

# EA Loss of Organic Carbon from Source Rocks During Thermal Maturation\*

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## Abstract

Decreases in pyrolysis yields during thermal maturation are generally factored into source-rock evaluations, however, decreases in total organic carbon (TOC) content are often ignored even though they may also be significant. For example, both theoretical calculations derived from a van Krevelen diagram and experimental pyrolysis measurements indicate organic carbon loss during generation and expulsion may be as high as 70% in type I kerogen and is approximately 50% in type II kerogen. TOC reduction is lowest in type III kerogen, but estimated losses still range from 12% to 20%. TOC losses during maturation are also supported by two recent field studies that examined Cretaceous units of the Rocky Mountain region. Empirical data from one these field studies indicate TOC reductions of 35% in mature source intervals containing type II-III kerogen.

Post-maturation TOC contents, however, can easily be restored to their initial values by using simple calculations that assume only a basic knowledge of organic matter type and thermal maturity level. In contrast, failure to adjust source-rock evaluations for TOC losses, particularly in the case of oil-prone type I and type II kerogen, can lead to errors in volumetric calculations of hydrocarbons generated. In the hypothetical basin evaluation described in this article, hydrocarbon yields were underestimated by 55% when TOC losses were not included in the volumetric assessment. By recognizing the potential for TOC reduction during maturation, the necessary corrections can be made, resulting in a more accurate and optimistic assessment of hydrocarbon potential.

## Introduction

Source-rock evaluation of horizons that are at advanced stages of thermal maturation is hindered by uncertainty regarding original hydrocarbon-generating potential of the organic matter. Although charts have been published (Orr, 1983; Espitalie et al., 1984) that allow estimation of original quality from measured organic content, pyrolysis yield, and thermal maturity level, this approach is not applicable much beyond the end of oil generation (approximately 1.4% Ro) where pyrolysis yields become uniformly low. At higher maturity levels, source-rock evaluation relies heavily upon (1) measurement of total organic carbon (TOC) content, (2) inferences drawn from optical analysis of organic matter, and (3) whatever information regarding organic preservation can be implied from depositional environment analyses.

TOC content is thus the least subjective and most quantitative measurement that can be made in evaluating rocks at elevated maturity levels, and consequently is a key parameter in estimating original hydrocarbon-generating capacity in such units. A literature review, however, indicates mixed opinions regarding the significance of TOC reduction during maturation and expulsion. Dow (1977) calculated that algal, liptinitic, and humic kerogens would undergo weight losses of 66%, 40%, and 16%, respectively, during a maturity increase equivalent to a vitrinite reflectance range of 0.6%-3.0% Ro. Durand-Souron (1980) used thermogravimetric analyses in an inert atmosphere to measure weight losses of approximately 75%, 65%, and 30% in kerogen types I, II, and III during simulated maturation. Assuming kerogen is composed principally of organic carbon, these weight loss estimates and measurements suggest substantial loss of carbon during hydrocarbon generation. In contrast, Hunt (1979) considers that the quantity of organic matter converted to oil in the source bed ranges from a few percent to about 15 percent.

Therefore, the purpose of this article is 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. By incorporating the method outlined, explorationists can obtain a more accurate assessment of original hydrocarbon-generating potential in areas that include mature and over-mature strata.

### **Theoretical Estimates of Organic Carbon Reduction**

The van Krevelen diagram shown in [Figure 1](#) provides a graphical representation of the changes that occur in the H/C and O/C atomic ratios of kerogens during progressive maturation. The maturation pathways of three reference kerogens (I, II, and III) and superimposed iso-reflectance lines of Durand and Monin (1980) provide a means for making some basic calculations of organic carbon loss. We will consider the H/C changes that occur within the zone of hydrocarbon generation, i.e. between 0.5% and 2.0% Ro. These calculations do not take into account organic carbon released in the form of carbon dioxide or hydrogen released in the form of water. Although production of carbon dioxide and water is relatively minor in types I and II kerogen during hydrocarbon generation, considerably larger volumes are lost from type III kerogen in the zone of oil generation (Tissot et al., 1974). Consequently, the estimates of carbon loss from type III kerogen will be too low.

The following assumptions, which can readily be modified to accommodate oils and gases of differing compositions as well as kerogens of intermediate composition, are made for the purpose of simplifying the calculations:

- 1) At 0.5% Ro, the H/C atomic ratios of kerogen types I, II, and III are approximately 1.50, 1.25, and 0.8, respectively ([Figure 1](#)).
- 2) Oil is generated at H/C values above 0.75, and methane is generated at lower values. All hydrocarbon generation ceases when the H/C ratio reaches a value of 0.5 ([Figure 1](#)).
- 3) The oil generated has an average composition. Hunt (1979) suggests an H/C value of 1.85 for a typical oil.
- 4) Methane (H/C=4.0) is the only gas generated, i.e. there is no generation of wet gas.

The H/C ratios of kerogen types I, II, and III at 0.5% Ro are used to assign hydrogen and carbon contents to the parent kerogens in [Figure 2](#). Oil generation is simulated by removing hydrogen and carbon atoms in the ratio 1.85:1 from the parent kerogens until the H/C ratios approach 0.75. Additional hydrogen and carbon atoms are removed in the ratio 4:1 to account for methane generation until the H/C ratio of the kerogens reaches 0.50. The total number of carbon atoms removed from each kerogen is expressed as a percentage of the initial carbon content.

The results suggest that TOC reductions during generation and expulsion are 70% for type I kerogen, 50% for type II, and 12% for type III. The reductions for oil-prone type I and II kerogens are particularly significant because they indicate the measured TOC contents of mature and over-mature rocks containing these kerogens will be very much lower than their pre-maturation values.

### **Experimental Simulation of Organic Carbon Reductions**

In order to experimentally verify the 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. Pyrolysis simulates the natural generation of hydrocarbons from kerogen during burial (Espitalie et al., 1977), and the maximum pyrolysis temperature employed (550°C) is sufficient to break all but the strongest bonds within the kerogen. The results demonstrate that pyrolysis measurably reduced the TOC values in all cases.

The TOC loss for each sample (as a percentage of initial TOC value) is plotted against the corresponding hydrogen index value in [Figure 3](#). Hydrogen index is a convenient measure of kerogen composition that is directly correlatable to H/C atomic ratio (Espitalie et al., 1977). Although considerable scatter is present, the data exhibit a linear trend of increasing organic carbon loss with increasing hydrogen index value. Possible causes of the scatter might include retention of some pyrolyzed hydrocarbons by the mineral matrix, incorporation of immature heavy bitumens in the pyrolysis yield, variable loss of carbon as carbon dioxide, and variable loss of sorbed water from the sediments. A linear regression of the data suggests that the following TOC reductions occur by the stage of full maturity:

<b><u>Kerogen in Sediment</u></b>	<b><u>TOC Reduction (<math>\Delta C</math>)</u></b>
Type I	66%
Type II	51%
Type III	20%

The results largely support the theoretical estimates previously discussed. The match is surprisingly good considering the H/C ratios of products evolved during anhydrous Rock-Eval pyrolysis are likely to be much more variable than the single values chosen for oil and gas in the models. The measured loss of organic carbon from type III kerogen is greater than the predicted loss, and this discrepancy 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 4](#). 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 ([Figure 5](#)). The strong similarity between the data trends in [Figure 4](#) and [Figure 5](#) is expected given that (1) pyrolysis closely simulates natural maturation, and (2) carbon reduction and hydrocarbon generation are directly related.

## Field Studies

It is difficult to measure maturation-induced TOC reductions in the field because organic content is generally quite variable over the distances or depths normally associated with significant maturation increases. Two recent field studies, however, provide data that support the theoretical and experimental estimates discussed in the preceding sections.

Burtner and Warner (1984) investigated the Mowry and Skull Creek shales from a number of Laramide basins in the northern Rocky Mountain region. Formation of the basins postdated deposition of the shales that mainly contain type II-III kerogens. They found that TOC values are anomalously low in the deepest and most mature portions of the basins and concluded that the organic carbon content was reduced by hydrocarbon generation and release of carbon dioxide. Burtner and Warner estimate (p. 462) that TOC reductions of approximately 35% have occurred in parts of the Powder River and Green River-Washakie basins. This figure is consistent with the theoretical and experimental estimates for type II-III kerogen.

In a second field study, Clayton and Bostick (1985) sampled a thin bed of Upper Cretaceous Pierre Shale within 2 meters of its contact with an igneous dike. The organic matter in the unaltered portion of the bed comprises poor type III kerogen (type IV of some authors) with hydrogen index values of only 60-80. Vitrinite reflectance increases towards the dike from 0.4% Ro in the country rock to 3.3% Ro at the contact, thus an extensive maturity range from immature to over-mature is represented. TOC values decrease 25% between 0.4% Ro and 1.4% Ro, a notable loss given the poor quality of the kerogen. In addition, the rock density was found to be uniform over the sampled interval, proving that the measured TOC reduction is due to loss of organic matter and not to changes in the mineral matrix. Clayton and Bostick (1985) consider it probable that substantial evolution of carbon dioxide took place as the rocks were heated by the dike. For that reason, the TOC loss associated with hydrocarbon generation was probably closer to the 10% loss that would be predicted from [Figure 3](#).

## TOC Adjustments and Application to Exploration

Using the theoretical and experimental data previously discussed, a simple technique for calculating initial TOC contents from measured residual TOC values was developed. This technique incorporates the maximum loss in organic carbon ( $\Delta C$ ) for a particular kerogen type and the extent of hydrocarbon generation ( $F$ ). The method also assumes a minimal knowledge of kerogen type and present maturity level. The experimental data in [Figure 3](#) suggest that  $\Delta C$  values of 0.65, 0.50, and 0.20 are typical of type I, II, and III kerogen, respectively. For various kerogen-maturity combinations,  $F$  can be approximated from the hydrogen index (HI) curves in [Figure 5](#) using the following relationship:

$$F = (HI_{\text{initial}} - HI_{\text{residual}})/HI_{\text{initial}} \quad (\text{i})$$

Immature organic matter will thus have  $F=0$ , while fully mature organic matter will have  $F=1$ .

Initial TOC contents can then be calculated from measured residual values using:

$$TOC_{\text{initial}} = TOC_{\text{residual}}/(1 - (F\Delta C)) \quad (\text{ii})$$

Values for F and FΔC that are appropriate for types I, II, and III kerogen over a range of maturity levels are shown in [Table 1](#). Values for kerogens with intermediate compositions could be derived in a similar manner. It can be seen from equations (i) and (ii) that low maturity source beds (F near zero) will have TOC contents that are virtually unchanged from their original values, while very mature horizons (F near 1) may have substantially reduced TOC levels.

Using the concepts developed in the first two equations, equation (iii) can then be used to calculate the quantity of hydrocarbons generated by rocks containing organic matter of known type and thermal maturity:

$$\text{mg HC/g rock} = \text{TOC}_{\text{initial}} \times F \times \text{HI}_{\text{initial}} = \text{TOC}_{\text{residual}} / (1 - (F\Delta C)) \times \text{HI}_{\text{initial}} \quad (\text{iii})$$

The units of this equation are parts of hydrocarbons per thousand parts of rock.

An example of the use of equations (ii) and (iii) in the source-rock evaluation of a hypothetical basin-wide source unit is shown in [Figure 6](#). It is assumed that the character of the kerogen in the unit and the present TOC and thermal maturity levels are known through either direct measurement or extrapolation.

Comparison of [Figure 6c](#) and [Figure 6d](#) indicates that the corrected TOC contents are similar to or slightly higher than the measured TOC contents in the southeastern part of the basin. This could be predicted given that most of the rocks there contain immature and marginally mature type III kerogen ([Figure 6a](#) and [Figure 6b](#)). However, corrected TOC values in the remainder of the basin are considerably higher than the measured values because the rocks range from mature to over-mature and contain type II kerogen.

The predicted yields of hydrocarbons per unit of rock based on measured and corrected TOC levels are shown in [Figure 6e](#) and [Figure 6f](#), respectively. While the northern part of the basin is the more favorable from the aspect of source conditions in both cases, high to very high hydrocarbon yields (>10 mg HC/g rock) are considerably more widespread when corrected TOC values are used in the calculations. If the source unit is assumed to have a uniform thickness throughout the basin, the total increase in hydrocarbon yield is approximately 55%.

Measurements or estimates of organic content, type, and thermal maturity are often combined as shown in [Figure 6e](#) to calculate the volume of hydrocarbons generated in a particular basin and to help rank the petroleum potential of several basins. This example demonstrates that exploration decisions based on volumetric calculations of hydrocarbons generated may be seriously in error if residual rather than initial TOC levels are used. The technique for restoring original TOC levels outlined here produces a more realistic evaluation of petroleum potential within a basin.

## Conclusions

- 1) Theoretical calculations and simulated maturation experiments indicate the TOC content of rocks can be substantially reduced during thermal maturation. Losses are most significant in type I and II kerogens where approximately 70% and 50%, respectively, of organic carbon content is released during hydrocarbon generation and expulsion. By comparison, carbon loss from type III kerogen is not as great with estimates of the decrease ranging from 12% to 20%. Furthermore, field data also exist that support significant TOC reductions for certain types of kerogen.

- 2) Measured TOC levels can be readily restored to their pre-maturation levels using data obtained during conventional source-rock evaluation.
- 3) Maturation-induced TOC reductions are most likely to affect source-rock recognition in beds containing marginal amounts of organic matter, and the use of rigid minimum TOC cut-off values without regard for kerogen type and thermal maturity will increase the probability of incorrect evaluation. Beds with high initial TOC content are less likely to be overlooked because they will often continue to be classified as "good" sources based on their residual TOC values.
- 4) Ranking of basins using hydrocarbons generated per volume of rock is likely to be incorrect if allowances are not made for maturation-induced TOC reductions. In particular, the evaluation will be overly pessimistic, and exploration opportunities could be missed if the corrections are not made.

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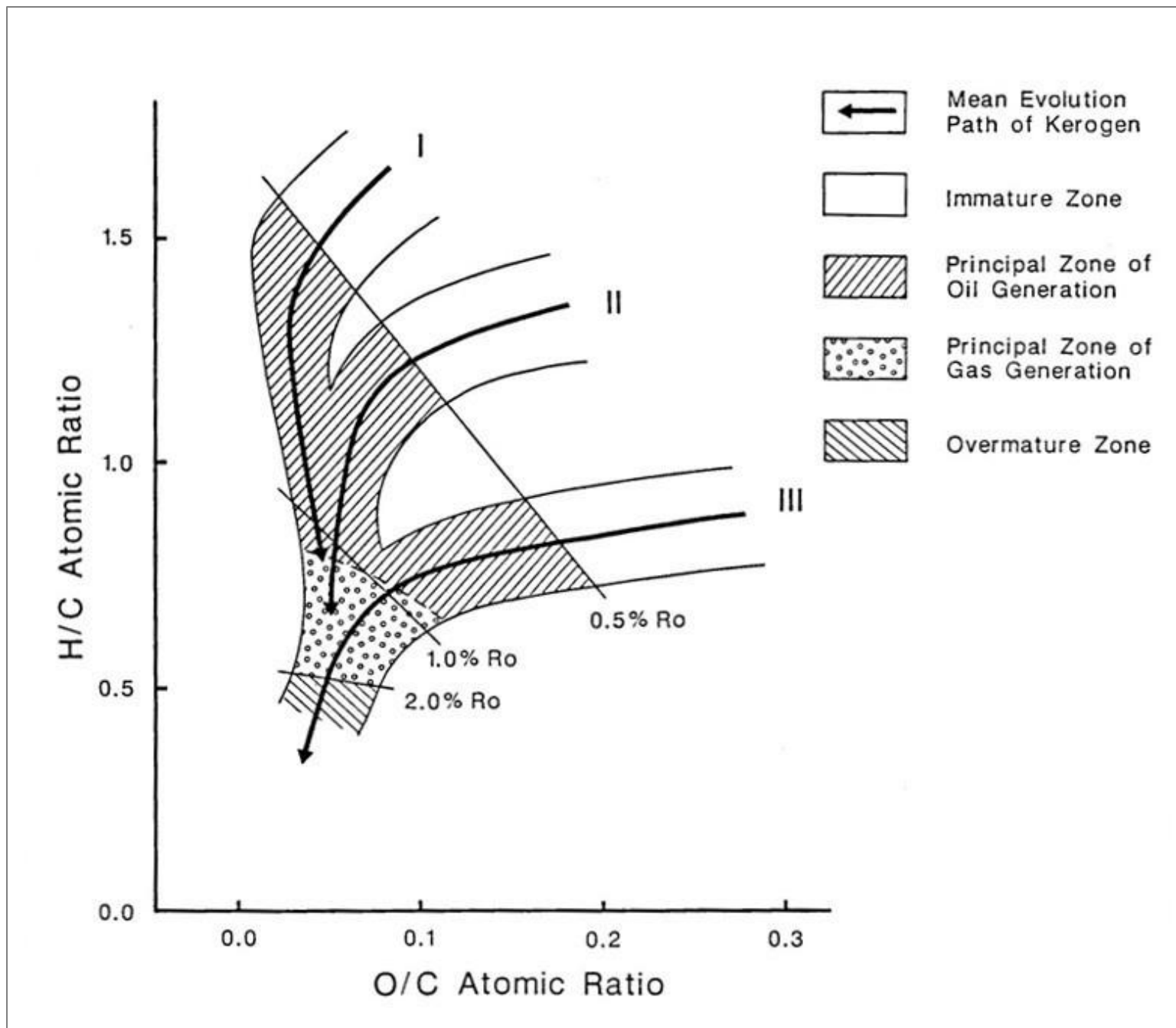


Figure 1. Maturation paths of type I, type II, and type III kerogens on a van Krevelen diagram. Modified after Durand and Monin (1980).



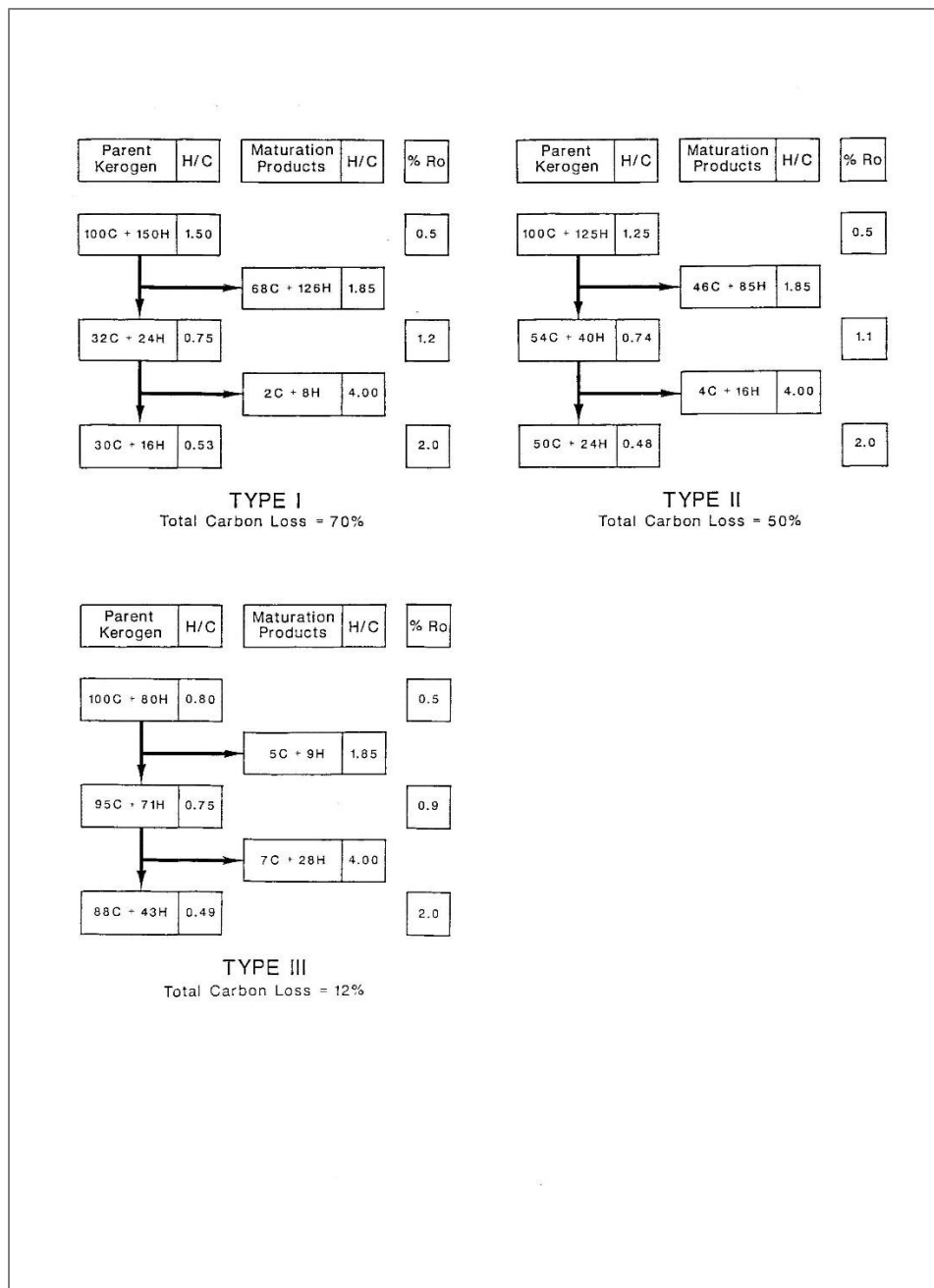


Figure 2. Percentage reduction in the carbon content of kerogens during maturation as estimated from the initial H/C ratios of the kerogens and the H/C ratios of the two principal types of hydrocarbons generated (assumed to be oil and methane).

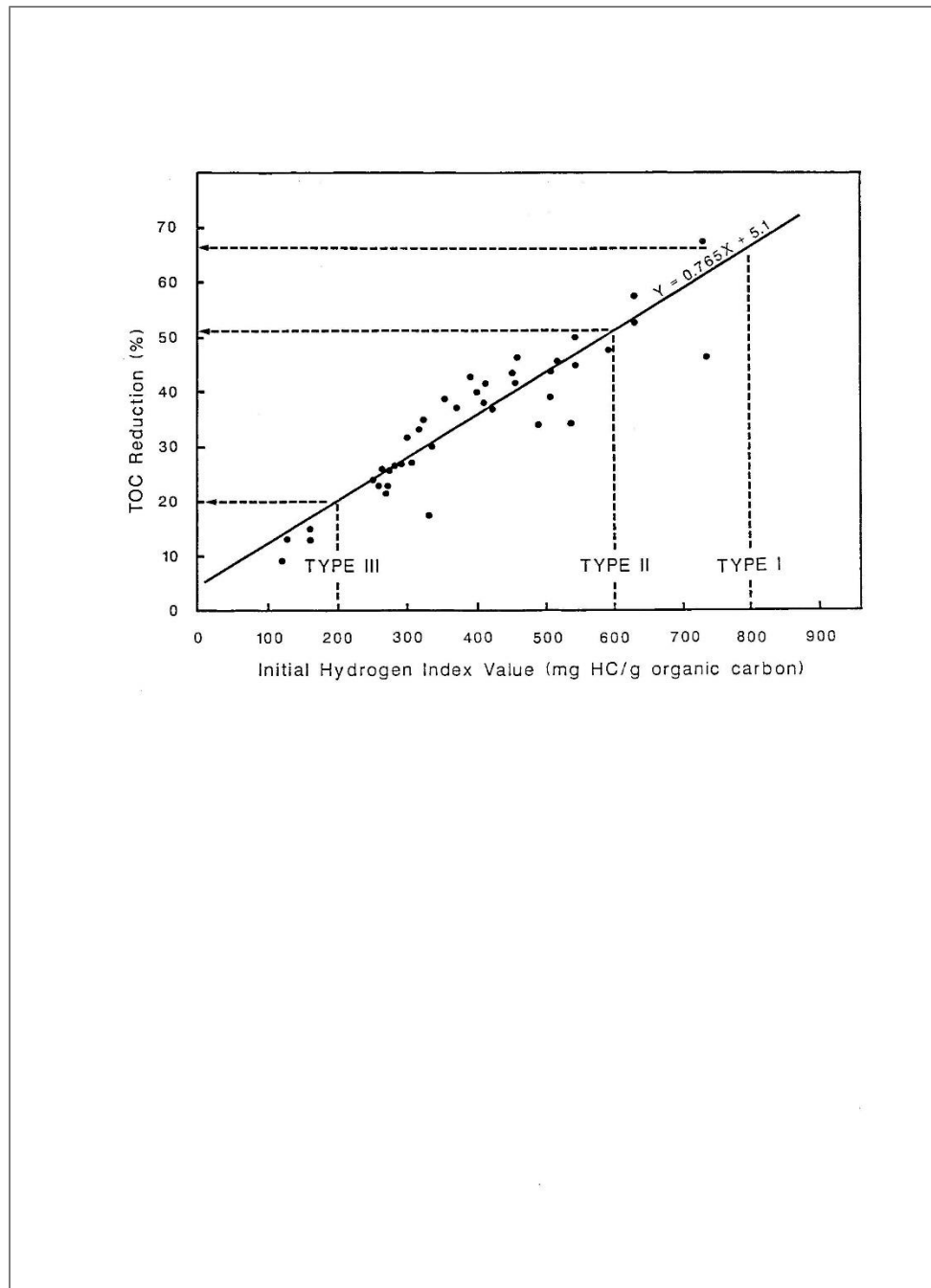


Figure 3. TOC reduction caused by pyrolysis of sediments as a function of their initial hydrogen index values.

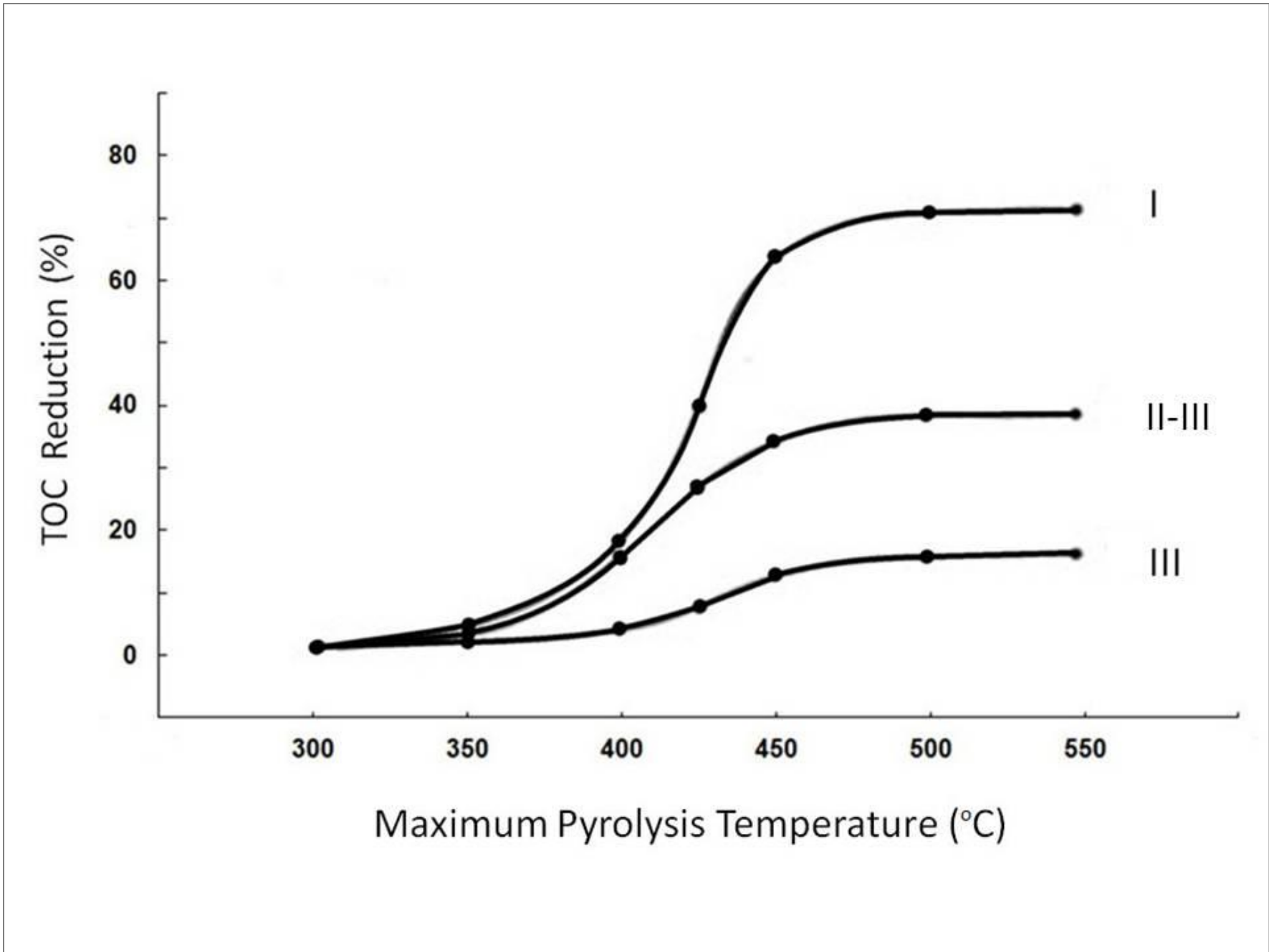


Figure 4. Carbon-loss curves for three sediments containing different types of kerogen.

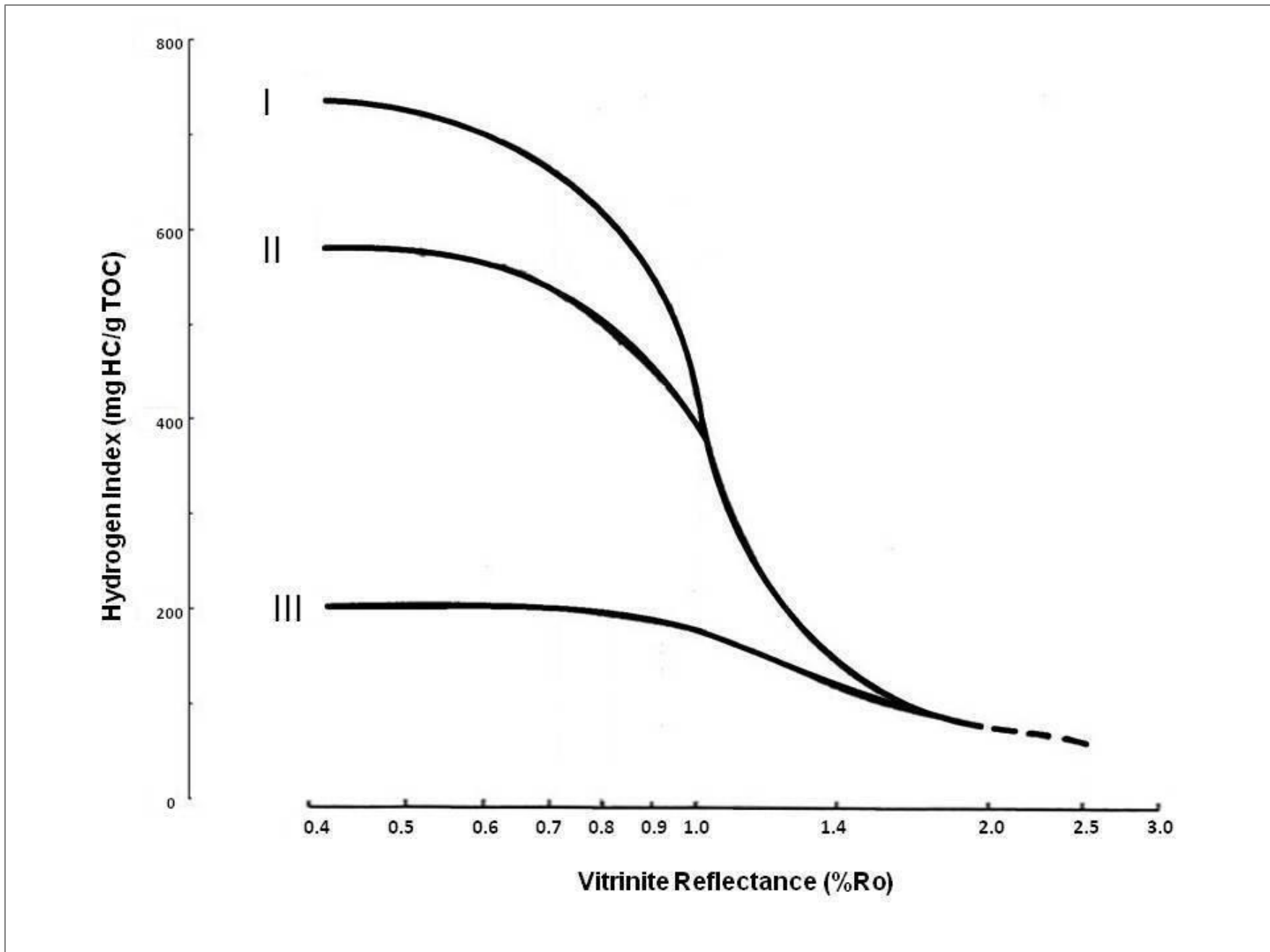


Figure 5. Hydrogen index-vitrinite reflectance curves derived through analysis of natural kerogens. Modified after Orr (1983).

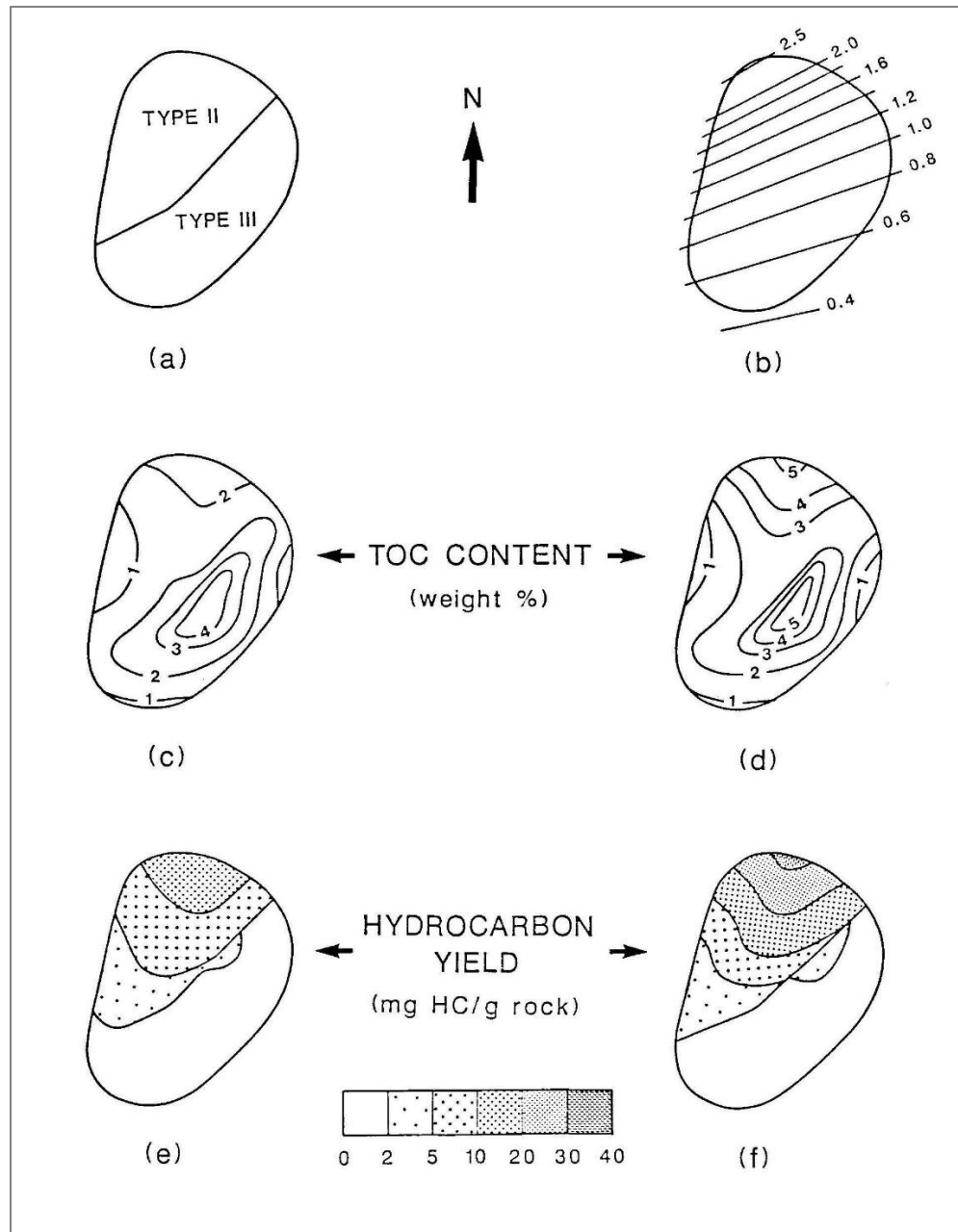


Figure 6. Hypothetical example demonstrating the effect of TOC reductions in basin analysis. Figure (a) shows the type of kerogen in the source unit, and (b) shows its thermal maturity (% Ro). Measured and restored TOC levels are shown in (c) and (d), respectively. Calculated hydrocarbon yields based on measured and restored TOC levels are shown in (e) and (f), respectively.

% Ro	F (I)	F (II)	F (III)	FΔC (I)	FΔC (II)	FΔC (III)
0.4	0.000	0.000	0.000	0.000	0.000	0.000
0.5	0.029	0.019	0.000	0.019	0.010	0.000
0.6	0.066	0.048	0.044	0.043	0.024	0.009
0.7	0.131	0.114	0.111	0.085	0.057	0.022
0.8	0.197	0.190	0.163	0.128	0.095	0.033
0.9	0.307	0.276	0.222	0.200	0.138	0.044
1.0	0.526	0.400	0.296	0.342	0.200	0.059
1.1	0.686	0.590	0.370	0.446	0.295	0.074
1.2	0.803	0.743	0.444	0.522	0.372	0.089
1.3	0.861	0.819	0.533	0.625	0.410	0.107
1.4	0.905	0.876	0.630	0.588	0.438	0.126
1.5	0.927	0.905	0.704	0.603	0.453	0.141
1.6	0.949	0.933	0.785	0.617	0.467	0.157
1.7	0.963	0.952	0.852	0.626	0.476	0.170
1.8	0.978	0.971	0.904	0.636	0.486	0.181
1.9	0.993	0.990	0.963	0.645	0.495	0.193
2.0	1.000	1.000	1.000	0.650	0.500	0.200

Table 1. Values for F and FΔC that are approximate for types I, II, and III kerogen over a range of maturity levels.