

Comparative Rock-Eval pyrolysis as an improved tool for sedimentary organic matter analysis

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Abstract—An improved Rock-Eval pyrolysis method is described for the global and exhaustive characterization of kerogen and bitumen in rock samples. Comparative pyrolysis is derived from the original Rock-Eval method of Espitalié *et al.*, it overcomes some of its inadequacies and allows a better exploitation of the pyrolysis data.

This new pyrolysis method is proposed mainly for routine analysis of bitumen in rock samples, using a double analysis of each sample (on whole rock and extracted rock). The difference between these two pyrolysis curves corresponds to the bitumen pyrolysis curve and is used for estimating the total bitumen content. The bitumen yield obtained in comparative pyrolysis as a good correlation with the bitumen yield obtained by the standard solvent extraction method with, however, some limitations due to the "mineral matrix effect". The bitumen pyrolysis curve is further subdivided into three fractions, which allow a quick and easy typing of bitumen products. This method has been successfully applied to basin analysis.

Key words—pyrolysis, Rock-Eval, source-rock characterization, kerogen, bitumen

INTRODUCTION

The well-known Rock-Eval pyrolysis method (Espitalié *et al.*, 1977, 1980, 1985/86) is now widely used for the standard characterization of sedimentary organic matter in petroleum exploration.

For a whole-rock sample, the pyrolysis recording of hydrocarbon generation as a function of temperature usually shows two well-defined peaks. Espitalié *et al.* (1977) stated that the first peak (S1) represents the free and adsorbed hydrocarbons already present, vaporized at 300°C, and that the second peak (S2) represents the hydrocarbons generated directly from the kerogen, by thermal cracking at 300–500°C. According to them, S1 is a measure of the bitumen content and S2 is a measure of the insoluble kerogen content, expressed in kg/ton of rock. The ratio $S1/[S1 + S2]$ (production index, PI) is an evaluation of the transformation ratio of kerogen into oil (in the absence of migration). The temperature T_{max} , recorded at the maximum of hydrocarbon generation during pyrolysis, is used in kerogen maturation rank evaluation. The hydrogen index, HI (S2/organic carbon), is used for characterizing the type and origin of the kerogen.

However, since the presentation of the original method in 1977, several authors have emphasized the difficulty of distinguishing bitumen from kerogen on the sole basis of thermal separation of hydrocarbon

products in fractions S1 and S2 (Clementz, 1979; Katz, 1983; Orr, 1983; Snowdon, 1984; Espitalié *et al.*, 1985/86; Peters, 1986). They have shown that, for rock samples rich in oil or bitumen, heavy hydrocarbons and degradation products of resins + asphaltenes are released in the S2 peak, at the same temperature range as for kerogen decomposition. This may be the source of inaccuracies and lack of representatives, giving rise to misleading interpretations. This is particularly true for bitumen-rich source rocks, reservoir rocks and polluted cuttings.

To overcome these drawbacks, it was first suggested to extract the suspect samples with organic solvent before analyzing them (Clementz, 1979). In this way, contamination of the S2 peak by heavy bitumen products is avoided. On the other hand though, the potential information available for the characterization of bitumen and hydrocarbons is completely lost.

In the hope of solving these problems, a new technique has been developed. It is an alternative pyrolysis method for the global and exhaustive analysis of insoluble and soluble fractions of sedimentary organic matter: comparative Rock-Eval pyrolysis (Delvaux, 1988).

PRINCIPLE OF COMPARATIVE PYROLYSIS

The basic principle of comparative pyrolysis is very simple. It comprises a double analysis of each sample by Rock-Eval pyrolysis. The first analysis is performed on a whole-rock sample. The second is

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carried out on a previously extracted sample with dichloromethane or chloroform. The key assumption is that the difference between the two pyrolysis curves corresponds to the bitumen pyrolysis curve.

It should be noted that this method has been especially designed for a rapid characterization of kerogen and bitumen in petroleum exploration. It cannot replace the more precise but more time-consuming classical methods of analysis.

The principle of the method is explained with the aid of a source-rock sample with a high bitumen content of 5.44 kg/ton of rock (Soxhlet extraction with dichloromethane, during 3×8 h). The Rock-Eval experiments were performed at a constant heating rate of $25^\circ\text{C}/\text{min}$, from 250 to 600°C , without an isotherm. The pyrolysis curve of the whole-rock sample [Fig. 1(A)] shows an incomplete separation of the S1 and S2 peaks: the valley between S1 and S2 is far from the base line level. This separation gives the amount of 2.25 kg HC/ton of rock for S1, and 6.89 kg HC/ton for S2. The same sample is previously extracted with dichloromethane and then pyrolyzed under identical conditions. The extracted-rock pyrolysis curve [Fig. 1(B)] contains only a very small S1 peak (residual solvent ?) and an S2 peak lower than the one of the whole-rock sample. The potential hydrocarbon content of the extracted rock (S1 + S2) is now 4.72 kg/ton of rock. As we can see easily, neither can the S1 content of whole rock (2.25 kg) be correlated with the solvent extract bitumen content (5.44 kg), nor can the S2 content of whole rock (6.89 kg) be correlated with the pyrolytic hydrocarbons from the insoluble kerogen (4.72 kg).

To overcome this problem, a differential curve is computed by subtracting the pyrolysis curve of the

extracted sample from that of the whole-rock sample. This new curve [Fig. 1(C)] represents the bitumen extracted by the solvent and is used for the calculation of the bitumen content (4.43 kg/ton of rock in the present sample).

As a result, the bitumen pyrolysis curve gives a hydrocarbon content which is much closer to the total bitumen content of the dichloromethane extract. On the other hand, the pyrolysis curve of the extracted rock represents more accurately the kerogen content. Now, the deficit between the bitumen yield in comparative pyrolysis (4.43 kg) and the bitumen yield in solvent (5.44 kg) represents only 18.6%, which is markedly less than the previous 58% with the classical Rock-Eval method. The remaining deficit may be explained by the so-called "mineral matrix effect", which is known to decrease the quantities of hydrocarbons expelled from the sample during pyrolysis (Espitalié *et al.*, 1980).

Comparative pyrolysis has been applied to 53 samples of various origin and bitumen content. The correlation diagrams of bitumen yield obtained by pyrolysis and that obtained by dichloromethane extraction are shown in Fig. 2. The S1 content in classical pyrolysis poorly represents the bitumen extracted, with a correlation coefficient of 0.81 and an angular coefficient of 0.41 (mean deficit of 59%). On the contrary, the bitumen content obtained by comparative pyrolysis shows a better correlation of 0.97 and a much better angular coefficient of 0.87 (mean deficit of only 13%).

A sample of asphaltic sandstone with very high bitumen yield (174.5 kg/ton of rock) was also analyzed. The hydrocarbon content of the bitumen pyrolysis curve is 165.0 kg/ton (95% of the solvent

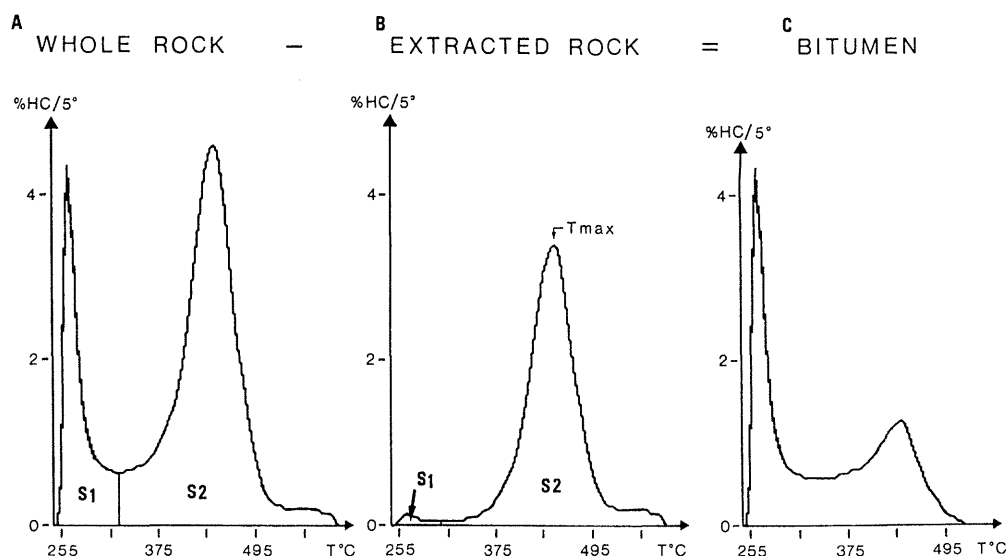


Fig. 1. Principle of comparative pyrolysis: double analysis of each sample by Rock-Eval pyrolysis (whole-rock sample and sample previously extracted with dichloromethane). Example of a rock sample with a dichloromethane extract bitumen content of 5.44 kg/ton of rock (percent hydrocarbon evolved for a temperature interval of 5°C , constant heating rate of $25^\circ\text{C}/\text{min}$). (A) Whole-rock pyrolysis curve: S1 = 2.25 kg/ton and S2 = 6.89 kg/ton. (B) Extracted-rock pyrolysis curve: S1 + S2 = 4.72 kg/ton. (C) Bitumen pyrolysis curve (4.43 kg/ton), obtained by subtracting the extracted-rock pyrolysis curve (B) from the whole-rock one (A).

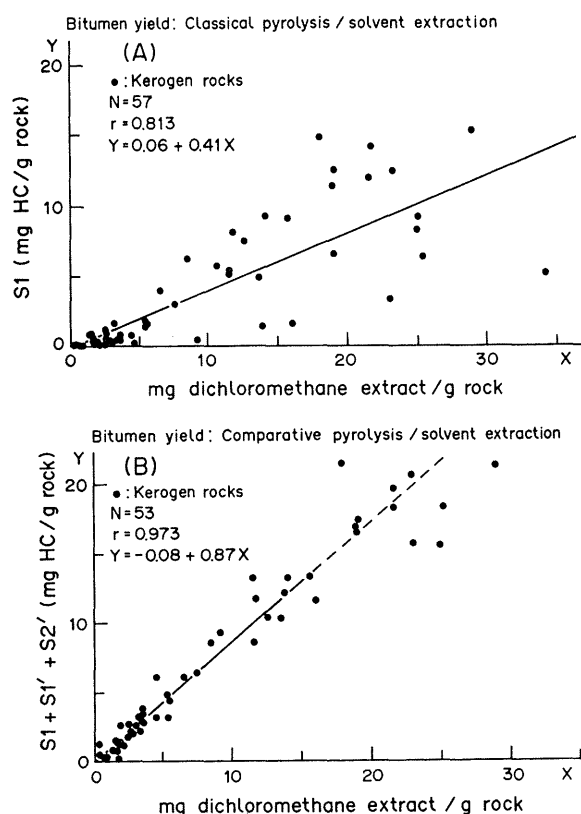


Fig. 2. Correlation of pyrolysis and solvent extract results for bitumen yield. (A) Classical pyrolysis ($S1 = \text{bitumen}$). (B) Comparative pyrolysis ($S1 + S1' + S2' = \text{bitumen}$).

extract yield). This experiment is evidence that, in the case of a sample with little mineral matrix effect, the comparative pyrolysis method appears relatively precise for bitumen content determination. In the case of a sample with a higher mineral matrix effect, the decrease in the amount of hydrocarbon released by pyrolysis should affect the whole-rock sample, as well as the extracted-rock sample. Consequently, it does not seem fitting to correct the bitumen yield given by the comparative pyrolysis method, to avoid changing the relative proportions of bitumen and kerogen in the results.

This method is not applicable for the analysis of bitumen in coals, because of their ability to retain solvent during the extraction process.

The bitumen pyrolysis curve represents the soluble organic matter as a whole and can be further subdivided into three fractions: $S1$, $S1'$ and $S2'$ (Fig. 3 + Table 1). The first separation is made by tracing a vertical line in the valley between the two peaks of the bitumen pyrolysis curve. The left peak is the $S1$ fraction, as in the classical method. A second separation is made inside the right peak, by tracing a base line from the previous valley, to the end of the right peak. The surface under the base line, which approximates the tailing of the $S1$ peak is the $S1'$ fraction and the surface over the base line is the $S2'$ fraction. Various analytical techniques have allowed us to identify their global composition [pyrolysis-gas chromatography (Py-GC), selective extraction by organic solvents, selective oxidation by potassium permanga-

nate (Delvaux, 1988)]. In particular, the oxidation rate of the $S2'$ fraction by a solution of potassium permanganate is similar to that of the $S2$ peak of the extracted rock. The $S2'$ fraction should therefore have a kerogen-like composition. Because of its solubility in dichloromethane it should be composed of resins + asphaltenes compounds. On the other hand, the oxidation rate of the $S1'$ fraction is similar to that of the $S1$ peak of the whole-rock sample, so the $S1'$ fraction should also be composed of hydrocarbons. Py-GC results show that the $S1$ peak contains hydrocarbons up to C_{20-25} and that the $S1'$ fraction contains hydrocarbons from C_{20-25} to C_{40} , depending on the temperature of the valley between the $S1$ and the [$S1' + S2'$] peaks (300–340°C).

As a result, we propose the following assumptions:

- $S1 = C_{1-25}$ free and adsorbed light hydrocarbons, volatilized at temperatures under 300–340°C;
- $S1' = C_{20-40}$ free and adsorbed heavy hydrocarbons, volatilized at temperatures over 300–340°C;
- $S2' = \text{hydrocarbons generated by thermal degradation of resins + asphaltenes at temperatures over 300–340°C.}$

The $S1$ fraction has virtually the same composition as that obtained by the original Rock-Eval method (Espitalié *et al.*, 1977). The $S2$ fraction of the original method corresponds to the sum ($S1' + S2' + S2$), i.e. not only hydrocarbons from kerogen decomposition but also hydrocarbons from resins + asphaltenes decomposition and volatilized free and adsorbed heavy hydrocarbons. In comparative pyrolysis, the $S2$ fraction only contains hydrocarbons from kerogen decomposition. The total bitumen content is expressed as the sum ($S1 + S1' + S2'$), which includes free and adsorbed hydrocarbons as well as hydrocarbons from the decomposition of resins + asphaltenes. The relationships between original Rock-Eval definitions and comparative pyrolysis definitions are presented in Table 1.

The definitions of kerogen and bitumen fractions in comparative pyrolysis are now closer to the definitions of kerogen and bitumen made by Durand (1980); kerogen = "organic matter insoluble in polar organic solvent" and bitumen = "the organic matter soluble in these solvents".

In comparative pyrolysis, $S2$ represents the kerogen content more accurately, because it is obtained from the extracted sample. The hydrogen index, HI, calculated from $S2$ and the organic carbon content, is also more precise. The same is valid for the temperature T_{max} of the $S2$ peak.

The accuracy of the subdivision of the bitumen pyrolysis curve into fractions $S1$, $S1'$ and $S2'$ has been controlled for 36 samples selected from those analyzed previously by comparative pyrolysis. The extracted bitumen was separated in saturates, aromatics and resins + asphaltenes fractions by medium pres-

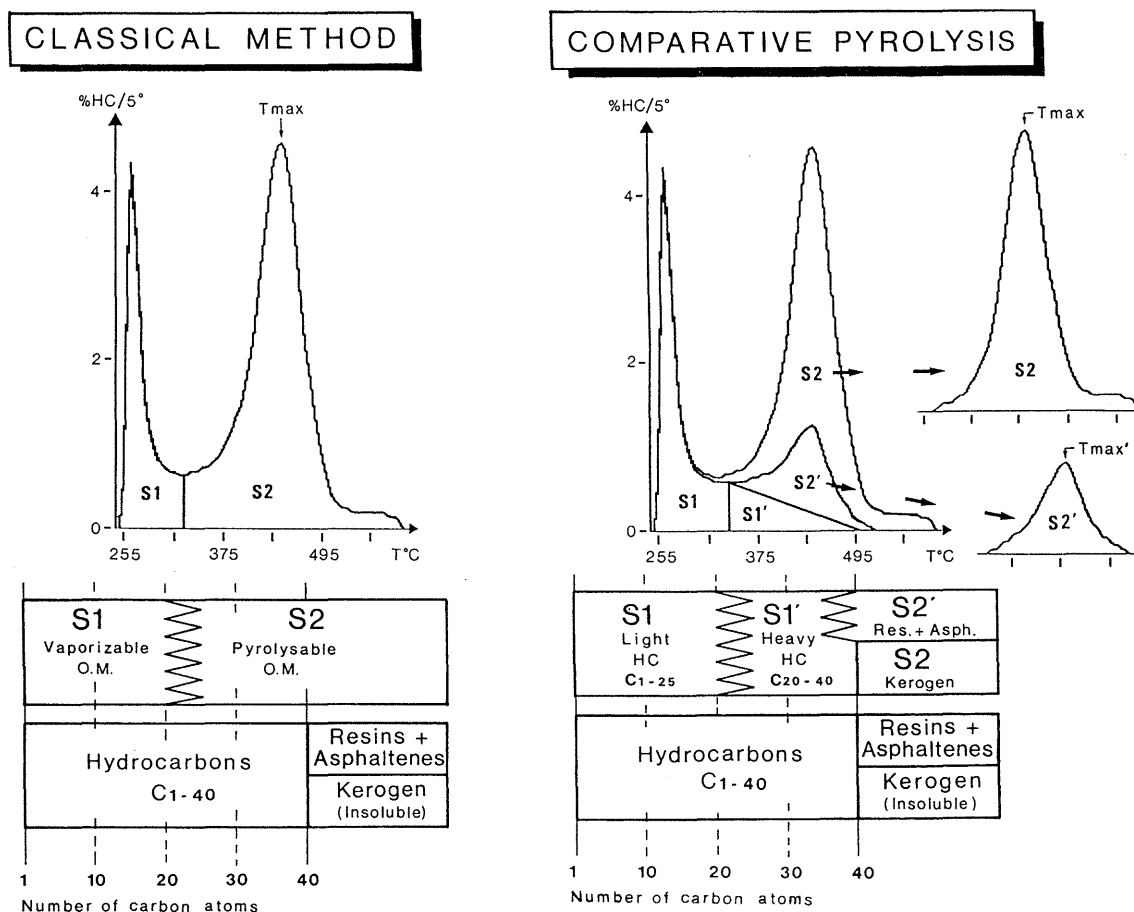


Fig. 3. Definition and composition of the main fractions of hydrocarbon pyrolysis products in classical pyrolysis (Espitalié *et al.*, 1977) and comparative pyrolysis. The comparative pyrolysis fractions are better representative of hydrocarbons, resins + asphaltenes and kerogen fractions. Percent hydrocarbon evolved for a temperature interval of 5°C.

sure liquid chromatography (MPLC), following the procedure of Radke *et al.* (1980).

The correlation diagrams in Fig. 4 show that the quantitative equivalence between the comparative pyrolysis hydrocarbon fraction (S1 + S1') and the MPLC saturates + aromatics fraction is relatively good, with a slight excess of hydrocarbons in the comparative pyrolysis results.

On the other hand, the correlation between the resins + asphaltenes content in comparative pyrolysis (S2') and the MPLC is worse, with a general deficit in the yield of resins + asphaltenes in comparative pyrolysis. This is probably due to the "mineral matrix effect" of Espitalié *et al.* (1980), which decreases the quantities of hydrocarbons released during pyrolysis, mainly for the heavy fractions of the bitumen.

NEW PARAMETERS FOR BITUMEN CHARACTERIZATION

The proportions of the four groups of organic components in a whole-rock sample are expressed by new transformation ratios:

—KTI, kerogen transformation index $[S1 + S1' + S2']/[S1 + S1' + S2' + S2]$, expressing the relative proportion of bitumen in the overall organic matter content (kerogen + bitumen);

—BTI, bitumen transformation index $[S1 + S1']/[S1 + S1' + S2']$, representing the relative proportion of hydrocarbons in the overall bitumen content;

—HTI, hydrocarbon transformation index $S1/[S1 + S1']$ expressing the relative proportion of light hydrocarbons (C₂₅⁻) in the overall hydrocarbon content.

The original production index, PI ($S1/[S1 + S2]$), of Espitalié *et al.* (1977) now corresponds to $S1/[S1 + S1' + S2' + S2]$ and expresses only the proportion of light hydrocarbons (C₂₅⁻) relative to the kerogen + bitumen content. It is, consequently, more suitable to use the new KTI to represent the bitumen proportion in whole-rock samples rather than the PI. The BTI and HTI are useful for determination of bitumen composition. The bitumen composition can also be represented in a ternary diagram S1-S1'-S2', which illustrates the relative concentration of light hydrocarbons, heavy hydrocarbons and resins + asphaltenes (see the example in Fig. 5).

The temperature T'_{max} recorded at the maximum of hydrocarbon generation during the pyrolysis of resins + asphaltenes may be used for estimating their maturation rank, in a similar manner to T_{max} , for kerogen (Fig. 5).

Table 1. New parameters in comparative pyrolysis and their relation with the classical Rock-Eval parameters, as defined by Espitalié *et al.* (1977)

<u>CLASSICAL METHOD</u> Whole Rock		<u>COMPARATIVE PYROLYSIS</u> Whole + Extracted Rock		
S1	Volatilization of Free and Adsorbed HC	S1	Volatilization of existing Light HC (C ₁₋₂₅)	B I T U M E N
S2	Pyrolysable HC (Kerogen +)	S1'	Volatilization of existing Heavy HC (C ₂₀₋₄₀)	
		S2'	H.C. from Pyrolysis of Resins + Asphaltenes	
S2		S2	H.C. from Pyrolysis of Kerogen	KE-RO-GEN
<u>HYDROGEN INDEX</u> (mg HC/g Org.C)				
HI	S2 / Organic C (Whole-Rock)	HI	S2 / Organic C (Extracted Rock)	

<u>CLASSICAL METHOD</u> Whole Rock		<u>COMPARATIVE PYROLYSIS</u> Whole + Extracted Rock	
<u>TEMPERATURE of MAXIMUM HYDROCARBON GENERATION</u> (°C)			
Tmax	S2 peak (Kerogen)	Tmax	S2 peak (Kerogen)
		Tmax'	S2' peak (Resins + Asph.)
<u>PRODUCTION INDEX</u>		<u>NEW TRANSFORMATION INDEX</u>	
PI	S1 / Whole O.M.	<u>Kerogen-Bitumen Tr. Index</u>	
		KTI	(S1+S1'+S2') / Whole O.M.
		<u>Bitumen-Hydrocarbon Tr. Index</u>	
		BTI	(S1+S1') / (S1+S1'+S2')
		<u>Hydrocarbon Tr. Index</u>	
		HTI	S1 / (S1+S1')

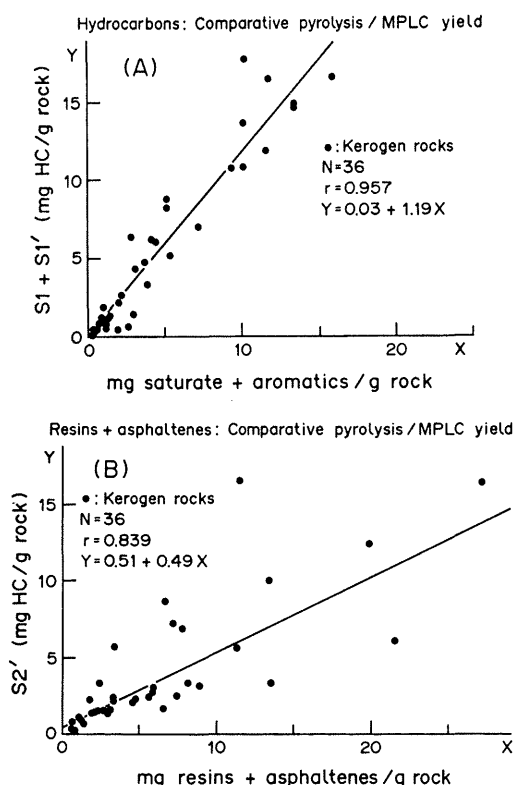


Fig. 4. Correlation of comparative pyrolysis and MPLC results for the yield of hydrocarbons (A) and resins + asphaltenes (B) fractions of the bitumen from 36 samples.

Comparative pyrolysis also provides curves for further geochemical characterization. The S2 and S2' curves are the basic recordings for kinetic analysis of kerogen and resins + asphaltenes (Delvaux *et al.*, 1990).

Comparative pyrolysis parameters are significant for rock samples with total hydrocarbon content ($S1 + S1' + S2' + S2$) > 0.2 kg/ton of rock and total organic carbon > 0.2%.

For rock samples satisfying these conditions, with a bitumen content > 3 kg/ton of rock, we have found standard deviations of 1.2–6.8% for KTI, BTI and HTI parameters. Comparative pyrolysis bitumen content shows a standard deviation between 1.9–6%, depending on the bitumen richness. The latter result is nearly as good as the standard deviation for dichloromethane extract (2.4–4%). For rocks of bitumen content < 3 kg/ton of rock, standard deviations are between 6.9–22.7% for KTI, and for BTI and HTI between 6–25% for comparative pyrolysis bitumen yield.

Therefore, we estimate that, in a first approach, the comparative pyrolysis results are sufficiently convenient to be used for the rapid characterization of insoluble as well as soluble sedimentary organic matter.

APPLICATION OF COMPARATIVE PYROLYSIS TO BASIN ANALYSIS

The comparative pyrolysis technique has been applied to the study of two boreholes.

The first one (Fig. 5) is the same well as used by Espitalié *et al.* (1977) for illustrating the original Rock-Eval method. The samples collected are homogeneous in composition (mixed type II–III source-rock), from 500 to 2500 m. Only the 2770 m sample is of type III kerogen. They cover a wide range of maturation rank, from the very immature to the mature oil rank. There has been little expulsion during thermal evolution, so that the bitumen produced was kept in place. The comparative curves depict the progressive appearance of soluble products as a function of depth. At 500 m, only resins and asphaltenes are present (inherited directly from living organic matter?). The resins + asphaltenes content increases with increasing depth and reaches its maximum at the beginning of the oil zone. Hydrocarbons appear progressively while the kerogen content decreases. The maturity indicators PI, KTI, T_{max} and T'_{max} show increasing values with depth. The compositional evolution of bitumen is illustrated by the S1–S1'–S2' ternary diagram.

The second borehole from Lower Zaire (Figs 6 and 7) is an example of a geochemical log plotted from comparative analysis, performed mainly on cuttings. Three zones are of petroleum interest: IABE type II immature source-rock; VERMELHA reservoir rock; and BUCOMAZI mature type I source-rock. The IABE immature source-rock contains bitumen in very small quantities and proportion but is relatively rich in resins + asphaltenes and heavy hydrocarbons. The BUCOMAZI mature source-rock contains bitumen in noticeable quantities, but in low proportion, and is composed mainly of resins + asphaltenes and light hydrocarbons. The VERMELHA reservoir rock mostly contains migrated oil, depleted in resins + asphaltenes.

CONCLUSIONS

Comparative pyrolysis is an improved Rock-Eval analysis method. It can be easily performed with the existing Rock-Eval device. With a double analysis of each of the samples, the analytical performance is strongly increased.

Comparative pyrolysis allows for a better distinction between kerogen and bitumen in a rock sample. This is particularly useful in the case of: (1) very immature source-rocks with inherited bitumen; (2) nearly mature or mature source-rocks; and (3) reservoir rocks. It offers new possibilities for:

- estimation of bitumen content;
- description of global bitumen composition;
- characterization of resins + asphaltenes;
- more precise kerogen analysis.

With the original method of Espitalié *et al.* (1977) this information was not directly available. It was

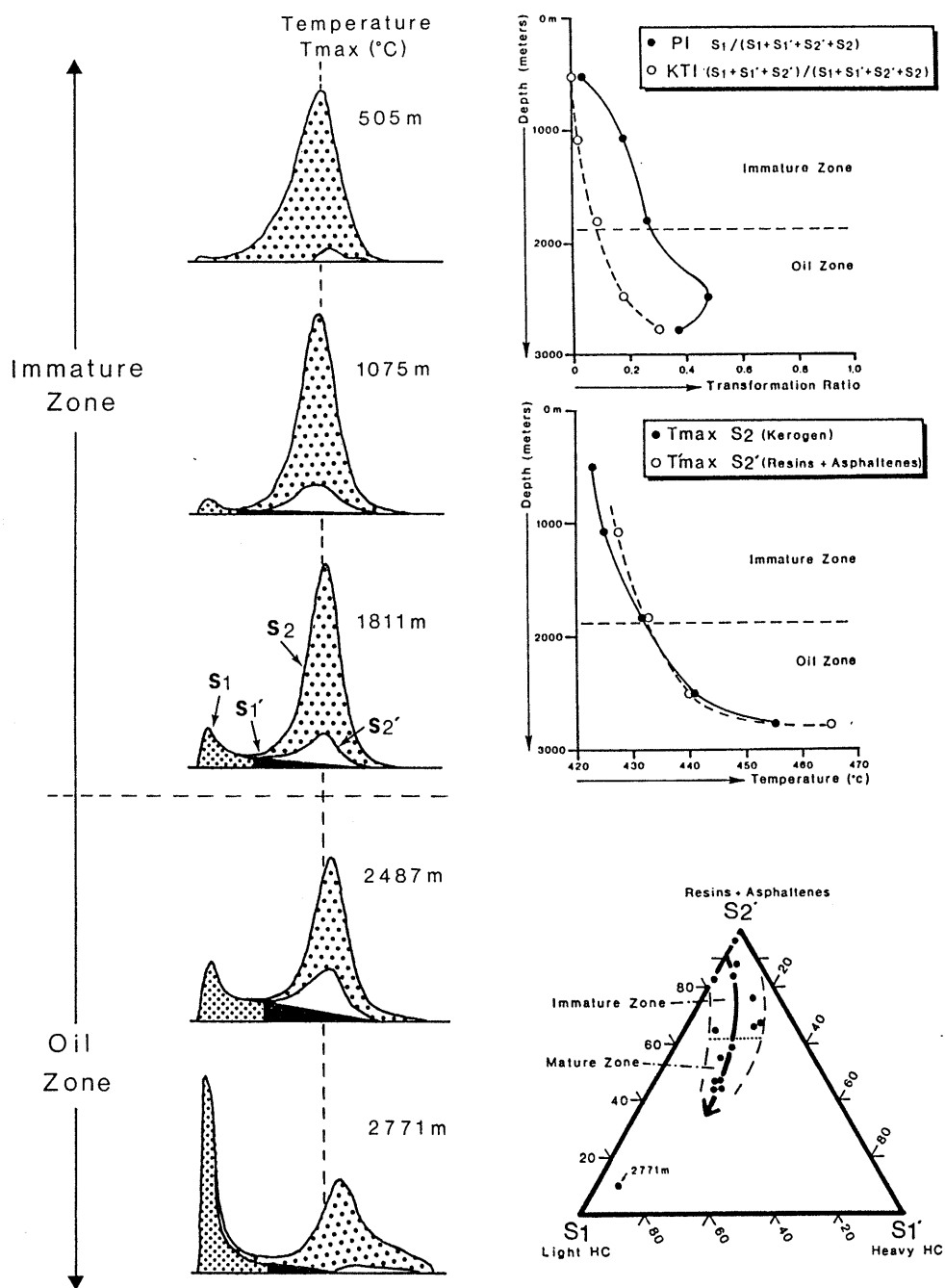


Fig. 5. Characterization of source-rock maturity and bitumen composition by comparative pyrolysis [for comparison, see Espitalié *et al.* (1977)]. The new transformation index KTI is a better indicator of bitumen generation than PI. The temperature T'_{max} of the $S2'$ peak may be used as an indicator of the thermal evolution of resins + asphaltenes, as is the temperature T_{max} of the $S2$ peak for kerogen. The ternary diagram illustrates the global bitumen composition.

unavoidable to have to extract relatively large quantities of rock and to perform MPLC analysis on the bitumen solution. These time- and sample-consuming operations may now be avoided by comparative pyrolysis. Because the bitumen itself is not analyzed, only the sample quantity necessary for the pyrolysis has to be extracted. Thus, several samples may be extracted simultaneously in the same device. This reduces the length of the analytical procedure.

The maturity of resins + asphaltenes is conveniently given by the temperature T'_{max} , but their type cannot be obtained directly. However, this infor-

mation can be obtained by kinetic analysis of the $S2'$ curve, following the method of Delvaux *et al.* (1990).

The comparative method has, however, some limitations which are mainly due to the "mineral matrix effect". This method has not been designed for a precise determination of bitumen quantity and quality but it is sufficiently accurate for a rapid characterization of bitumen in routine analysis. This method is of great interest in petroleum exploration, for the rapid analysis of a large amount of rock samples.

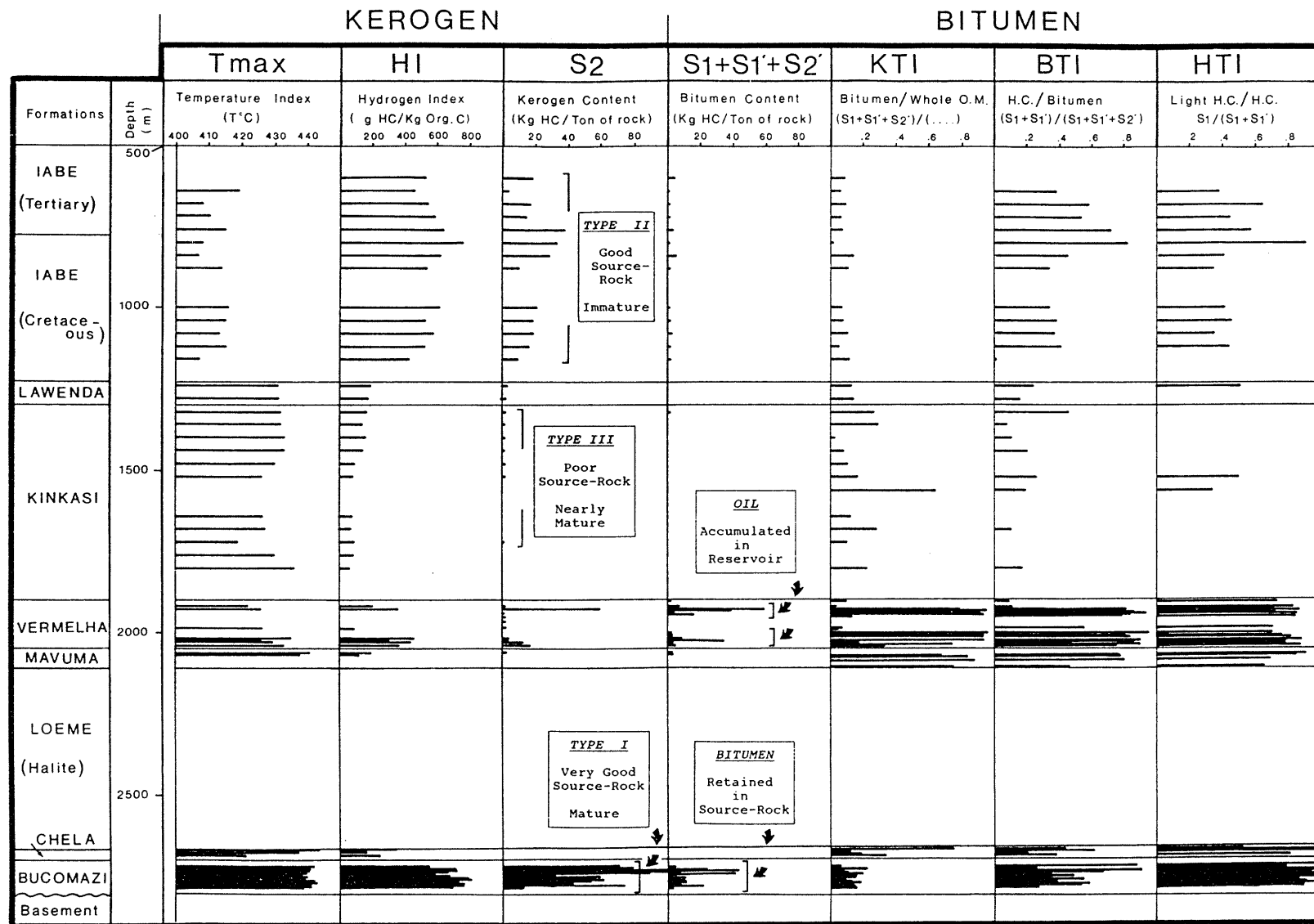


Fig. 6. Example of a geochronological log plotted from comparative pyrolysis performed on a well from Lower Zaire.

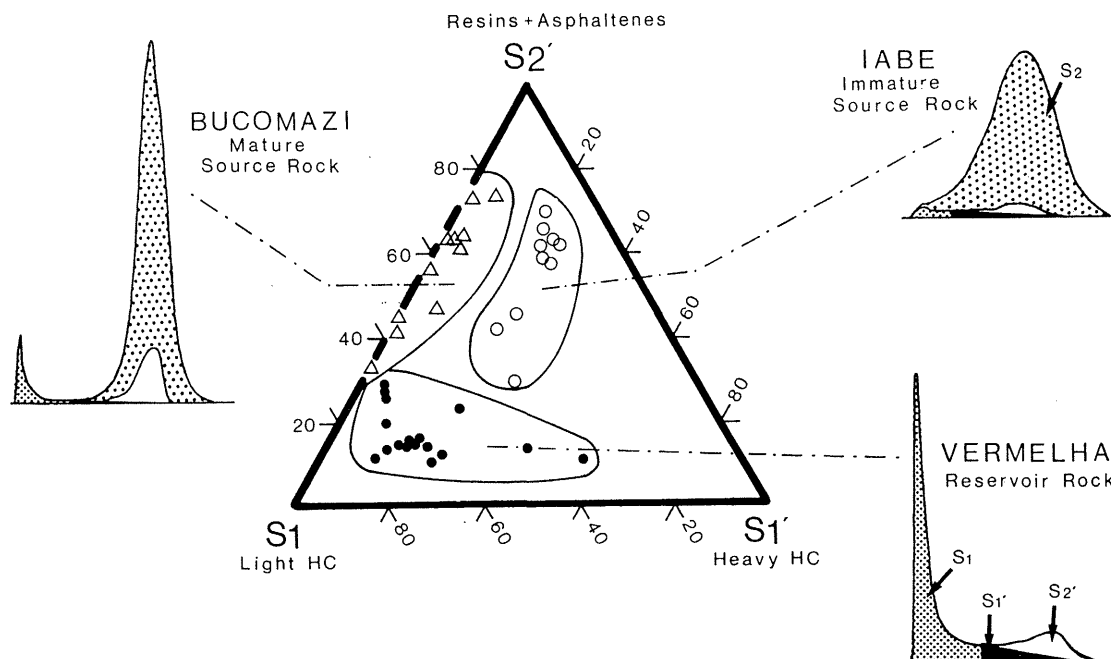


Fig. 7. Bitumen characterization in a ternary diagram and typical comparative pyrolysis curves for the same well as in Fig. 6.

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