



High microscale variability in Raman thermal maturity estimates from shale organic matter

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ABSTRACT

Raman spectroscopy has recently received attention as a means to estimate thermal maturity of organic matter in petroleum generating source rocks to complement more traditional approaches such as vitrinite reflectance and programmed pyrolysis. While many studies have observed positive correlations between source rock thermal maturity and Raman spectral parameters, little attention has been given to the degree of variation in the Raman response across individual organic grains, especially for shales or mudrocks with highly dispersed organic matter. Here the spatial variation in Raman estimates of thermal maturity within individual organic grains is assessed from shales from the Boquillas, Marcellus, Niobrara, and Woodford Formations. The thermal maturity parameters extracted from Raman spectra can vary widely across distances of $\leq 5 \mu\text{m}$ within the same organic grain. These results illustrate the high degree of chemical heterogeneity inherent to the organic matter within these source rocks. Additionally, the spatial pattern of the Raman parameters, as revealed by 2D Raman mapping, imply that organic matter structure is influenced by associations with mineral surfaces within the surrounding rock matrix. Chemical heterogeneity and matrix effects directly impact the Raman response from these types of materials and thus the extracted thermal maturity estimate. These findings highlight the care which must be adopted when making Raman measurements of organic matter within source rock matrices, especially for samples which feature highly dispersed, heterogeneous organic matter as found in petroliferous mudrocks.

1. Introduction

The thermal history of preserved organic matter (OM) within shale rocks is one of the key parameters required to evaluate the petroleum-generating ability of these materials (Dow, 1977). The most common thermal maturity proxies are based on measurements of light ($\lambda = 546 \pm 10 \text{ nm}$) reflectance from vitrinite macerals or programmed pyrolysis of a small amount ($\sim 100 \text{ mg}$) of powdered rock sample (e.g., Peters, 1986; Hackley and Cardott, 2016). However, there are instances in which these traditional approaches are challenged. In some cases, formations contain source rocks with little or no vitrinite. Examples include pre-Devonian shales deposited prior to the evolution of woody plants (the source of vitrinite) as well as marine formations in which algal and microbial input are the dominate OM source. Similarly, organically lean or high maturity source rocks are difficult to analyze by programmed pyrolysis due to detection limit considerations (Peters, 1986).

Raman spectroscopy has been used since the late 1980s and early 1990s as a tool to evaluate the thermal history of OM in sedimentary rocks, e.g. (Beny-Bassez and Rouzaud, 1985; Jehlička and Bény, 1992; Wopenka and Pasteris, 1993). In the past 10 years, there has been increased interest in using this approach as a thermal maturity proxy because it is fast, does not rely on the presence of specific organic macerals, requires very little sample, and is potentially non-destructive. While many studies have reported correlations between source rock thermal maturities and Raman spectral parameters (Spötl et al., 1998; Kelemen and Fang, 2001; Beyssac et al., 2002, 2003; Rahl et al., 2005; Lünsdorf et al., 2014, 2017; Romero-Sarmiento et al., 2014; Wilkins et al., 2014, 2015, 2018; Zhou et al., 2014; Lünsdorf and Lünsdorf, 2016; Schmidt Mumm and Inan, 2016; Bonoldi et al., 2016; Lünsdorf, 2016; Lupoi et al., 2017; Sauerer et al., 2017; Schito et al., 2017; Xueqiu et al., 2017; Cheshire et al., 2017; Childress and Jacobsen, 2017; Baludikay et al., 2018; Henry et al., 2018; Khatibi et al., 2018), only a few studies have examined the effect of sample heterogeneity on the

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Table 1

Shale geologic reference materials (GRMs) information and bulk geochemical parameters. Total organic carbon (TOC) data from LECO TOC analyzer. Programmed pyrolysis data from Wildcat Technologies Hydrocarbon Analyzer with Kinetics (HAWK) where T_{\max} = temperature of S2 peak maximum, HI (hydrogen index) = $(S2/TOC) \times 100$, OI (oxygen index) = $(S3/TOC) \times 100$, PI (production index) = $S1/(S1 + S2)$.

Formation	Sample ID	Basin	Long.	Lat.	Age	TOC (wt%)	Programmed pyrolysis						
							S1 (mg-HC/g-Rock)	S2 (mg-HC/g-Rock)	S3 (mg-CO ₂ /g-Rock)	T _{max} (°C)	HI	OI	PI
Boquillas	ShBOQ	Gulf Coast	101.2111	29.7028	Late Cretaceous	5.0	1.4	31	0.7	422	620	14	0.04
Woodford	ShWFD	Anadarko	97.1489	34.3520	Devonian-Mississippian	8.0	1.2	44	0.6	427	550	7.8	0.03
Marcellus	ShMAR	Appalachian	77.9884	42.9787	Middle Devonian	6.8	4.6	20	0.2	436	300	2.7	0.19
Niobrara	ShNIO	Denver-Julesburg	105.2315	40.2230	Late Cretaceous	2.5	2.1	4.4	0.2	455	180	8.4	0.32

Raman response from probed OM (Beyssac et al., 2003; Lünsdorf et al., 2014; Henry et al., 2018). Furthermore, to our knowledge, there have been no reports on the variability of the Raman response from within individual organic grains embedded in shale matrices, although recent work employing coupled atomic force microscopy and infrared spectroscopy suggest this variability may be limited (Yang et al., 2017).

Raman spectra of source rock OM are typically dominated by two broad peaks centered at $\sim 1600\text{ cm}^{-1}$ and 1350 cm^{-1} , generally assigned to the E_{2g} C–C vibrations of sp^2 carbon atoms in aromatic rings and to A_{1g} vibrational modes which arise due to disorder and defects in the aromatic lattice, respectively (Wang et al., 1990; Ferrari and Robertson, 2001; Sauerer et al., 2017). These peaks are referred to as the G and D bands in analogy to the Raman spectrum of graphitic materials where G stands for graphite and D stands for disorder. The Raman spectrum of single crystalline graphite does not feature a D band (Tuinstra and Koenig, 1970; Wang et al., 1990). Due to resonance enhancement effects between aromatic ring moieties within carbonaceous materials and the excitation wavelengths used in most Raman measurements (Ferrari and Robertson, 2001; Jorio et al., 2011) the strong signal from the G and D peaks can obscure the signal from other Raman active chemical groups within the Raman probe volume. Hence, efforts to extract correlations to thermal maturity from the Raman spectra of source rocks have focused exclusively on the analysis of these two peaks. Analysis of the G and D peaks is generally approached by spectral deconvolution through iterative peak fitting (Wopenka and Pasteris, 1993; Beyssac et al., 2002, 2003; Rahl et al., 2005; Wilkins et al., 2014; Lünsdorf and Lünsdorf, 2016; Sauerer et al., 2017), although several authors have pointed out that this approach can be subject to operator biases (Lünsdorf et al., 2014; Wilkins et al., 2014; Lupoi et al., 2017; Henry et al., 2018). Raman thermal maturity estimates are then made by empirical correlation between the extracted Raman peak parameters and another thermal maturity proxy such as vitrinite reflectance or T_{\max} .

The present research assesses the spatial variation in common Raman parameters used to estimate thermal maturity from individual organic grains within four proposed U.S. Geological Survey shale geologic reference materials (GRMs) from the Boquillas, Marcellus, Niobrara, and Woodford Formations. These GRMs are representative of several important U.S. shale plays, vary in thermal maturity from immature through the oil window, and feature highly dispersed OM embedded in a fine-grained mineral matrix characteristic of sedimentary mudrocks. While the Raman response can vary between different OM types present in shale source rocks due to compositional differences amongst them and their own innate heterogeneity (Beyssac et al., 2003; Lünsdorf et al., 2014; Henry et al., 2018), variation of the Raman response from within individual OM grains of the same type (e.g., kerogen, solid bitumen, etc.) should be greatly reduced. However, differences in Raman signal from within individual OM grains could reflect spatial variation in the chemical domains present across micron scales and/or may also imply that the local molecular structure across

shale OM grains is influenced by associations with the surrounding mineral matrix (Baldock and Skjemstad, 2000; Kennedy et al., 2002). We thus hypothesize that: (i) variation of Raman thermal maturity values extracted across single OM grains of the same type will be low, (ii) the presence of spatially distinct chemical domains or localized organic-mineral interactions within single OM grains will be reflected in high variation for the Raman parameters, and (iii) the observed Raman variation will decrease as the thermal maturity of the shale GRMs increases and chemical heterogeneity is lost with the concomitant increase in OM aromaticity (Lünsdorf, 2016). To test these hypotheses we characterized the four shale GRMs using programmed pyrolysis and optical petrography and then evaluated the spatial variation of the extracted Raman parameters used for thermal maturity estimates across short distances ($\leq 5\text{ }\mu\text{m}$) within individual OM grains of the same type through Raman microscopy mapping. Our findings are discussed in the context of understanding chemical variation within source rock OM and highlight the care which must be adopted when using Raman to evaluate the thermal maturity of petroleum source rocks, especially for shales and mudrocks which feature highly dispersed, heterogeneous OM.

2. Materials and methods

2.1. Samples

The four shale samples analyzed in this study are all proposed U.S. Geological Survey GRMs relevant to U.S. unconventional petroleum plays (<https://www.eia.gov>). The purpose of these proposed GRMs is to serve as quality control and assurance standards for mineralogical and organic and inorganic geochemical studies on shale and mudrock systems. General sample information is provided in Table 1 and is taken from Birdwell and Wilson (2017). The Boquillas sample (ShBOQ) is representative of the Late Cretaceous (Cenomanian-Turonian) Boquillas Shale of the Gulf Coast basin and was collected from a road cut on US-90 west of Del Rio in Val Verde County, Texas. The Marcellus sample (ShMAR) is representative of the Middle Devonian Marcellus Shale in the Appalachian Basin and was collected at the Oatka Creek outcrop in the village of Le Roy in Genesee County, New York. The Niobrara sample (ShNIO) is representative of the Late Cretaceous Niobrara Shale in the Denver-Julesburg Basin and was collected at the CEMEX quarry near Lyons in Boulder County, Colorado. The Woodford sample (ShWFD) is representative of the Devonian-Mississippian Woodford Shale in the Anadarko Basin and was collected at a road cut on I-35 near Ardmore and Springer in Carter County, Oklahoma. All samples were supplied as crushed rock chips from the U.S. Geological Survey Reference Material Project (https://crustal.usgs.gov/geochemical_reference_standards/).

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