# Final Report
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## Introduction

Vitrinite reflectance (%$R_o$) is arguably the most widely cited measure of the thermal maturity of a potential source rock, as well as an important parameter used in thermal/burial history modeling of sedimentary basins (Dow, 1977; Tissot and Welte, 1984; Mukhopadhyay, 1994). Nevertheless, it is increasingly apparent that the use of vitrinite reflectance as an indicator of source rock maturity and/or paleotemperature assessment can suffer from two shortcomings, retardation and suppression, both of which result in erroneous maturation estimates. Indeed, suppression of vitrinite leads to an underestimation of thermal maturity and, therefore, an underestimated burial depth (Price and Barker, 1985; McTavish, 1978, 1998; Samuelsson and Middleton, 1998; Lo, 1993; Carr, 1999, 2000). Sediments that accumulate in reducing marine environments and, consequently, are rich in liptinite- or exinite-dominated (hydrogen-rich) kerogens appear to be most prone to suppression (Price and Barker, 1985).

It is clear that the inability to recognize suppression/retardation of vitrinite or recycled vitrinite presents a problem that must be recognized to fully understand the maturation level and the thermal/burial and perhaps expulsion history of a potential source rock. The completed research addressed the relative accuracy of vitrinite reflectance data from Upper Devonian black shale units of western New York State. The results, though somewhat ambiguous, indicates that these black shale deposits have been subjected to vitrinite suppression, although the amount of suppression remains unknown.

## Approach

Twenty-seven sample couplets of coalified woody material (i.e., plant stems, bark) and host black shale were collected from Upper Devonian black shale units of western New York State, including the Middlesex Shale, Rhinestreet Shale, Pipe Creek Shale, and Dunkirk Shale, specifically from Chautauqua and Erie counties. We have been unable to collect enough coalified plant remains from the Marcellus Shale, but this work is continuing. Our approach was predicated on the view that vitrinite-rich coal and coalified material, being less prone to suppression (Bostick and Foster, 1975), yields more accurate maturity values. However, we also recognized that coal and coalified plant material in black shale that accumulated during marine transgressions, as likely occurred during deposition of some Devonian black shale units (e.g., Baird and Brett, 1991; Lash, 2006), can be affected by suppression. The collected sample couplets were sent to a commercial lab where vitrinite reflectance, Rock-Eval parameters, and total organic carbon (TOC) content were determined.

## Discussion

Coalified plant remains and disseminated vitrinite recovered from shale appear to record similar levels of thermal maturity, suggesting a lack of suppression. For example, Rock-Eval $T_{max}$ values of both sample sets are essentially identical; coalified plant debris = $441.3^{o}$ C ($\pm$ $3.8^{o}$ C); shale = $441.9^{o}$ C ($\pm$ $1.9^{o}$ C). Similarly, the measured mean vitrinite reflectance of both sample sets is the same; coalified plant debris = 0.76% (± 0.06); shale = 0.78% (± 0.08). However, the likelihood of suppression is suggested by scatter plots of $\%R_o$ and Rock-Eval $T_{max}$ that show a random distribution of data (Fig. 1), quite unlike the expected positive correlation reflecting increasing thermal maturity (e.g., Dembicki et al., 1983; Peters, 1986; Hunt, 1996).

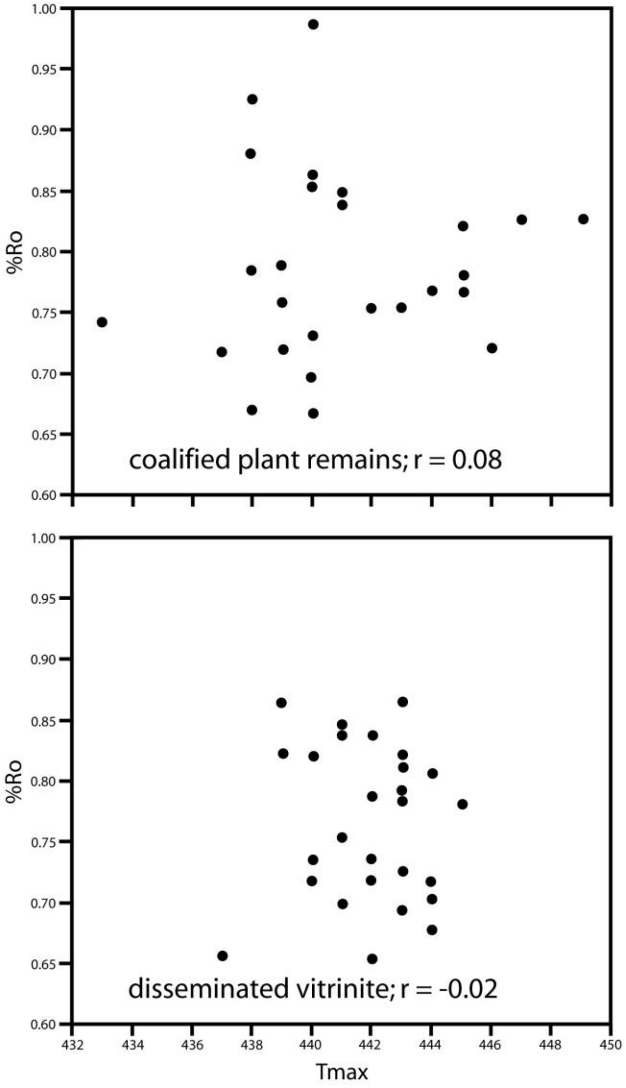

**Figure 1:** ***Plots of Rock-Eval $T_{max}$ versus $\%R_o$ for coalified plant remains and disseminated vitrinite in shale samples collected from the same location as the plant remains. Note the lack of any statistically valid relationship of the two parameters.***

Interestingly, there is no consistent relationship of the vitrinite reflectance of coalified woody material and the host black shale from which the coalified plant remains were collected (Fig. 2). Specifically, essentially equal numbers of sample couplets are defined by a higher reflectance of the plant remains as a characterized by host shale reflectance in excess of that of coalified plant remains (Fig. 2). This relationship is especially important because it negates the possibility of defining an algorithm capable of estimating a true reflectance from measured reflectance.

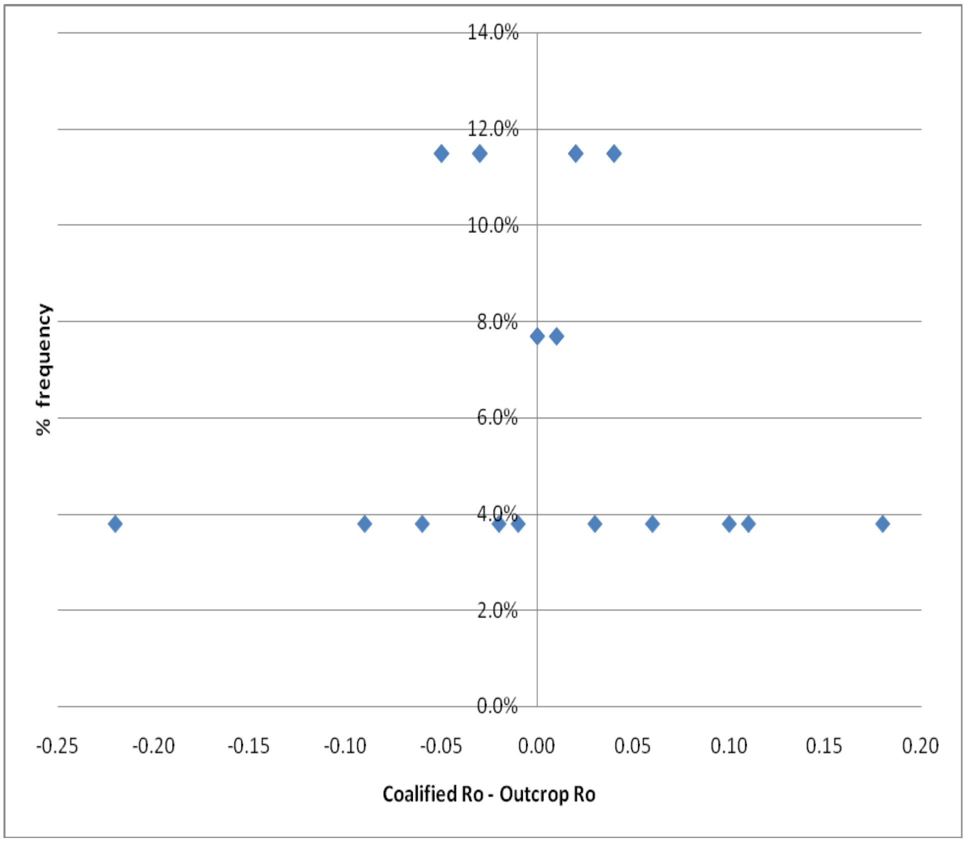

**Figure 2:** ***Frequency plots of the difference between the vitrinite reflectance of a coalified plant sample and the host shale (outcrop) sample. Note the lack of any consistent relationship.***

Results of the NYSERDA research appear to confirm what some have suggested about chemical differences between vitrinites formed in humic coals and coaly shales compared with those formed in shales with large amounts of sapropelic type II kerogen (Price and Barker, 1985). Black shale deposits of the Appalachian Basin would be classified as the latter. Teichmüller (cited in Hunt, 1996) has pointed out that wood remains in organic-rich shales like those studied in the NYSERDA-funded work have a much lower reflectance than vitrinite grains sampled from accompanying normal coals and organic-lean shale and siltstone. Tiechmüller argues that differences in measured $\%R_o$ are caused by variations in source material and early diagenetic effects. Indeed, George et al. (1994) have pointed out that marine-influenced coal deposits display vitrinite suppression. The significance of this to the present work is two-fold; (1) the Devonian black shales of western New York (and perhaps the entire basin, for that matter) would have been buried deeper than heretofore modeled and (2) the units would have entered the oil window sooner than predicted.

Future research efforts stemming from the NYSERDA-funded investigation will address collecting organic-lean, gray shale samples for %$R_o$ analysis. Such deposits, which may not have experienced the level of diagenetic alteration as that which affected the black shale (e.g., George et al., 1994), may provide a more accurate means of assessing the thermal maturity of immediately over- and underlying black shale.

## Thermal/Burial Modeling

We have recently started to model the burial history of the Devonian shale succession in conjunction with Platte River Associates, Boulder, Colorado. As an example, the burial/thermal history of the Upper Devonian Dunkirk Shale was modeled using the Platte River BasinMod1D software package. We used well API# 22531, a deep test well in central Chautauqua County, western New York, ~ 20 km south of the Lake Erie shoreline. The well log was subdivided into 17 units (Fig 3), each of which was defined in terms of lithologic proportions based on analysis of the gamma-ray and density logs. For each of the 17 units, physical properties such as porosity and thermal conductivity are based on the proportions of various end-member lithologies, including sandstone, shale, black shale, limestone, siltstone, and coal. Our model assumes steady-state heat flow and that the modern geothermal gradient of 28.13$^o$C/km, calculated by use of bottom hole temperatures, has existed throughout the life of the basin. Basement heat flow used in the model is 49 mW/m$^2$ and was assumed to be constant through time; the modern average surface temperature of 9$^o$C was also used in this model. Future modeling will vary a number of parameters, including heat flow, geothermal gradient and paleo-surface temperature, over time. The described model does not take into account elevated heat flow that could have been related to activity along the Rome Trough. However, the location area of this study is probably far enough from the trough so that this would not have been a factor. The model uses the 0.64% $R_o$ of the Dunkirk Shale for calibration and makes the reasonable assumption that peak burial depth was reached by the end of the Permian, ~250 MY. Finally, the model includes the formation of a Pennsylvanian forebulge early in the Alleghanian organic cycle (Lash and Engelder, 2007). The deep test well model suggests that the Dunkirk Shale entered the oil window at about 270 MY and that the Marcellus Shale had entered 10 MY earlier (Fig. 3). The peak burial depth of the Dunkirk Shale in this part of the basin is estimated to be 2.7 km (Fig. 3). Interestingly, the model suggests that no unit of the test well entered the gas window (Fig. 3). It is important to emphasize that thermal models are only as accurate as the calibrating data, in this case, the measured %$R_o$ of the Dunkirk Shale. We expect the begin this type of work in earnest in the latter half of 2008 and into 2009 as a means of assessing the level of thermal stress sustained by potential Devonian and Ordovician source rocks in western NewYork.

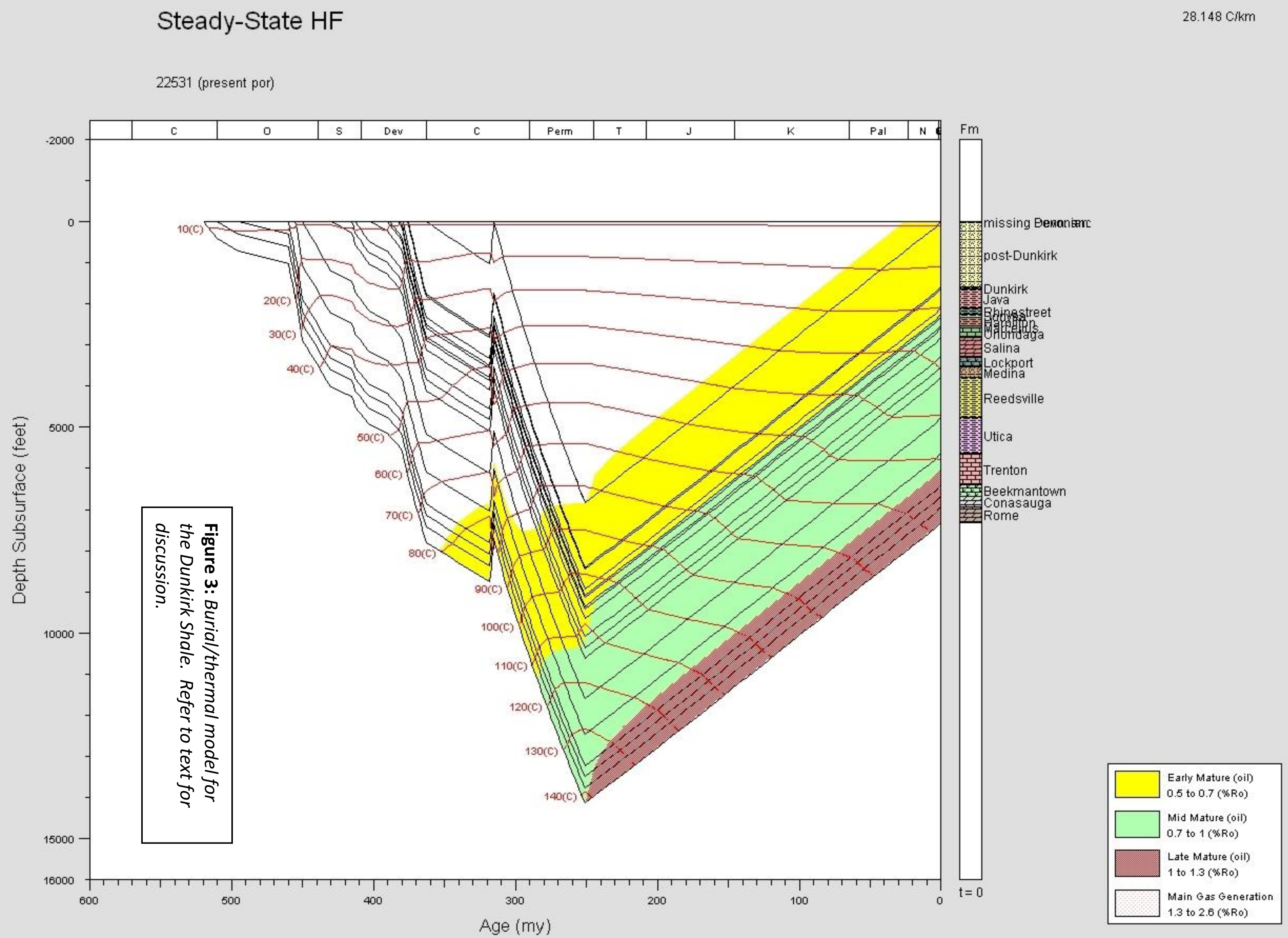

**Figure 3:** *Burial/thermal model for the Dunkirk Shale. Refer to text for discussion.*

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