PS Loss of Organic Carbon from Source Rocks During Thermal Maturation: Past, Present, and Future*

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Abstract

Much of this poster focuses on the work of Daly and Edman (1987) that used both theoretical and experimental methods to demonstrate the loss of organic carbon from source rocks during thermal maturation. Then, using the theoretical and experimental data generated from this study, a simple technique that assumes only a basic knowledge of organic matter type and thermal maturity level was developed for calculating initial TOC contents from measured residual TOC values. The purpose of this work was to clearly document the magnitude of organic carbon loss during maturation and provide a straightforward method for restoring initial TOC levels during a basin evaluation program. This study therefore represents one of the earliest accounts documenting the importance of TOC loss during maturation. At the time this work was done, although decreases in pyrolysis yields during thermal maturation were generally factored into source rock evaluation, reductions in TOC were often ignored. Unlike earlier work such as that of Dow (1977) and Durand-Souron (1980), which indicates mixed opinions regarding the significance of TOC reduction during maturation and expulsion, Daly and Edman (1987) combined and compared the results of theoretical calculations derived from a van Krevelen diagram with the results of two different experimental approaches both of which used a Leco carbon analyzer to measure TOC and a Rock-Eval to provide pyrolysis data. This combined approach indicates that organic carbon loss during generation and expulsion may be as high as 70% in Type I kerogen, is approximately 50% in Type II kerogen, and ranges from 12% to 20% in Type III kerogen. In addition, the combined approach provides a simple technique for calculating initial TOC contents from measured residual TOC values that extends beyond the limited thermal maturity levels (end of the oil window, approximately 1.4 %Ro where pyrolysis yields become uniformly low) of charts yielding original kerogen quality published by Orr (1983) and Espitalie et al., (1984). TOC content is thus the least subjective and most quantitative measurement that can be made in evaluating rocks at elevated maturity levels, and, by incorporating the method used by Daly and Edman (1987), explorationists could have obtained a more accurate assessment of volumetric calculations regarding the amounts of hydrocarbons generated in areas that include mature and overmature strata. Based on the work of Daly and Edman (1987), TOC loss during thermal maturation was quickly incorporated into Platte River's BasinMod 1D basin modeling program. Another notable development during this same time period includes among the first uses of well logs to identify and calculate total organic carbon in organic-rich rocks (Passey et al., 1990). The methods and concepts developed in the 1980's and 1990's have often been updated and modified to fit the needs of exploration and production in

unconventional reservoirs. Additional methods for the back calculation of original TOC have been developed, and work continues to be done on the use of well logs to determine TOC content, thermal maturity, and porosity. For example, the skeletal density of kerogen varies with its maturity, and the typical range is from 1.1g/cc for low maturity kerogen up to 1.6g/cc for high maturity kerogen. Another point of interest is where does the TOC that is lost during generation and maturation go? Among the developments since Daly and Edman (1987) is more detailed work on the type of hydrocarbon (oil, volatile oil, condensate/wet gas, dry gas etc.) that is generated and expelled at a given maturity level. Furthermore, assuming 35% carbon loss due to generation, there is about a 9.80% porosity increase due to organic carbon decomposition that creates space for hydrocarbon storage (Jarvie, 2006). The creation and assessment of organic porosity is a focal point of interest for unconventional resource plays (Katz and Arango, 2018). Rob Reed did some of the first work on documenting organic porosity with an SEM of the Barnett Shale he took in 2007. Loucks et al., 2009 followed up on this work by providing a model for the development of organic nanopores as a function of increasing thermal maturity in organic-rich mudstones. With regard to future work, below are some of the topics that merit further investigation:

1) There will likely be continued work on the origins of organic porosity and improvements in back calculation of original TOC.
2) It is also likely that the use of logs, particularly NMR T1, T2 and diffusion data will continue to be used to characterize porosity, subsurface fluid types, saturations, and wettability.
3) While 3D seismic data is being used routinely by numerous companies to predict the mechanical properties and density of various formations, there has yet to be a direct link made between TOC loss during organic carbon conversion and the associated changes in rock properties (House, 2018).

Loss of Organic Carbon from Source Rocks During Thermal Maturation: Past, Present, and Future

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Past

Daly and Edman (1987) combined and compared the results of theoretical calculations derived from a van Krevelen diagram with the results of two different experimental approaches both of which used a Leco carbon analyzer to measure TOC and a Rock-Eval to provide pyrolysis data.

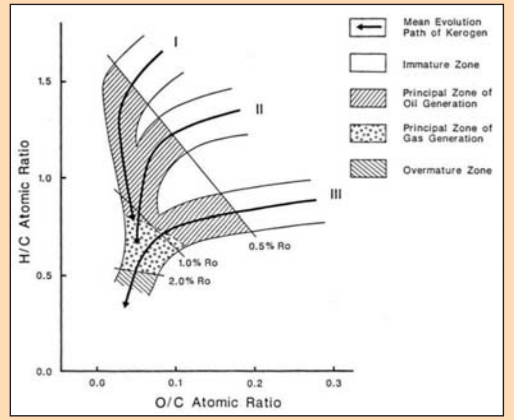

Figure 1. Van Krevelen diagram used for theoretical calculations of TOC loss.

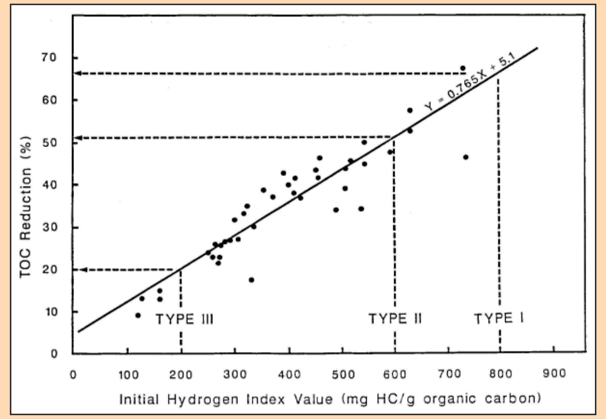

Figure 2. TOC loss (as a % of initial TOC value) vs. HI.

The theoretical calculations derived from a van Krevelen diagram (Figure 1) suggest TOC reductions during generation and expulsion are 70% for type I kerogen, 50% for type II, and 12% for type III. Then, in the first experiment that showed estimated reductions in organic carbon content induced by thermal maturation, TOC contents of 40 immature rocks were measured with a Leco carbon analyzer prior to Rock-Eval pyrolysis and again after pyrolysis. The TOC loss for each sample (as a percentage of initial TOC value) is plotted against the corresponding hydrogen index value in Figure 2. A linear regression of the data in Figure 2 suggests that at full maturity the TOC reductions are 66% for type I kerogen, 51% for Type II kerogen, and 20% for type III kerogen. The measured loss of organic carbon from type III kerogen is greater than the predicted loss, which probably reflects the relatively large amount of carbon dioxide generated by type III kerogen that was not accounted for in the model.

In a second experiment, seven splits of each of three immature rock samples were pyrolyzed in a Rock-Eval. As in the previous experiment, TOC values were measured both before and after pyrolysis. A different maximum pyrolysis temperature was used for each of the seven splits in order to follow the rate of carbon loss with increasing thermal alteration. The results are shown in Figure 3. In each case, the rate of carbon loss is low to begin with, increases rapidly at moderate pyrolysis temperatures and decreases again at high temperatures. This pattern is similar to that produced by the hydrogen index values of naturally matured kerogens.

In addition, this combined approach provides a simple technique for calculating initial TOC contents from measured residual TOC at elevated maturity levels. This technique incorporates

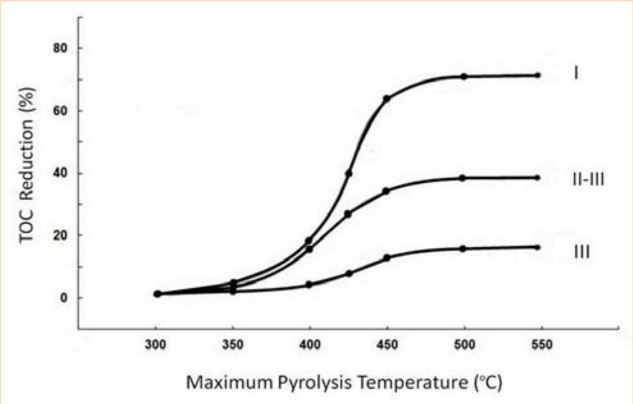

Figure 3. Carbon-loss curves for three sediments containing different types of kerogen.

the maximum loss in organic carbon (ΔC) for a particular kerogen type and the extent of hydrocarbon generation (TR). Values for kerogens with intermediate compositions can be derived in a similar manner.

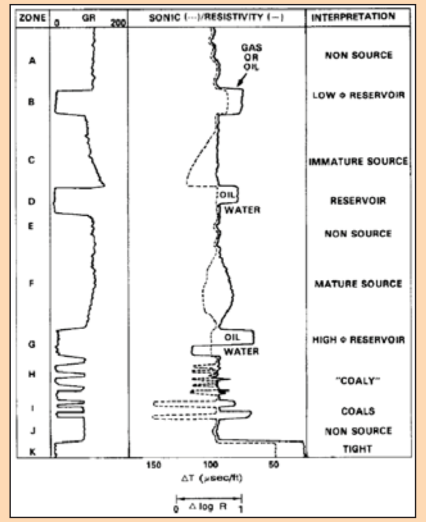

Figure 4. Schematic guide for the interpretation of a wide variety of features observed on Δlog R overlays. From Passey et al., (1990).

TOC content is thus the least subjective and most quantitative measurement that can be made in evaluating rocks at elevated maturity levels, and, by incorporating the method used by Daly and Edman (1987), explorationists can obtain a more accurate assessment of volumetric calculations regarding the amounts of hydrocarbons generated in areas that include mature and overmature strata. The complete Daly and Edman (1987) PDF manuscript and methodology will soon be available on line. Although Cooles et al., (1986) recognized that the organic carbon content of mature source rocks is much less than their initial immature values, their algebraic model of TOC assumes residual carbon (inert carbon) remains constant during the main phase of petroleum generation. This is an assumption that Burnham (1989) has stated is good for type II and III sources (less than 10-20% error) but is poor for type I (50% error).

Based on the work of Daly and Edman (1987), TOC loss during thermal maturation was quickly incorporated into Platte River's BasinMod 1D basin modeling program.

Another notable development around this same time period includes among the first uses of well logs to identify immature and mature source rocks (Figure 4; Passey et al., 1990). However, these log calculations (Schmoker, 1981; Meyer and Nederlof, 1984; Herron 1991; etc.) only serve to identify source rock intervals and do not provide quantitative methods to calculate initial TOC.

Present

There appears to be a gap in the published literature between about 1987 and 2006 regarding updating methods to calculate TOC reduction with increasing maturity although it is likely these computations were included in basin modeling programs used during this time period. However, as interest in unconventional plays increased, Jarvie et al., (2007) applied the equations of Claypool (Peters et al., 2006) to calculate initial TOC in unconventional plays. As unconventional plays became more prevalent and commercially attractive, interest in TOC loss evolved and changed emphasis. Specifically, considerable research has been conducted regarding how conversion of organic matter into hydrocarbons creates additional intraparticle kerogen porosity in which oil and gas can be stored (Romero-Sarmiento et al., 2013). Almost simultaneously, Jarvie (2006) and Reed (2007) used two different methods (Figures 5 and 6) to show that pore space is created in organic matter as TOC decreases with the generation and expulsion of hydrocarbons. According to Romero-Sarmiento et al., (2013), organic porosity starts to appear as soon as kerogen transformation begins.

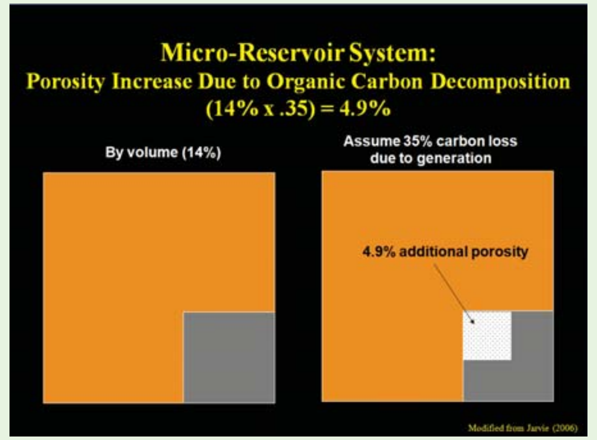

Figure 5. If a rock sample is 14% organic carbon by volume (7 wt.%), then assuming 35% carbon loss upon generation, then there is a 4.9% porosity increase in the organic carbon. From Jarvie (2006).

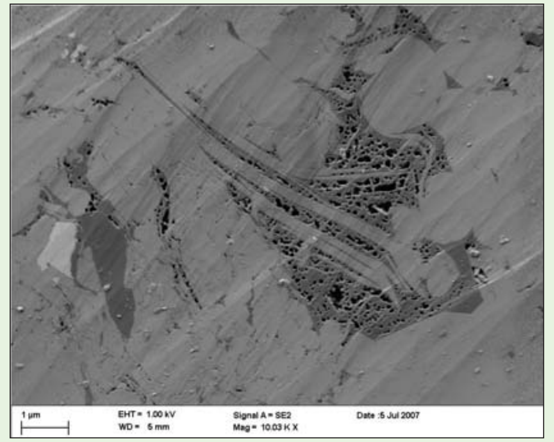

Figure 6. SEM image from the Barnett Shale showing microporosity. From Reed (2007).

In order to enhance earlier methods for determining original TOC, Romero-Sarmiento et al., (2013) developed a new approach for determining TOC_o using an inversion procedure in a petroleum system modeling analysis based on observed TOC, maturity, and a detailed kerogen kinetic scheme. Their 3D model (TemisFlow®) computes organic contributions to shale porosity and TOC variations through time as a result of both thermal cracking and expulsion (Figures 7 and 8). However, Katz and Arango (2018) have found many contradictions in the existing literature regarding where and when organic porosity develops, the influence of organic carbon content and kerogen type, its mode of formation etc. These authors also found that organic pore size often affects the role organic porosity plays in liquid-rich plays (Figure 9). Finally, with increasing thermal maturity, kerogen becomes denser, harder and more brittle (Bousige et al., 2016). There are a number of different technologies that can detect these changes. Therefore, it is important to use a variety of tools to investigate the extent of "sweet spots" in unconventional plays.

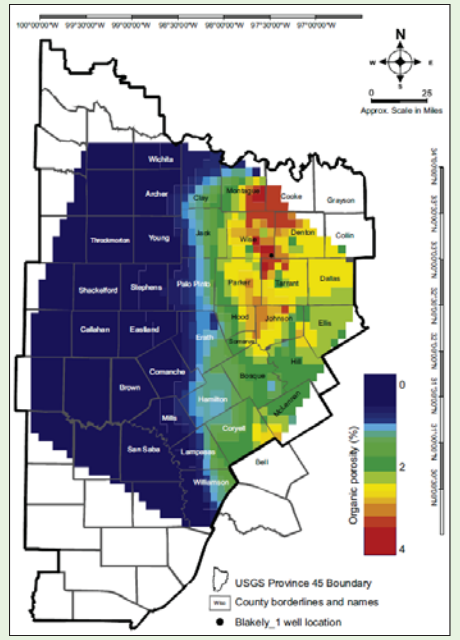

Figure 7. Computed organic porosity in the Lower Barnett Shale. From Romero-Sarmiento et al., (2013).

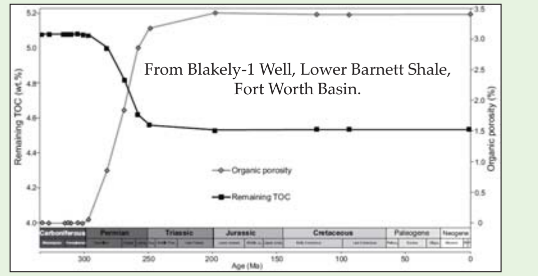

Figure 8. Calculated evolution of TOC and organic porosity through time. From Romero-Sarmiento et al., (2013).

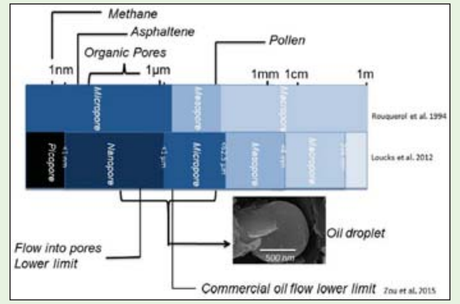

Figure 9. Pore size classification scheme and comparison. From Katz and Arango (2018).

Future

New methods from multiple disciplines are being developed, and advances in geochemistry need to be included in calibrating new data sets from the various disciplines used to identify TOC loss and its relationship to maturity, organic porosity creation, and the types of hydrocarbons present in the organic pores.

In addition to geochemical approaches, advanced wireline logs (Anand and Ali, 2016) help in determining the density and porosity of organic matter and resolving the signatures of different fluids such as bitumen and hydrocarbons in organic matter and inter-particle organic pores and clay-bound and inter-particle water.

While analysis and inversion of carefully acquired modern 3D seismic data is capable of estimating porosity, TOC, matrix strength and any property affecting the behavior of seismic waves, the latest work on rock property changes occurring as hydrocarbons mature and are expelled has not yet specifically addressed the changes due to organic matter transformation (House and Edman, 2019).

This poster is dedicated to the memory of Alan Daly, a splendid colleague and an outstanding geochemist.