S_1 peak of Rock-Eval analysis: What does it represent for unconventional hydrocarbon resource assessment?

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Introduction

Capable of generating a suite of parameters (i.e. S_1, S_2, TOC, Tmax, HI and OI) from a single analysis to provide information on sedimentary organic matter richness, type and thermal maturity of a rock sample, Rock-Eval pyrolysis has probably been the most widely used analytical technique for assessing the quality and quantity of petroleum hydrocarbons associated with shale source rocks and tight reservoirs. However, the effectiveness of these apparently meaningful parameters can be affected by several factors such as sample contamination from drilling mud, sample storage and preparation as well the nature of the sample itself, which has not been made aware to many geologists and needs detailed investigation. For example, despite routine use of the Rock-Eval S_1 peak to estimate the amount of free liquid hydrocarbons present in the rock systems (Peters, 1986; Jarvie 2012), what S_1 represents chemically for particular shale or tight reservoir samples and how it is affected by the sample condition are not clear to many geologists and engineers. This study especially focuses on the effects of sample storage, preparation and contamination on the S_1 peak.

Method

As Rock-Eval analysis is a bulk rather than a compositional analytical technique, the S_1 peak is a bulk response of the instrument's flame ionization detector (FID) to the total amount of hydrocarbons released from the sample at 300°C. It does not distinguish indigenous hydrocarbons from invaded components. In the current study, we employed a compositional thermal analytical technique, thermal desorption-gas chromatography-mass spectrometry/flame ionization detection (TD-GC-MS/FID) to characterize the molecular composition of the Rock-Eval S_1 peak in an attempt to quantify the effect of contamination and sample handling/storage. In contrast to bulk quantitative results from Rock-Eval analysis, the TD-GC-MS/FID technique produces a molecular level compositional distribution of the hydrocarbons thermally released from the rock sample. This enables detection and quantification of any external contaminants, and allows identification of the compositional variation of free hydrocarbons among different samples and over time.

Results

Shown in Figure 1 are the GC-FID traces of S_1 peak for a Triassic Montney shale/siltstone core sample and a Jurassic Nordegg shale core sample from Alberta, Canada. It is clear that the Rock-Eval S_1 peak for the Montney shale/siltstone sample is mainly comprised of drilling mud additives (nC_{14} alkene and diesel) associated with mud invasion during coring. The peaks labelled as "toluene" and "solvent" are not indigenous to the Montney core but likely the result of core preparation performed before its arrival in the lab. Even for the Nordegg shale core, mud additives (i.e. nC_{12} to C_{14} n-alkenes) can account for more than 18% of the S_1 peak.

The absence of $<nC_{12}$ hydrocarbon components from the Jurassic Nordegg shale in Figure 1 indicates that the shale core sample has likely experienced significant evaporative loss to its light end hydrocarbons during core handling and storage as well as sample preparation before analysis. The effect of evaporative loss on the light hydrocarbons is better illustrated in Figure 2 where both the Rock-Eval S_1 peak values and molecular compositions are compared among a freshly prepared Ordovician Lorraine Shale core sample and the same powdered shale sample after being either stored in a sealed container or exposed to air without preservation measures. The freshly ground shale sample contains abundant hydrocarbons as light as the gaseous C_3 to C_4. However, the C_3-C_7 hydrocarbons are absent from the Ordovician Lorraine Shale sample just after a week of storage in a capped vial. In fact, there is also partial loss of higher molecular weight hydrocarbons such as C_{11} (Fig 2 middle). Moreover, significant evaporative loss of light hydrocarbons can take place within hours when the crushed shale sample is exposed to open air (Fig 2 lower). This confirms that S_1 peak from Rock-Eval analysis cannot be used to represent the free oil content of shale and tight reservoirs systems without proper calibration.

Despite their ease of evaporative loss from core, our study suggests that light oil components in shale cores may be preserved well enough for geochemical and geological assessment if appropriate analysis can be completed immediately after conventional coring at well site. This is apparent from Figure 2 (upper) where hydrocarbons as light as propane and butane are present in the Ordovician Lorraine Shale core even after 6 months of storage at ambient conditions. Had the core been analyzed immediately after coring or been preserved with waxing or freezing, more light hydrocarbons would have been detected, producing a more reliable S_1 peak for resource assessment. Extensive TD-GC-FID/MS analysis on core samples of various lithology and TOC contents indicates that the extent of evaporative loss of light hydrocarbons depends greatly on the matrix permeability and the TOC content of the shale and tight reservoir sample, as well as the oil quality (e.g. API gravity, Michael et al. ,2013).

Conclusions

Rock-Eval S_1 peak is not always representative of the crude hydrocarbons generated by source rocks. Because of potential contamination from drilling mud and evaporative loss during sample storage and preparation before lab analysis, proper correction should be applied when S_1 value is used for hydrocarbon resource characterization and assessment. The advanced TD-GC-MS/FID can complement Rock-Eval analysis to fingerprint and quantify the composition of S_1 peak, and is suggested to be carried out on selected samples as a QA/QC for Rock-Eval results.

References

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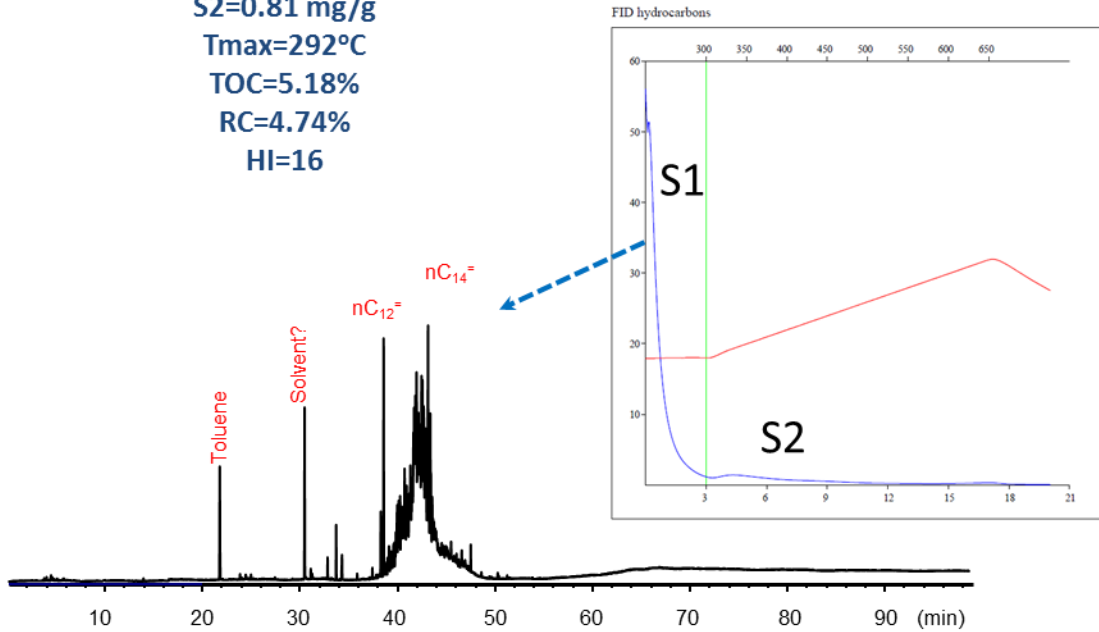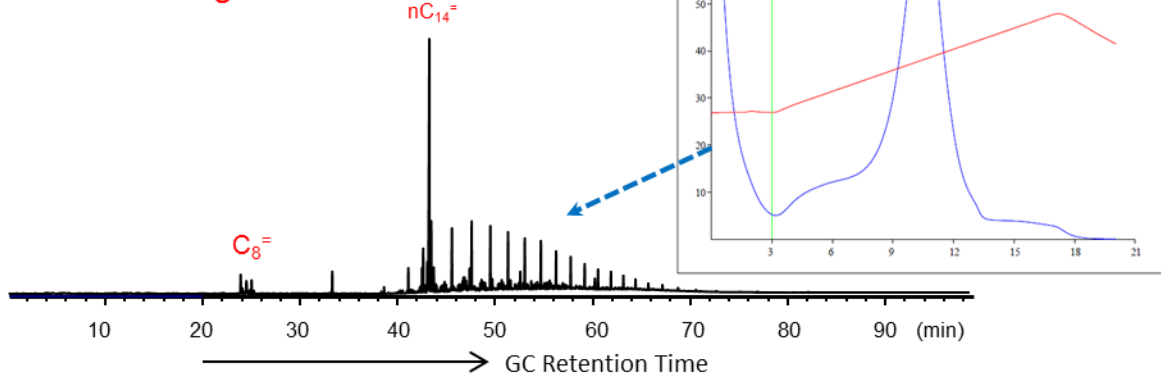
Fig1. FID-pyrograms from Rock-Eval analysis and TD-GC-FID traces showing the hydrocarbon composition of the corresponding S_1 peaks for (upper) a Triassic Montney shale/siltstone core; and (lower) a Jurassic Nordegg core sample. $nC_{12}^=$ and $nC_{14}^=$ are alkenes used as drilling mud additives.
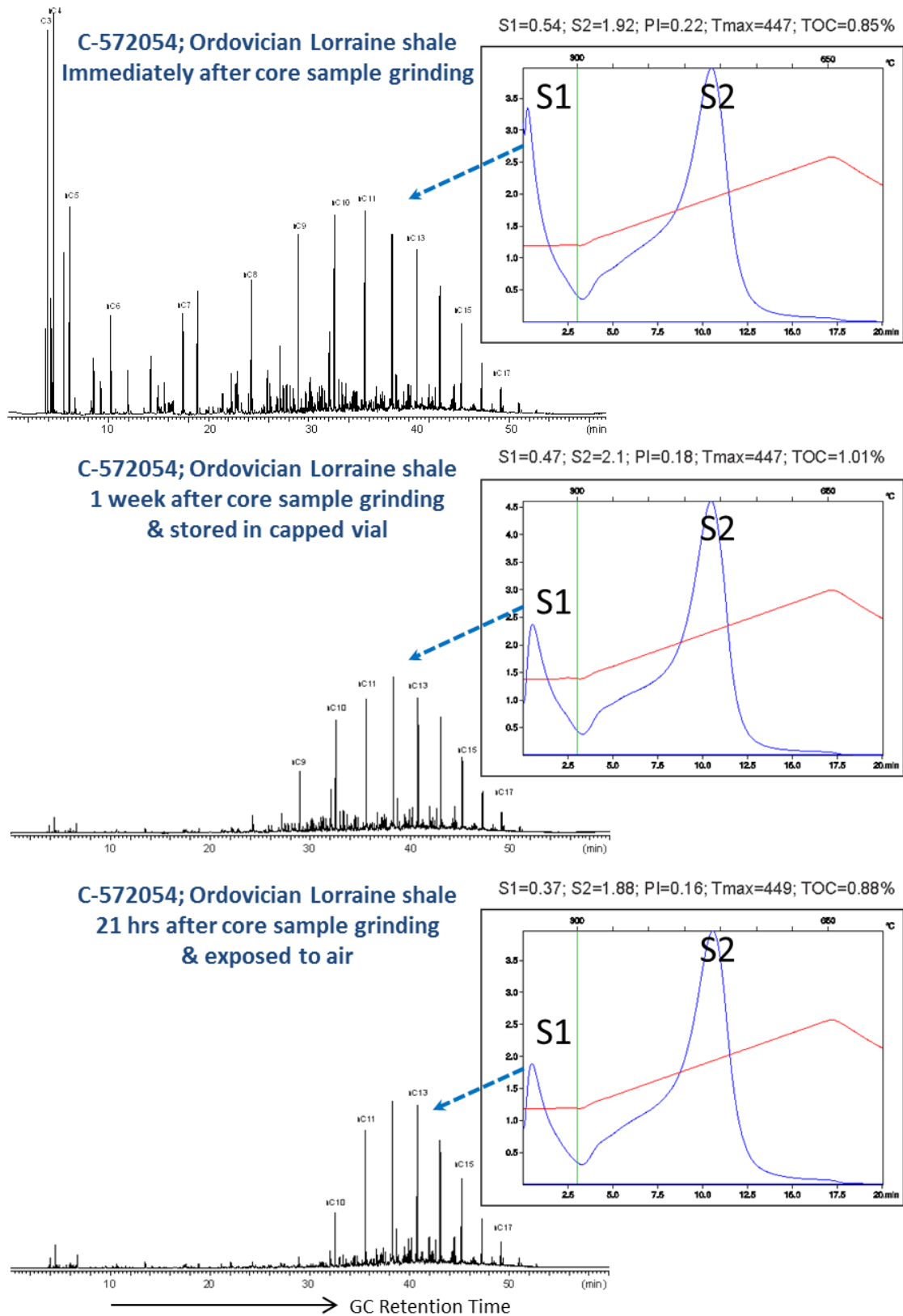
Fig 2. TD-GC-FID traces showing the composition of free hydrocarbons represented by Rock-Eval S_1 peak for a Ordovician Lorraine shale core sample (upper) immediately after grinding; (middle) 1 week after grinding and stored in sealed container; and (lower) 21 hours after grinding and exposed to air. Note that the core was taken during water well drilling and stored at ambient conditions for 6 months before lab analysis.