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Critical considerations when assessing hydrocarbon plays using Rock-Eval pyrolysis and organic petrology data: Data quality revisited

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ABSTRACT

The dramatic increase in exploration for unconventional hydrocarbon resources has inherently fuelled the need for new source-rock geochemical data. The need for new data comes along with an increasing number of new users, many of whom do not possess the background to interpret accurately and evaluate the quality of data sets generated by different geochemical screening techniques (e.g., Rock-Eval pyrolysis, vitrinite reflectance). Here, datasets from Rock-Eval pyrolysis, vitrinite reflectance, and LECO TOC analyses are scrutinized and compared to show how failing to recognize good vs. bad datasets can dramatically change interpretations during prospect or play appraisals. Detector saturation, contamination of the sample with drilling fluid, and suppression of both Tmax and vitrinite reflectance, are examples of complications that could compromise the validity of the results and the play or prospect reviews derived from them. In addition, misconceptions such as: "LECO TOC is better than Rock-Eval 6 TOC", expressed by many users, are a consequence of the lack of understanding of how different screening techniques and instrumentation work. A solid understanding of these pitfalls and limitations can provide inexperienced geoscientists and engineers with the required support to improve risk maps for hydrocarbon-charge analysis and source-rock evaluations, when using classic guidelines for interpreting results.

1. Introduction

Source-rock evaluation (also known as geochemical screening) is arguably the most critical step during the initial assessment of hydrocarbon plays, especially when dealing with unconventional systems such as shale–gas and shale–oil systems (Jarvie, 2012a,b). Geochemical screening of source rocks has a threefold purpose: to assess the quantity, quality, and thermal maturity of the sedimentary organic matter (OM) from the perspective of hydrocarbon generation, retention, and expulsion. These assessments are routinely performed via open-system programmed pyrolysis (quality, quantity, and thermal maturity, via Rock-Eval pyrolysis), organic petrography (quality and thermal maturity, via visual kerogen analysis and vitrinite reflectance), and LECO TOC combustion (quantity).

Over the past 30 years these techniques have been the "workhorse" of the energy industry when it comes to source-rock evaluation. Lately, the industry has seen a new "boom" due to exploration oriented toward the discovery and production of unconventional resources (e.g., Curtis, 2002; Jarvie, 2012b, 2014; Jarvie et al., 2007; Milliken et al., 2013). The character of these unconventional plays has focused most of the attention on the description of source rocks, which have the potential to generate and store hydrocarbons (Jarvie, 2012a,b). This renewed interest in source-rock geochemistry parallels a new wave of geologists, geophysicists, and engineers, some of whom do not have background in geochemistry.

Although promising and encouraging from the data-generation point of view, such a massive amount of new data falling into the hands of these relatively untrained new users (and many poorly-trained regular users of geochemistry datasets) can generate confusion, especially when an effort is made to follow classic guidelines to interpret geochemical results (e.g., Espitalié, 1986; Jarvie, 1991; Jones, 1987; Katz, 1983; Peters, 1986; Peters and Cassa, 1994) (Table 1). An effort has been made to cover the interpretative gaps and deficiencies left by these classic guidelines. Snowdon (1995) was the first to document Tmax suppression in certain rocks with a hydrogen index (HI) ≥150 mg HC/g TOC. Baskin (1997) presented the H/C atomic ratio as a better way to estimate thermal maturation, and also pointed out complications in correlating H/C ratio with HI derived from Rock-Eval 2 instruments. Sykes and Snowdon (2002) developed a set of guidelines for interpreting Rock-Eval results for coaly source rocks (coals, shaly coals, and carbonaceous shales and mudstones). Dembicki (2009) exposed and documented in detail the three most common errors made when interpreting source-rock data for play or prospect appraisals (or as he defined them in this paper "The TOC myth", "The Rock-Eval Fallacy", and "The vitrinite reflectance deficiency"). These limitations, considerations, and misconceptions usually prompt users to overestimate/underestimate resource density, and to misidentify oil-prone from gas-prone organic matter.

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Table 1
Summary of classic guidelines for interpreting common source-rock evaluation parameters (modified from Peters, 1986; Peters and Cassa, 1994; Baskin, 1997). The cut-offs and subdivisions presented in these classic guidelines should be used with caution (see text for details).

Quantity of organic matter	TOC (wt.%)	S2 (mg HC/g rock)	S1 (mg HC/g rock)
Poor	<0.5	<1.0	0.0–0.5
Fair	0.5–1.0	1.0–5.0	0.5–1.0
Good	1.0–2.0	5.0–10.0	1.0–2.0
Very good	2.0–4.0	10.0–20.0	2.0–4.0
Excellent	>4.0	>20.0	>4.0

Kerogen type (organic matter quality)	Atomic H/C[a]	Hydrogen index[a] (mg HC/g TOC)	S2/S3	Main product at peak maturity
III	<0.8	50–200	<3	Gas
II/III	0.8–1	200–300	3–5	Gas & oil
II	1–1.2	300–600	5–10	Oil & gas
I	>1.2	>600	>10	Oil

Maturity of organic matter	VR_o (%)	Alginite coloration	Tmax (°C)	Production index
Immature	<0.60	Greenish yellow	<435	<0.10
Early	0.60–0.75	Golden yellow	435–445	0.10–0.15
Peak	0.75–0.90	Dull yellow	445–450	0.25–0.40
Late	0.90–1.35	Orange-red	450–470	>0.40
Postmature	>1.35	Non-fluorescing	>470	–

[a] The values listed and the kerogen classifications derived from them apply only to immature samples.

Despite the effort made by the above authors (and many more here not mentioned) with respect to interpreting geochemical screening results, many aspects concerning quality assurance/quality control issues (QA/QC) in such datasets have been left out of these reviews. It is not uncommon to hear in industry gatherings or project meetings expressions such as "total organic carbon (TOC) values from LECO analysis are more reliable than those from a Rock-Eval 6" and "Rock-Eval 2 analysis is more reliable than Rock-Eval 6 analysis". With such claims, it is evident that there are some pitfalls, limitations, and misconceptions regarding QA/QC of geochemical screening results that still need to be addressed.

In this study, rock samples of Devonian to Paleogene-age, covering a wide range of lithologies (marls, and carbonates vs. siliciclastics), OM content (organic-lean vs. organic-rich), OM quality (oil-prone vs. gas-prone), and type of play (conventional vs. unconventional), were analyzed by Rock-Eval pyrolysis/TOC, LECO TOC, and reflected-light microscopy. The data sets resulting from these analyses were scrutinized and compared to show that, when quality control is inadequate, source-rock evaluation becomes problematic and interpretations can be misleading and contradictory, in addition to interpretative issues, some of which were summarized above. Our main purpose is to familiarize both experienced and inexperienced interpreters with a set of critical situations, pitfalls, and limitations that routinely occur when performing source-rock analysis using Rock-Eval pyrolysis and organic petrography, in addition to other issues related to the interpretation of results (e.g., Dembicki, 2009; Devine, 2014; Jarvie, 2014). The QA/QC issues here presented are commonly overlooked when using geochemical screening data.

2. Methods

2.1. Sample selection and preparation

The samples analyzed were carefully selected from a large in-house inventory of rocks from Devonian to Paleogene-age. The rock samples were selected based on their level of analytical complexity to demonstrate the effects of QA/QC issues on interpretation during source-rock analysis. The selected rock samples were first pulverized to ~100 μm size in sufficient quantities to allow subsampling of aliquots for the different geochemical analyses. Detailed procedures are summarized below.

2.2. Total organic carbon analysis (TOC)

TOC analyses were performed using a LECO SC-632 sulfur/carbon analyzer and a Rock-Eval 6 Turbo.

2.2.1. LECO TOC analysis

Approximately 250–500 mg of previously pulverized rock were required for LECO TOC analysis. To remove inorganic carbon in the form of carbonates, chemical treatment of the sample was required prior to analysis. To achieve this, samples were treated with hydrochloric acid (HCl) for 12–24 h with intermittent stirring. At the end of this time or when the dissolution of carbonates was observed to be complete (no effervescence with stirring or additional acid), the samples were rinsed free of the HCl solution by using distilled water. The samples were then dried to eliminate moisture prior to analysis. Prepared samples were then combusted at ~1100 °C inside the oven of a LECO SC-632 analyzer and the amount of carbon dioxide (CO_2) generated was measured by an infrared cell. Selected samples were analyzed in duplicate to QA/QC for the homogeneity of the aliquots taken and analytical precision. Precision was better than ±0.2%.

2.2.2. Rock-Eval 6 TOC analysis

For TOC analysis with a Rock-Eval 6, sample preparation is described in the next section (see Open-system programmed pyrolysis (Rock-Eval pyrolysis)). A detailed description of the TOC determination using Rock-Eval 6 instrumentation can be found in Behar et al. (2001). Briefly, for each sample 60 mg of pulverized material were first thermally decomposed in a pyrolysis oven to obtain the weight % of pyrolyzable carbon (PC) and pyrolyzable mineral-carbon. Hydrocarbons and both CO_2 and carbon monoxide (CO) were simultaneously detected via a flame ionization detector (FID for hydrocarbons) and infrared cells (IR cells for CO_2 and CO). Subsequently, each sample was combusted in an oxidation oven to obtain the weight % of residual carbon (RC) and oxidized mineral-carbon (oxiMinC). The temperature program for pyrolysis was 300 °C isothermal for three minutes followed by a 25 °C/min ramping from 300 °C to 650 °C; oxidation program was 300 °C isothermal for 30 s followed by a 25 °C/min ramping from 300 °C to 850 °C, held isothermal for 5 min at 850 °C.

2.3. Open-system programmed pyrolysis (Rock-Eval pyrolysis)

For both Rock-Eval 2 and Rock-Eval 6 analysis, samples were pulverized to ~100 μm size. If samples were in contact with oil-based mud contamination (OBM), they were extracted using organic solvents. A strong azeotropic mixture of chloroform–methanol (89:11 v/v) was used and extraction time was 24 h. After solvent extraction, the samples were dried inside an oven at 50 °C for 4 h, with a constant flow of nitrogen gas.

2.3.1. Rock-Eval 6 analysis (RE6)

Temperature programs and detection of free hydrocarbons (S1), thermally-cracked hydrocarbons (S2), and CO and CO_2 from thermal decomposition of OM (S3) are listed above and are described in detail by Behar et al. (2001). Once pulverized, 60 to 70 mg of sample were weighed and placed inside metal crucibles. The weighing effort must be precise, so that weight-associated biases can be ruled out.

2.3.2. Rock-Eval 2 analysis (RE2)

Analyses were carried out using 100 mg of 100-mesh pulverized sample and followed standard operating parameters described in Espitalié et al. (1985) and Espitalié (1986).