than 100 reliable measurements in each sample to construct robust reflectance histogram populations. In organically lean samples, the number of measurements was compromised in order to measure only reliable macerals with well-polished surfaces. Red/Green quotient values (Q = relative intensity at 650 nm/relative intensity at 500 nm) were determined under standard conditions (filters: excitation 450–490, beam splitter 510, barrier 420 nm) for dolomite crystals.

The predominant maceral types in the Utica Shale samples are bitumen, chitinozoans, and minor graptolites. The measured bitumen and chitinozoan reflectance values were converted to the equivalent vitrinite (random) reflectance values ($\%VRo_{eqv.}$) using the Bertrand (1990); $VRo_{eqv.} = (RB + 0.03)/0.96$) and Bertrand and Malo (2001); $VRo_{eqv.} = (VR_{chi} - 0.014) / 1.127$) equations, respectively. Results show that samples from the deeper intervals of the Utica Shale have $VRo_{eqv.}$ of 2.12% occurring within the dry gas zone. Intermediate and shallow Utica samples have $VRo_{eqv.}$ of 1.17% and 1.24% respectively, and occur at the end of the oil window and the onset of the wet gas zone (Table 2). Organic petrology and geochemistry of Utica Shale samples are discussed in detail in Haeri-Ardakani et al. (in press). The dominant organic matter particles in the Montney Formation samples are solid and granular bitumen. The Montney samples cover a wider range of VRo, form onset of the oil window (0.8%) to the dry gas window (2.35%, Table 1).

Table 1
Well locations and depths of the Utica Shale and Montney Formation samples.

Formation	Latitude	Longitude	Depth from (m)	Depth to (m)
Utica	46.52650	−71.77789	1997.88	2030.45
	46.36245	−72.42747	700.15	751.95
	46.75649	−71.46467	342.15	514.00
Montney	55.11067	−120.187401	3743.83	3744.20
	55.387678	−120.182253	3060.17	3134.84
	55.525588	−121.039161	3849.11	3870.62
	55.945206	−120.599792	2130.46	2348.27
	55.806772	−119.725794	2035.78	2122.91

Table 2
Summary statistics of VRo and Q measurements of Utica Shale and Montney Formation samples.

Formation	Maturity level	Depth (m)	VR_{eqv}	Q_{core} min–max (mean), *n*	Stdev	Q_{rim} min–max (mean), *n*	Stdev
Utica	Oil window	422.1	1.28	0.97–1.61 (1.15), 17	0.18	0.97–1.03 (0.99), 5	0.03
		424.2	1.04	1.10–1.40 (1.34), 13	0.27	–	–
		426	1.1	1.10–1.32 (1.20), 11	0.08	1.07–1.10 (1.09), 3	0.01
		473.65	1.06	0.95–1.41 (0.92), 14	0.14	0.88–0.92 (0.89), 3	0.03
		514	1.31	0.81–1.25 (1.01), 10	0.16	0.75–0.90 (0.82), 5	0.06
		700.15	1.19	1.10–1.40 (1.21), 14	0.08	1.01–1.10 (1.07), 3	0.05
		705.05	1.35	0.99–1.34 (1.18), 14	0.09	0.99–1.03 (1.01), 3	0.03
		710.3	1.25	0.99–1.41 (1.13), 14	0.10	–	–
		715.25	1.21	0.97–1.30 (1.11), 16	0.09	–	–
		736.85	1.12	1.03–1.63 (1.23), 22	0.15	–	–
		740.5	1.19	1.03–1.65 (1.27), 8	0.22	–	–
		745.55	1.27	1.08–1.63 (1.18), 15	0.16	1.01–1.03 (1.02), 2	0.02
		750.1	1.35	1.10–1.74 (1.27), 18	0.19	0.95–1.03 (0.98), 10	0.03
	Dry gas window	1999.55	1.97	1.50–2.16 (1.70), 6	0.24	1.61–1.82 (1.72), 2	0.15
		2003.37	2.04	1.43–1.78 (1.55), 11	0.09	1.10–1.81 (1.51), 4	0.29
		2005.9	2.11	1.50–2.04 (1.81), 12	0.21	1.56–1.65 (1.61), 2	0.06
		2008.7	2.09	1.34–2.33 (1.90), 6	0.41	0.86–1.10 (0.99), 3	0.13
		2014.9	2.09	1.40–1.70 (1.53), 12	0.12	0.92–1.34 (1.10), 8	0.14
		2017.02	2.33	1.60–2.10 (1.71), 14	0.13	1.67–1.74 (1.71), 2	0.05
		2021.95	2.27	1.52–1.70 (1.59), 8	0.05		
		2024.6	2.22	1.56–2.13 (1.77), 13	0.20	1.52–1.69 (1.69), 3	0.09
		2028.75	1.95	1.63–2.24 (1.79), 8	0.20	1.30–1.52 (1.41), 2	0.15
Montney	Oil window	2110.05	0.78	0.79–1.74) (1.10), 5	0.37	–	–
		2079.58	0.87	0.75–1.74 (1.17), 9	0.28	1.23–1.30 (1.27), 2	0.46
		2122.91	1.17	0.75–1.96 (1.09), 6	0.44	0.88–1.47 (1.18), 2	0.42
		2134.88	1.27	0.73–1.21 (0.99), 10	0.22	0.73–0.92 (0.83), 2	0.14
	Dry gas window	2326.26	1.44	0.79–1.54 (1.34), 10	0.59	1.01–1.21 (1.11), 2	0.14
		3849.11	1.61	1.19–1.52 (1.33), 4	0.14	–	–
		3867.08	1.79	0.88–1.83 (1.23), 10	0.27	1.12–1.39 (1.18), 2	0.18
		3060.17	2.15	0.97–2.68 (1.41), 9	0.62	–	–
		3743.83	2.35	1.28–1.52 (1.41), 5	0.10	–	–
		3068.87	2.39	0.95–2.13 (1.58), 6	0.43	–	–
		3132.12	2.53	1.25–1.91 (1.49), 7	0.22	–	–