

# ROCK-EVAL 6 APPLICATIONS IN HYDROCARBON EXPLORATION, PRODUCTION, AND SOIL CONTAMINATION STUDIES

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LES APPLICATIONS DE ROCK-EVAL 6 DANS L'EXPLORATION ET LA PRODUCTION DES HYDROCARBURES, ET DANS LES ÉTUDES DE CONTAMINATION DES SOLS

Le succès d'une exploration pétrolière repose sur l'analyse détaillée du système pétrolier dans une zone donnée. L'identification des roches mères potentielles, la détermination de leur maturité, de leurs paramètres cinétiques et de leur répartition sont réalisées au mieux à partir d'exams rapides d'échantillons de roches (carottes ou déblais) au moyen de la pyrolyse Rock-Eval. Cette technique a été utilisée en routine pendant une quinzaine d'années et elle est devenue un outil standard pour l'exploration des hydrocarbures.

Cet article décrit comment les nouvelles fonctionnalités de la dernière version de l'appareil Rock-Eval (Rock-Eval 6) ont permis une expansion des applications de la méthode en géosciences pétrolières. Des exemples d'applications nouvelles sont illustrés dans les domaines de la caractérisation des roches mères, de la géochimie de réservoir et des études environnementales incluant la quantification et la description des hydrocarbures dans des sols contaminés.

ROCK-EVAL 6 APPLICATIONS IN HYDROCARBON EXPLORATION, PRODUCTION, AND SOIL CONTAMINATION STUDIES

Successful petroleum exploration relies on detailed analysis of the petroleum system in a given area. Identification of potential source rocks, their maturity and kinetic parameters, and their regional distribution are best accomplished by rapid screening of rock samples (cores and/or cuttings) using the Rock-Eval apparatus. The technique has been routinely used for about fifteen years and has become a standard tool for hydrocarbon exploration.

This paper describes how the new functions of the latest version of Rock-Eval (Rock-Eval 6) have expanded applications of the method in petroleum geoscience. Examples of new applications are illustrated for source rock characterization, reservoir geochemistry, and environmental studies, including quantification and typing of hydrocarbons in contaminated soils.

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## LAS APLICACIONES DE ROCK-EVAL 6 EN LA EXPLORACIÓN Y LA PRODUCCIÓN DE LOS HIDROCARBUROS, Y EN LOS ESTUDIOS DE CONTAMINACIÓN DE LOS SUELOS

El éxito de una exploración petrolera se funda en el análisis detallado del sistema de hidrocarburos en un área determinada. La identificación de las rocas madre potenciales, la determinación de su grado de madurez, de sus parámetros cinéticos y de su distribución, se llevan a cabo de mejor modo tomando como punto de partida exámenes rápidos de muestras de rocas (testigos o residuos de perforación) por medio de la pirólisis Rock-Eval. Se ha aplicado esta técnica en rutina durante unos quince años y ha llegado a ser una herramienta estándar para la exploración de los hidrocarburos.

Se describe en este artículo cómo las nuevas funcionalidades de la última versión del aparato Rock-Eval (Rock-Eval 6) han permitido una expansión de las aplicaciones en geociencias petroleras. Se ilustran diversos ejemplos de nuevas aplicaciones en los sectores de la caracterización de las rocas madre, de la geoquímica de yacimiento y de los estudios medioambientales en que se incluyen la cuantificación y la descripción de los hidrocarburos en los suelos contaminados.

## INTRODUCTION

Characterizing the organic matter from sedimentary rocks is one of the main objectives of organic geochemistry and is now widely recognized as a critical step in the evaluation of the hydrocarbon potential of a prospect. During the last two decades, various authors (e.g., Barker, 1974; Claypool and Reed, 1976; Espitalié *et al.*, 1977 and 1984; Clementz *et al.*, 1979; Larter and Douglas, 1980; Horsfield, 1985; Peters and Simoneit, 1982; Peters, 1986) have used pyrolysis methods to provide data on the potential, maturity and type of the source rocks in different sedimentary basins.

Among these techniques, Rock-Eval pyrolysis has been widely used in the industry as a standard method in petroleum exploration. This technique uses temperature programmed heating of a small amount of rock (100 mg) in an inert atmosphere (helium or nitrogen) so as to determine (Fig. 1): the quantity of free hydrocarbons present in the sample ( $S_1$  peak) and the amount of hydrocarbons and compounds containing oxygen ( $CO_2$ ) that are produced during the thermal cracking of the insoluble organic matter (kerogen) in the rock ( $S_2$  and  $S_3$  peaks respectively).

Furthermore, the Total Organic Carbon (TOC) content of the rock is determined by oxidation under air, in a second oven, of the residual organic carbon after pyrolysis ( $S_4$  peak). The method has not evolved much over the years. However, the new Rock-Eval 6 apparatus incorporates major changes in the methodology. As a consequence, new scientific applications of the method are proposed.

As we will see in the following, some of these applications are new and therefore expand the fields of use of Rock-Eval methodology, while others are mainly improvements of the existing method. In this respect, we will first present the Rock-Eval 6 functions and we will then detail their different applications (use of mineral carbon determination in carbonate sequences, application of new oxygen indices, application of high temperature  $T_{max}$  (temperature measured at the top of the  $S_2$  peak), and use of the improved total organic carbon (TOC) determination). Finally, we will illustrate more specific applications of Rock-Eval 6 data in reservoir geochemistry and in soil contamination studies.

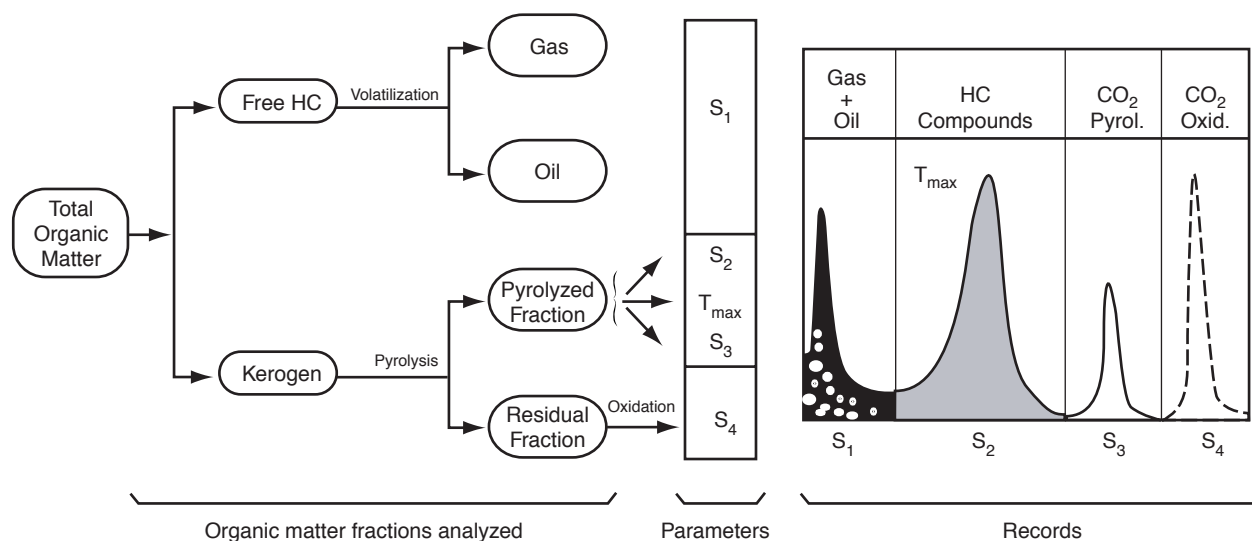


Figure 1

General diagram showing the different fractions of the total organic matter of analyzed rocks, the corresponding parameters and their recordings.

## 1 METHODOLOGY: ROCK-EVAL 6 NEW FUNCTIONS

A number of technical changes have been introduced in Rock-Eval 6. They lead to the new functionalities described in the next paragraphs.

### 1.1 New Temperature Range for the Pyrolysis and Oxidation Ovens

In Rock-Eval 6, programmed heating of both the pyrolysis and the oxidation ovens is conducted from 100°C (instead of 180°C in the previous versions) up to 850°C (instead of 600°C in the previous versions).

Pyrolysis at temperatures up to 850°C is necessary for complete thermal degradation of terrestrial type III organic matter. Previous studies have shown that thermal cracking of terrestrial organic matter is not always complete at 600°C and therefore the corresponding  $S_2$  peak can be underestimated. The consequence is a possible underestimation of the petroleum potential for type III source rocks. By increasing the maximum pyrolysis temperature in Rock-Eval 6, the measure of the hydrogen index ( $HI = S_2/TOC$ ) is more accurate and the range of validity of  $T_{max}$  is extended to higher values.

Another important outcome of this new functionality is a better determination of kinetic parameters for

type III organic matter. For such samples, we frequently observed pyrolysis curves that did not return to the baseline when using the low heating rates. This experimental problem was a source of uncertainty in the determination of the kinetic parameters for type III source rocks.

The oxidation temperature of the sample has also been increased (up to 850°C) in order to avoid incomplete combustion of refractory material, such as heavy oils, tar-mats, coke or pyrobitumen in source rocks or reservoir rocks, or polyaromatic hydrocarbons (PAH) in soils from polluted sites. This new functionality has resulted in a better TOC determination. As we will see later, high temperature oxidation also allows mineral carbon determination, which is one of the main improvements provided by Rock-Eval 6.

The initial pyrolysis temperature has been reduced to 100°C instead of 180°C to allow detailed study of the free hydrocarbons in rocks. This is particularly useful for the analysis of cuttings on site (oil shows during drilling), for reservoir studies (better evaluation of API gravity from Rock-Eval data) and especially for soil contamination studies where contaminants are often very light hydrocarbon compounds (gasoline, diesel oil, jet fuel). In conjunction with this lower temperature, it is now possible to select the temperature program in order to optimize the separation of these light compounds, thus approaching a separation according to bubble points.

Furthermore, the location of the thermocouple that drives the ovens has been changed. In Rock-Eval 6, the thermocouple is now located in the crucible immediately below the sample (Fig. 2) instead of against the oven wall as it was in Rock-Eval 2.

Therefore, the measured temperature is very close to the real sample temperature. As a result, the temperature measurement is more accurate. As illustrated in Figure 2, the shape of the crucible has also been

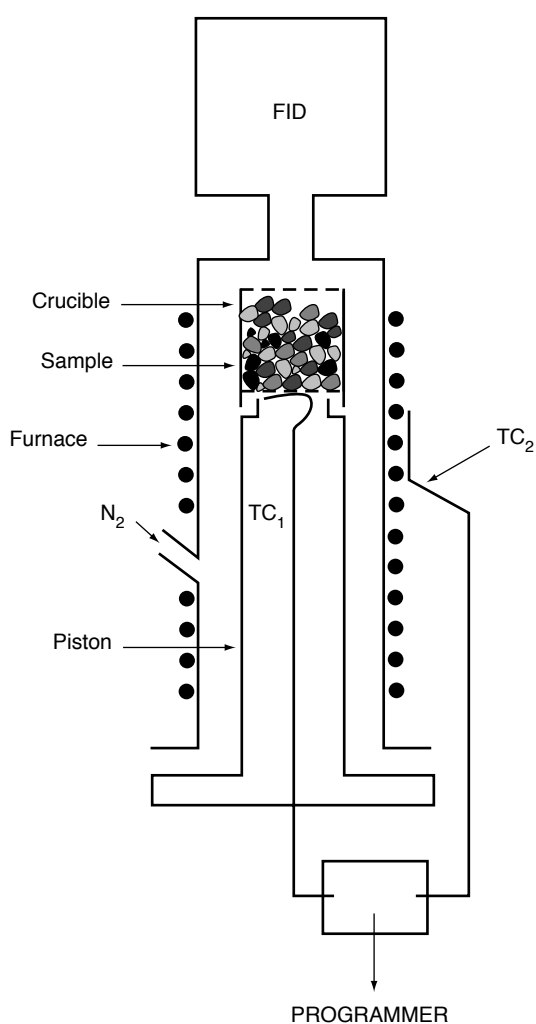
changed in order to accommodate the thermocouple ( $TC_1$ ). The second thermocouple ( $TC_2$ ) is used to ensure continuity of temperature control when the crucible is removed from the pyrolysis oven at the end of the analysis. The same is true for the oxidation oven.

## 1.2 Continuous On-Line Detection of CO and CO<sub>2</sub> with Infra-Red Detectors

For earlier versions of Rock-Eval, the CO<sub>2</sub> released during pyrolysis was trapped and quantified using a catharometer. Although the S<sub>3</sub> peak quantifies the total CO<sub>2</sub> yield, it does not reflect its temperature-programmed release during kerogen cracking. This limits interpretation of the S<sub>3</sub> response. Similarly during oxidation, the CO<sub>2</sub> released was trapped at 600°C and then quantified by the catharometer. For practical reasons, CO was not analyzed during pyrolysis or oxidation.

These limitations have led us to add sensitive infrared detectors to Rock-Eval 6, that are capable of continuous on-line recording of the amount of both CO and CO<sub>2</sub> released during pyrolysis and oxidation of samples. As a result, five characteristic curves are obtained for each sample analyzed using Rock-Eval 6 (Fig. 3): (1) the amount of hydrocarbons (flame ionization detector, FID trace of S<sub>1</sub> and S<sub>2</sub> peaks), (2–3) CO and CO<sub>2</sub> produced during pyrolysis (CO and CO<sub>2</sub> pyrolysis curves), (4–5) CO and CO<sub>2</sub> produced during oxidation (CO and CO<sub>2</sub> oxidation curves). The sixth curve in Figure 3 is the superposition of CO and CO<sub>2</sub> curves and is very useful for a rapid visualization of the presence or absence of carbonate in the sample.

As shown in following results, continuous recording of both CO and CO<sub>2</sub> has revealed a number of useful new parameters. For instance, the character of CO and CO<sub>2</sub> pyrograms produced can be used to distinguish the types of kerogen in rock samples. The different peaks on the pyrograms represent different classes of functional groups containing oxygen (e.g. ethers, carboxyls, carbonyls) which vary from one organic matter type to another. This approach has already been successfully used for CO pyrograms from immature to early mature source rocks (Daly and Peters; 1982). This new functionality allows measurement of the mineral carbon in the rock in addition to the classical organic carbon determination. Furthermore, mineral type determination (e.g. calcite, dolomite, siderite) is possible.



Furnace open: temperature controlled by  $TC_2$   
 Furnace closed: temperature controlled by  $TC_1$

Figure 2  
 Schematic diagram indicating the location of the thermocouple for temperature regulation in the pyrolysis oven.

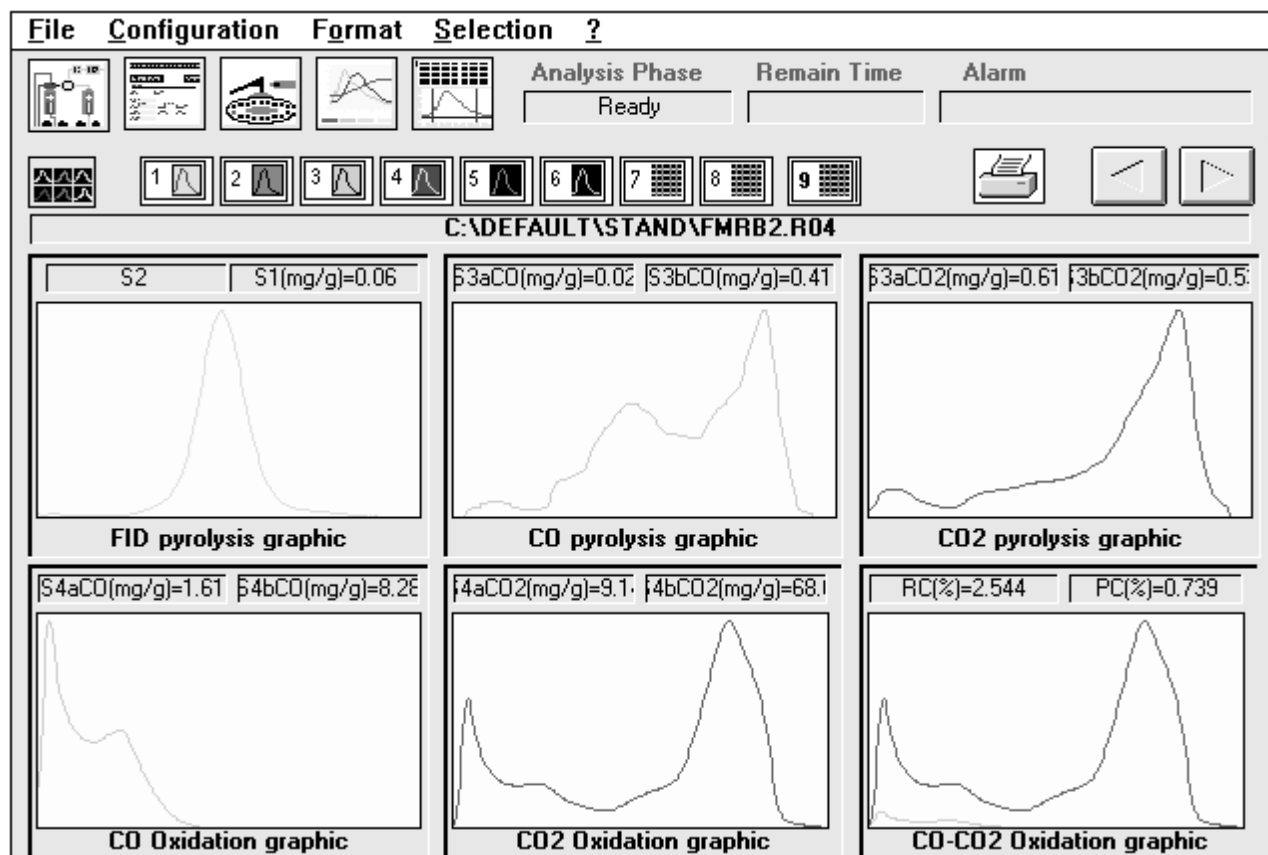


Figure 3  
 Illustration of Rock-Eval 6 standard recordings for hydrocarbons, CO and CO<sub>2</sub> during the pyrolysis and oxidation phases.

### 1.3 Processing of Multi-Heating Rates Cycles

Because of new applications of the Rock-Eval methodology to reservoir geochemistry and soil contamination studies, it was necessary to allow enough flexibility in the apparatus to account for the variety and the specificity of the hydrocarbons to be detected and quantified. For example, in soil contamination studies, the residence time of the S<sub>1</sub> peak and the starting heating rates are critical for a good determination of pollutants. For Rock-Eval 6, there is now a true “temperature versus time” function, meaning that initial temperatures, heating rates and residence times can be adjusted by the user for any specific application. In addition, a number of pre-programmed cycles are available that have already been successfully tested for soil

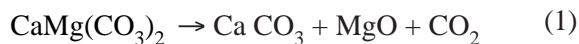
contamination studies and for reservoir geochemistry (e.g., detection of tar-mats).

## 2 RESULTS

### 2.1 Mineral Carbon Determination

The amount of mineral carbon is calculated by addition of the CO<sub>2</sub> released during pyrolysis above 400°C and the CO<sub>2</sub> from carbonate decomposition during the oxidation phase from 650°C to 850°C (Fig. 4). Carbonate minerals such as magnesite and siderite begin to decompose when the pyrolysis temperature approaches 400°C whereas dolomite and calcite (the most important minerals in carbonate sequences) decompose during oxidation (Fig. 5). In this figure, we can observe that dolomite oxidative

decomposition gives two characteristic peaks corresponding to the following reactions:



and at higher temperature



Calcite decomposition occurs at about 800°C and is indicated by a single peak.

Because of this sequential decomposition of the carbonate minerals during the analytical cycle, it is possible to quantify the amount of mineral carbon and estimate which species is dominant in the sample.

Although it is less abundant than calcite and dolomite, siderite is quite common in source rocks, particularly in fermentation zones where the preservation of organic matter is enhanced (Curtis, 1977; Berner, 1981). Its range of decomposition temperature is large, from 400°C to 650°C, and therefore it can interfere, during pyrolysis, with the CO<sub>2</sub>

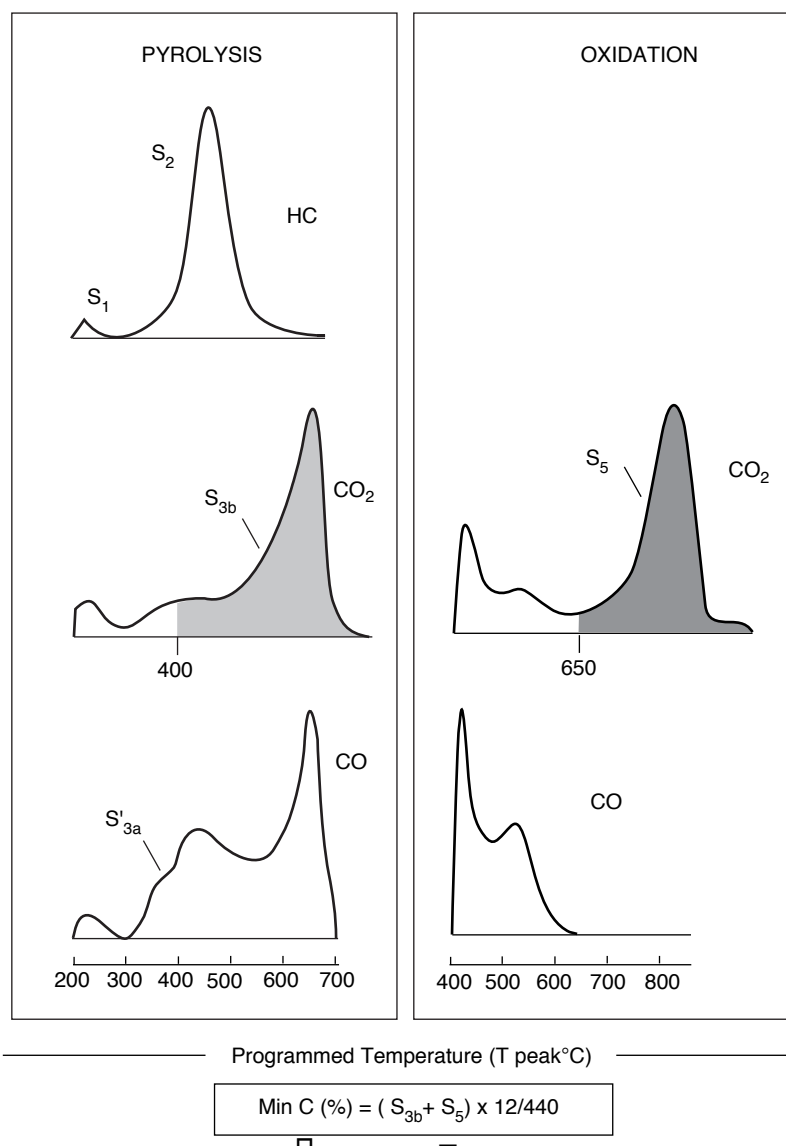


Figure 4

Principle of determining mineral carbon content (MINC; %) using CO<sub>2</sub> pyrolysis and oxidation curves.

released by the oxygenated functions in the organic matter. In Rock-Eval 6, thanks to the continuous on-line recording of CO and CO<sub>2</sub> released during pyrolysis, it seems that the combination of S<sub>3</sub>CO, S<sub>3</sub>CO<sub>2</sub> values and T peak CO<sub>2</sub> (temperature at the maximum of CO<sub>2</sub> pyrolysis curve; "T<sub>max</sub> CO<sub>2</sub>") on bulk rocks can point out very rapidly when and where siderite is occurring.

Samples with siderite present S<sub>3</sub>CO values greater than 5 mg CO/g rock, S<sub>3</sub>CO<sub>2</sub> greater than 10 mg CO<sub>2</sub>/g rock and T peak CO<sub>2</sub> in the 485–520°C temperature range. As a result, we have a very good indicator of the presence of siderite in source rock samples which in turn may be used as a redox indicator of the whole series (siderite occurs only in specific environments).

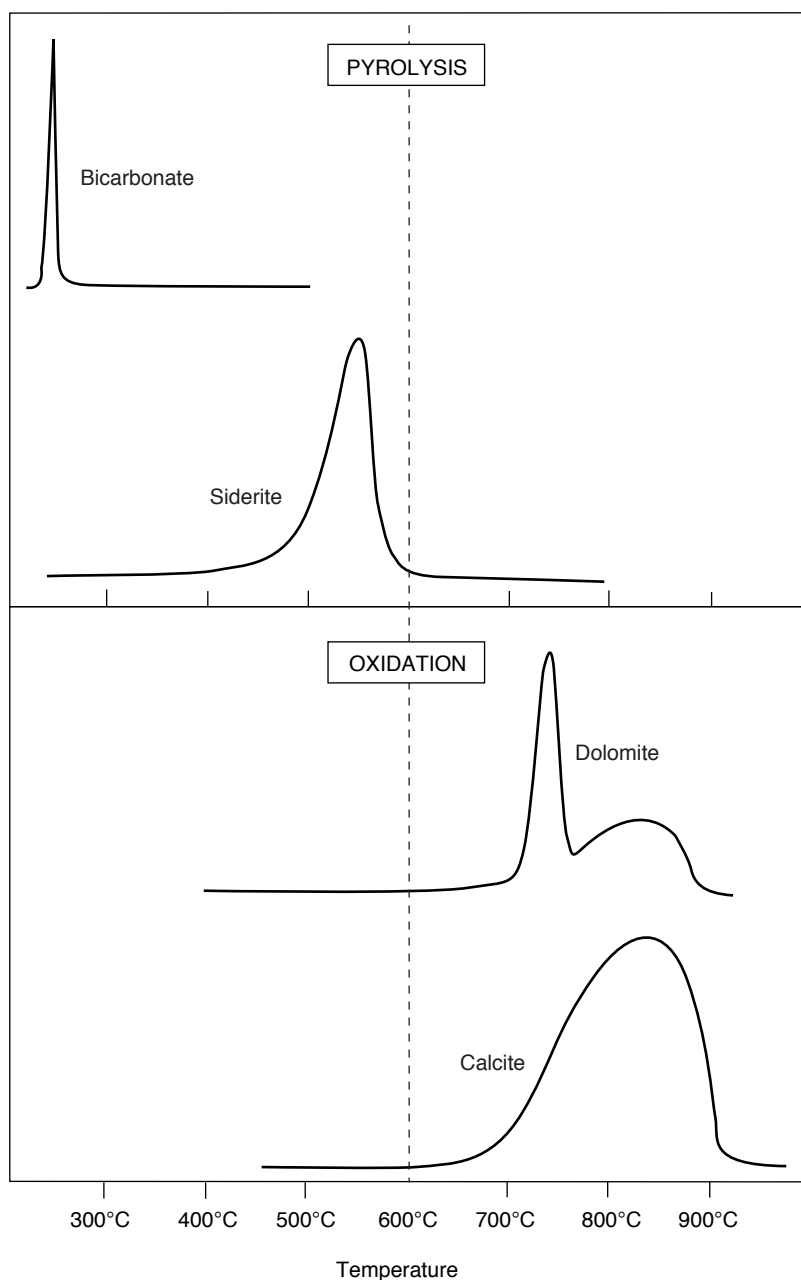
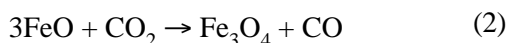


Figure 5

Rock-Eval 6 response of different types of carbonate minerals illustrating their progressive decomposition with increasing temperature.

Furthermore, the comparison of a series of bulk rocks and acid-treated rocks indicated that, when a great deal of siderite is present, we can observe the production of CO during pyrolysis according to the following set of chemical reactions:



Once siderite is removed by acid treatment, the CO production stops, resulting in small values of  $S_3\text{CO}$  (organic CO alone).

Mineral carbon content based on Rock-Eval 6 analysis correlates well with that obtained by routine chemical attack techniques throughout the range observed in most sedimentary rocks (0–12%; Fig. 6).

This rapid estimate of both the organic and mineral carbon is very useful in studies of the relationship between organic matter and mineral carbon in carbonate petroleum systems. Such work has been successfully conducted recently by van Buchem et al. (1996) on the Upper Devonian mixed carbonate-siliciclastic system of western Canada. These authors show a distinct pattern in plots of the carbonate versus organic carbon content within each sequence, each

being characteristic of the equilibrium between carbonate precipitation, organic matter dilution, and occurrence of dysaerobic conditions.

## 2.2 Organic Carbon Determination

Like previous Rock-Eval systems, Rock-Eval 6 determines the amount of organic carbon by adding pyrolyzed carbon (PC) and residual carbon (RC). Nevertheless, the continuous CO and CO<sub>2</sub> detection has improved PC and RC quantification (Fig. 7).

Pyrolyzed carbon is computed from:

- the hydrocarbon compounds released in peaks  $S_1$  and  $S_2$ , assuming that they contain about 83% of the organic carbon;
- the CO released during pyrolysis up to 500°C ( $S'_{3a}$  peak);
- the CO<sub>2</sub> released during pyrolysis up to 400°C ( $S_{3a}$  peak). To avoid interference from the release of pyrolytic CO<sub>2</sub> from carbonate minerals such as siderite, only the first part of the CO<sub>2</sub> pyrolysis curve is taken into account. Likewise, in order to avoid possible interference caused by Boudouard's reaction, where the CO<sub>2</sub> released early during carbonate decomposition can react with the residual carbon to produce CO ( $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ ), we limit

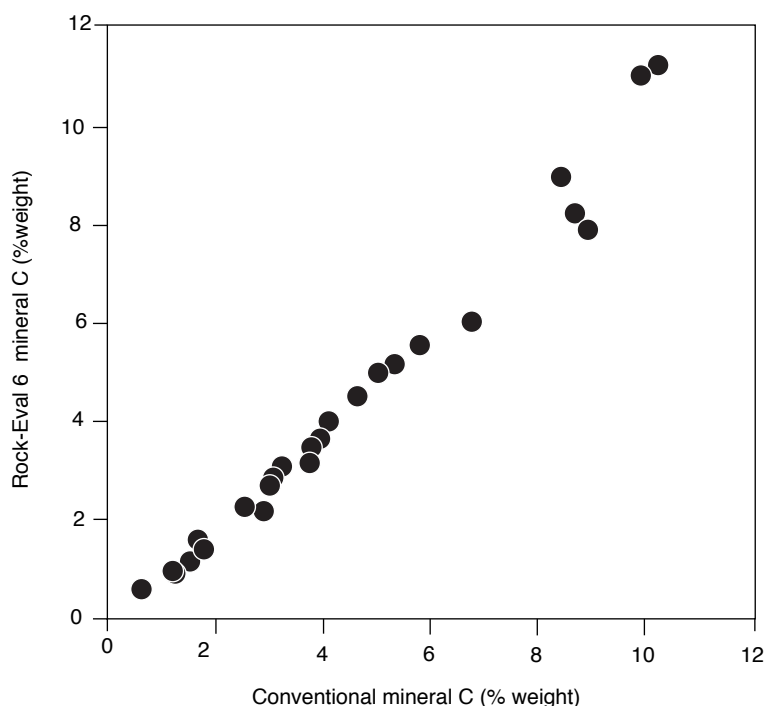


Figure 6  
 Comparison of mineral carbon determination using Rock-Eval 6 and acid attack.



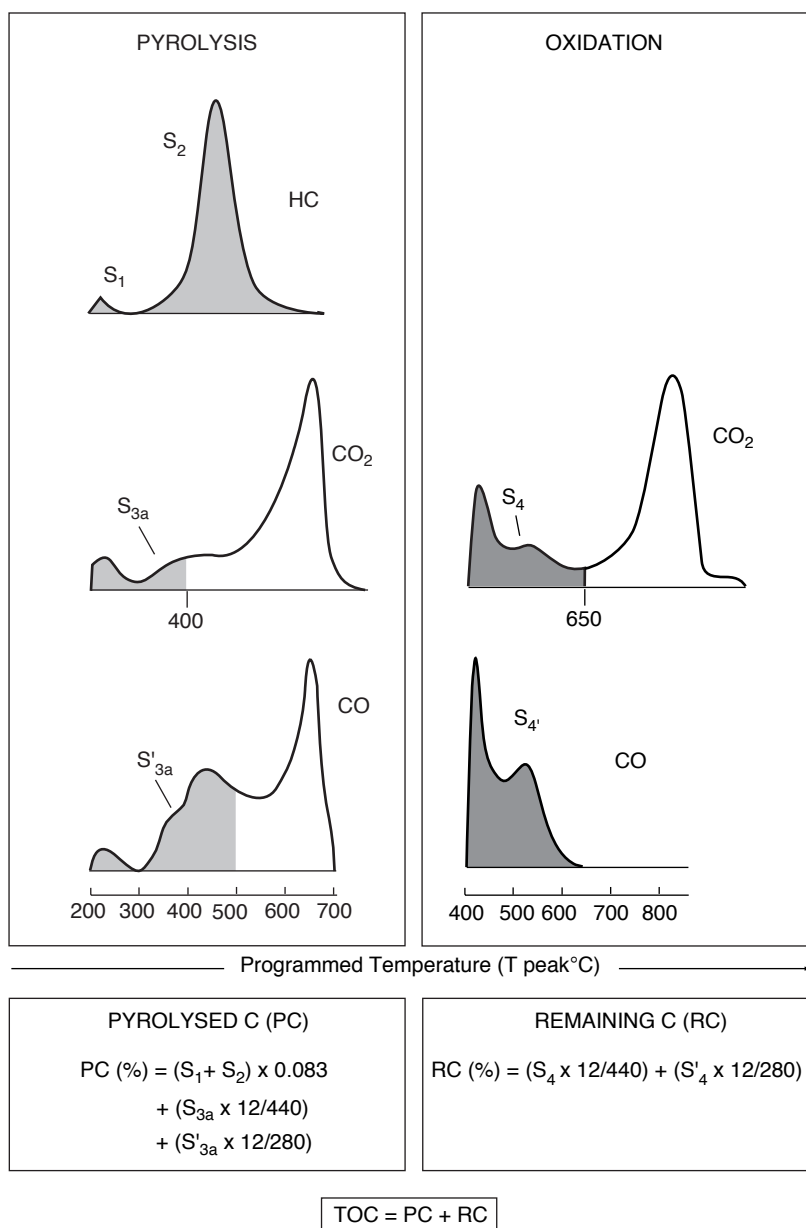


Figure 7

Principle of determining total organic carbon content (TOC; %) using FID, CO<sub>2</sub> pyrolysis and oxidation curves to calculate the amounts of pyrolyzed carbon (PC) and residual carbon (RC).

the calculation for CO to a temperature of 500°C. The residual carbon is obtained during the oxidation phase by summing the organic carbon oxidized into CO (S<sub>4</sub>' peak) and CO<sub>2</sub> up to 650°C (S<sub>4</sub> peak). At higher temperatures, there is no more CO production and the remaining CO<sub>2</sub> comes generally from the decomposition of carbonates.

The progress made in organic carbon determination has brought higher performance as a whole (Fig. 8;

comparison between TOC measurements using Rock-Eval 6 and LECO), but this is particularly true when dealing with coal samples where Rock-Eval 2 response was often poor. The organic carbon now measured for mature coal samples (Vitrinite Reflectance (R<sub>o</sub>) > 2%) is drastically improved since high temperature oxidation allows complete combustion of the organic matter, thus providing the true residual carbon in the sample (Fig. 9).

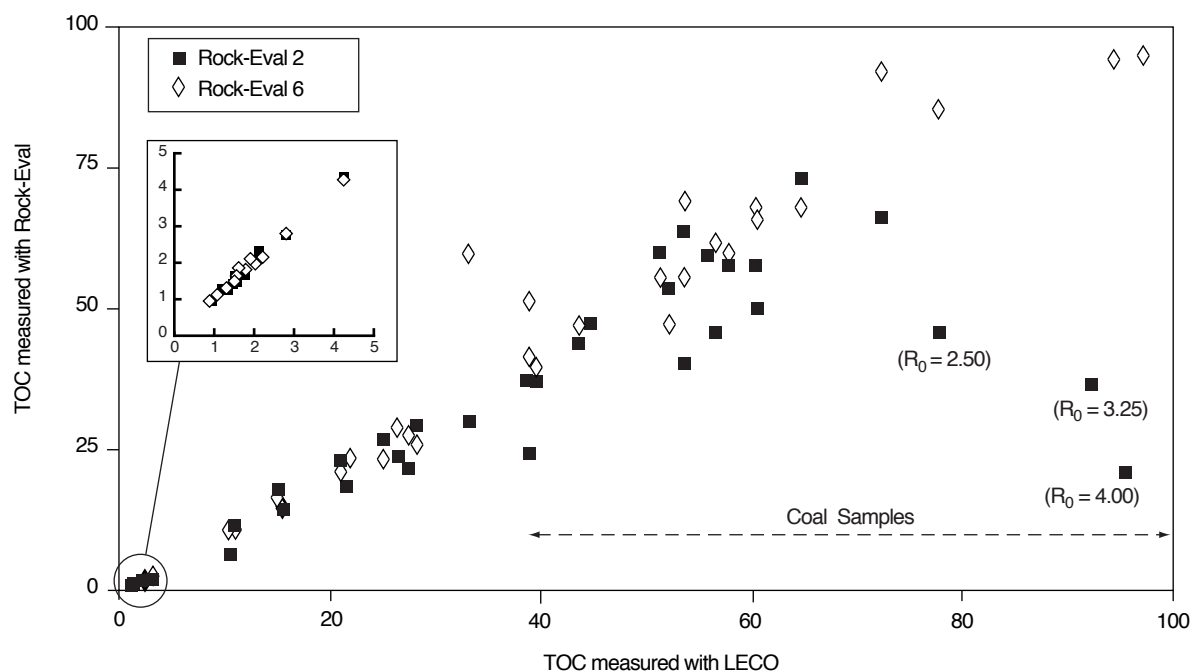


Figure 8  
 Comparison of organic carbon determination using Rock-Eval 6 and LECO.

### 2.3 Oxygen Index Determination

In the previous Rock-Eval apparatus, the oxygen index (OI in  $\text{mgCO}_2/\text{g TOC}$ ) is calculated from the amount of  $\text{CO}_2$  released and trapped over the  $300^\circ\text{C}$  to  $390^\circ\text{C}$  pyrolysis range. For Rock-Eval 6, both  $\text{CO}$  and  $\text{CO}_2$  are continuously monitored during the programmed pyrolysis of a rock sample. From these curves, oxygen indices specific to  $\text{CO}_2$  ( $\text{OI}_{\text{CO}_2}$ ) and to  $\text{CO}$  ( $\text{OI}_{\text{CO}}$ ) can be defined (Fig. 10). The combination of these two values gives the true oxygen index of the sample ( $\text{OI}_{\text{RE6}}$ ).

This improvement in the calculation of the oxygen index allows the use of the  $\text{OI}_{\text{CO}_2}/\text{OI}_{\text{CO}}$  ratio and the  $\text{OI}_{\text{RE6}}$ , to estimate changes during source rock deposition. For instance, on a series of source rock samples from the Bucomazi formation (Fig. 11), we were able to differentiate between “basin fill” versus “sheet drape” geological assemblages where the organo-facies variations depend upon paleoenvironment of deposition (Lafargue and Burwood, 1997). These differences were also illustrated by the

$\text{CO}$  and  $\text{CO}_2$  pyrolysis curves that vary from one depositional environment to the other thus indicating variations in the chemical composition of the organic matter (Fig. 12).

This modification of the apparatus improves its application to studies of organic facies variations in recent sediments, where the organic matter is rich in oxygenated functions.

### 2.4 Residual Petroleum Potential ( $S_2$ ) and High Temperature $T_{\text{max}}$

For Rock-Eval 6, the final pyrolysis temperature is  $850^\circ\text{C}$  instead of  $600^\circ\text{C}$ . As a consequence, the petroleum potential of many type III rock samples is increased and the resulting hydrogen index is more representative. Another improvement of this high temperature pyrolysis is the ability to measure high  $T_{\text{max}}$  values for type III samples with vitrinite reflectance values ( $R_0$ ) greater than 2%. Figure 13 shows differences between the  $S_2$  peaks obtained by Rock-Eval 2 and Rock-Eval 6 for coal samples with a

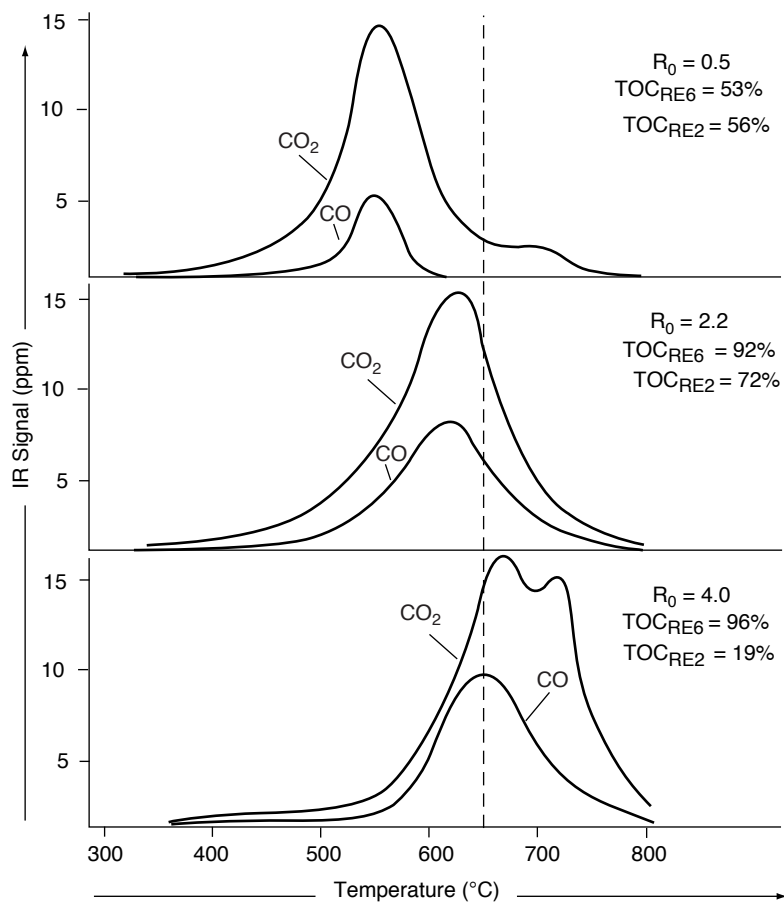


Figure 9

Examples of oxidation curves for a series of coal samples at increasing maturity. The resulting TOC calculation shows the differences between RE6 and RE2 measurements.

large range of maturities. The figure shows that the value of  $S_2$  changes significantly and that  $T_{max}$  values over  $600^\circ\text{C}$  are significant and are not an artifact of the measurement caused by very small  $S_2$  peaks. The correlation between  $T_{max}$  and  $R_o$  (Fig. 14) is thus extended to the very mature samples, which was not possible with the previous apparatus.

In type III source rocks, small residual potential  $S_2$  makes it difficult to know whether there is any remaining gas potential. When such source rocks are located in thrust zones, it is very important to determine their relative maturities in different parts of the thrust in order to reconstruct the deformation kinematics of the basin. This reconstruction requires maturity measurements that were difficult to obtain with previous versions of Rock-Eval when the samples were highly mature. In addition, determination of the residual potential for gas and the role of coal maturity

on its retention properties is also of interest for the evaluation of coal bed methane (Scott *et al.*, 1994).

### 3 ROCK-EVAL 6 ENLARGED APPLICATIONS

This section describes how the new functions of Rock-Eval 6 expand applications of the method in reservoir geochemistry and in soil contamination studies.

#### 3.1 Reservoir Geochemistry

Geochemistry of reservoirs is an area of growing interest with remarkable economic importance because it can be used to evaluate reservoir continuity during field appraisal, to identify non-productive reservoir zones, and to analyze commingled oils for production allocation calculations (e.g. Kaufman, 1990; England

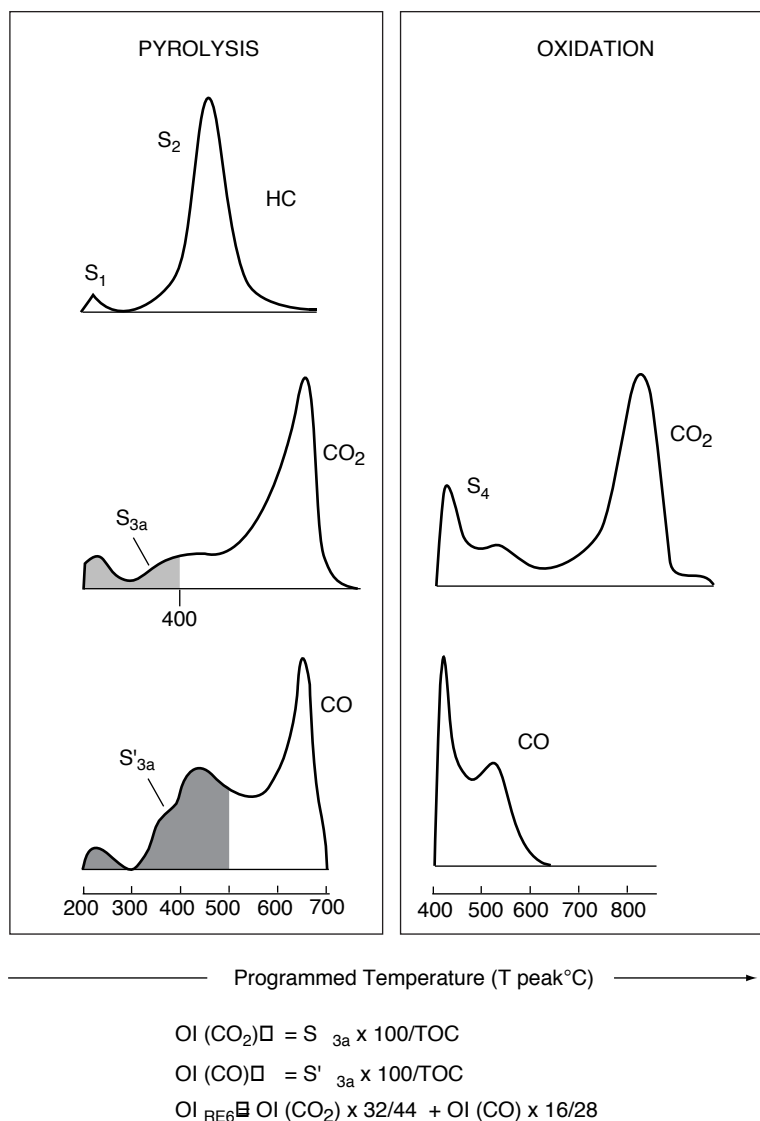


Figure 10  
 Principle of determining the oxygen indices using CO<sub>2</sub> and CO pyrolysis curves.

and Cubitt, 1995). The Rock-Eval method has already been successfully applied in reservoir geochemistry, especially for the detection of tar-mats and for the prediction of oil API gravities (Trabelsi *et al.*, 1994). For reservoir geochemistry, the main advantage of Rock-Eval 6 is its capability to perform both pyrolysis and oxidation of the sample up to 850°C at various rates.

Figure 15 is an example of Rock-Eval 6 results for four different reservoir rocks: three sandstones and one carbonate. The first sample represents a conventional

oil accumulation that produces a large S<sub>1</sub> peak and a smaller S<sub>2</sub> peak. Almost no CO and CO<sub>2</sub> are generated during oxidation.

The second sample shows a small S<sub>1</sub> peak, a bimodal S<sub>2</sub> peak (small S<sub>2a</sub> and large S<sub>2b</sub>) and significant amounts of CO and CO<sub>2</sub> released during oxidation. This sample is from a conventional tar-mat, i.e. a reservoir rock accumulated with crude oil enriched in resins and asphaltenes. For the last sandstone reservoir, we still observe the S<sub>1</sub>, S<sub>2a</sub> and S<sub>2b</sub> peaks but we also observe an important CO<sub>2</sub> peak produced during

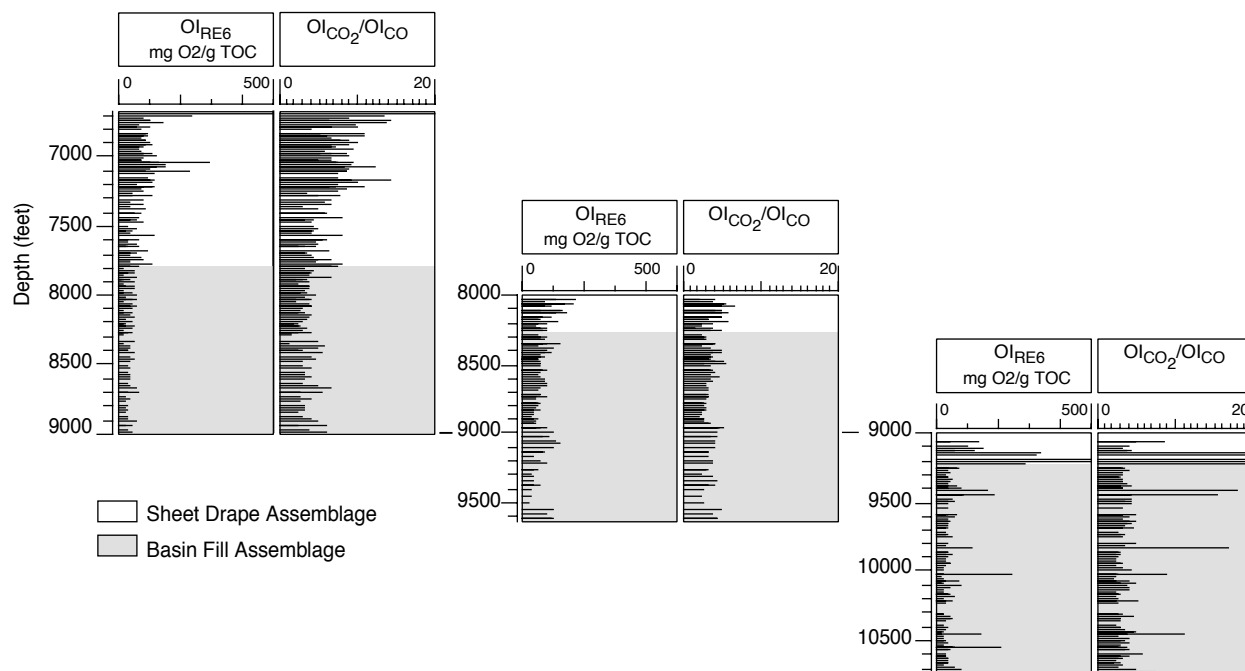


Figure 11

Correlation of Rock-Eval 6 oxygen indices across different wells of the Lower Congo Basin illustrating the transition from basin fill to sheet drape assemblages.

oxidation at high temperature (near 800°C). Since we also observed this peak in the rock sample after decarbonation, it cannot be caused by carbonate decomposition of minerals in the sandstone matrix. This peak corresponds to the combustion of refractory material associated with pyrobitumen in the sample. Therefore it seems possible, from the comparison of the oxidation curves of two tar-mat levels, to distinguish a conventional tar-mat deposited in the reservoir from a pyrobitumen produced by in-place secondary cracking of an oil accumulation. This distinction is very important since it can guide exploration and production strategies in oil fields with tar-mats.

The carbonate reservoir sample shows the same pattern in the FID trace as that observed for the conventional tar-mat in the sandstone reservoir. This is typical of the large amounts of resins and asphaltenes present in the rock. During the oxidation phase of the sample, the strong CO<sub>2</sub> production at about 500°C and the CO production correspond to the residual organic carbon, whereas the very large amount of CO<sub>2</sub> produced at higher temperature corresponds to the decomposition of the carbonate matrix.

### 3.2 Soil Contamination Studies

Due to its economic, environmental and industrial importance, the characterization of soils contaminated by hydrocarbons is another area where research is very active. Rock-Eval 6 expands the application of pyrolysis methodology to oil-contaminated sites by making it possible to start the analysis at low temperature (100°C). Furthermore, heating rates can be adjusted so as to release the different petroleum cuts (e.g., gasoline, diesel oil, heavy oils, lubricant oils, gas plant distillation residues). In this application (called Pollut-Eval), the vaporized hydrocarbons are identified by the FID and the signal is integrated for full quantification. A complete carbon mass balance is then carried out through oxidation of the residue and continuous quantification of CO<sub>2</sub> by the infrared detectors.

For these types of studies, the apparatus is equipped with a cooled autosampler that reduces the loss of light compounds. The equipment thus provides the parameters needed to characterize a contaminated site: what pollutant, how much and where? Due to the short duration of the analysis (30 min), the time needed to

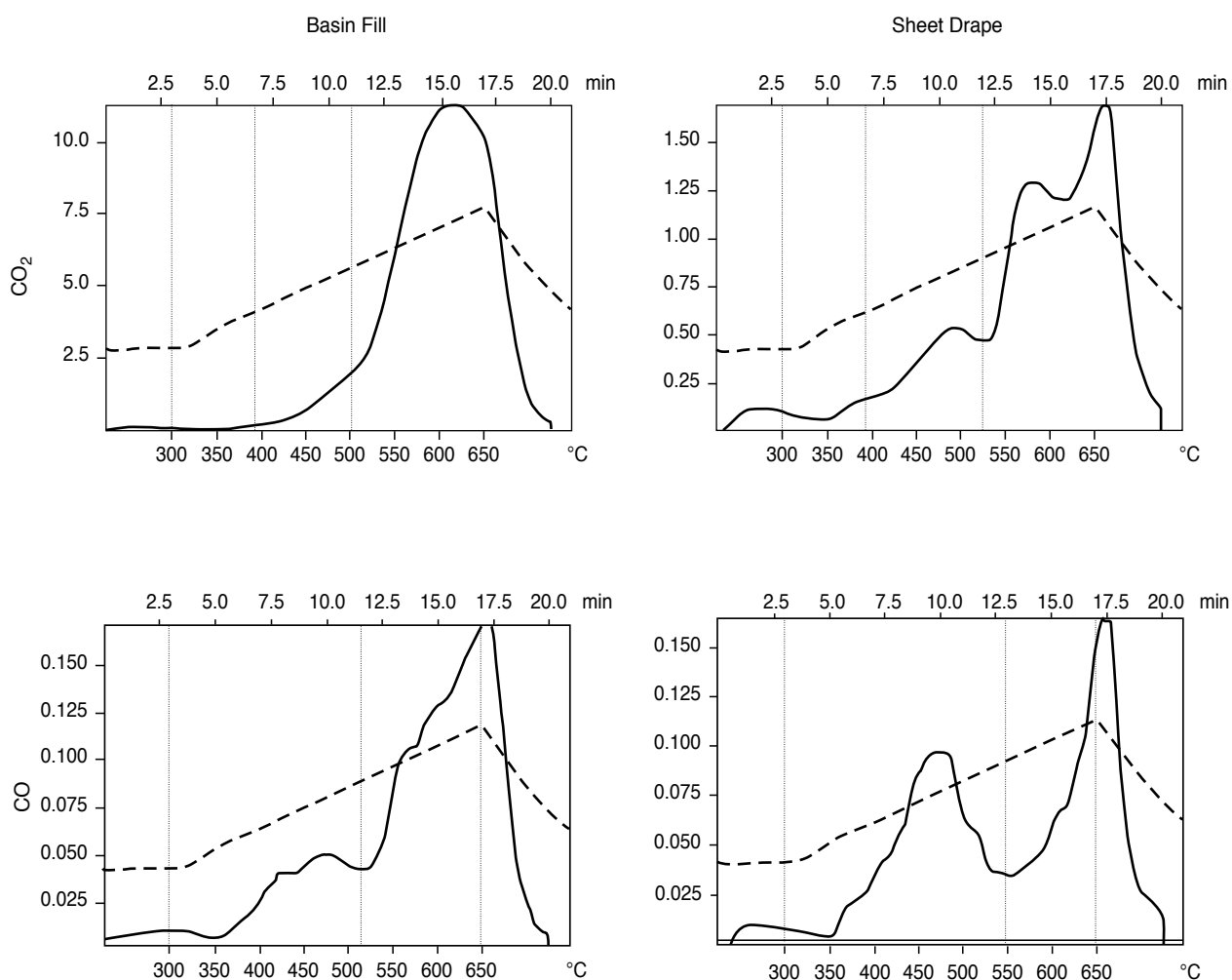


Figure 12

CO<sub>2</sub> and CO pyrolysis curves illustrating the differences in the composition of the organic matter in the basin fill and sheet drape organo-facies.

evaluate the extent of a contaminated site is drastically decreased compared to routine techniques that involve the extraction of the pollutant prior to its analysis by chromatography, infrared or chromatography-mass spectrometry. Furthermore, when applied on site, the measurements can be used to optimize the drilling program (Ducieux *et al.*, 1997).

Rock-Eval 6 data can be correlated to standard environmental data such as infrared response. They are also complementary to infrared or gas chromatographic analyses because they allow rapid screening of a large number of samples, thus helping to identify the samples that are worthy of additional study. An example of the

application of Rock-Eval 6 data for two industrial sites is presented in Figure 16. The upper part of the figure shows contamination by diesel oil and polyaromatic hydrocarbons in a soil near an old gas plant. The FID trace indicates two main peaks corresponding to the mixture of these hydrocarbons and the CO and CO<sub>2</sub> traces during oxidation are characteristic of the combustion of the heavy residue accompanying these products in the pollution. The second example is taken from contaminated soil near a service station. Light gasoline-range compounds are released early during pyrolysis and no significant amounts of CO and CO<sub>2</sub> are recorded during oxidation.

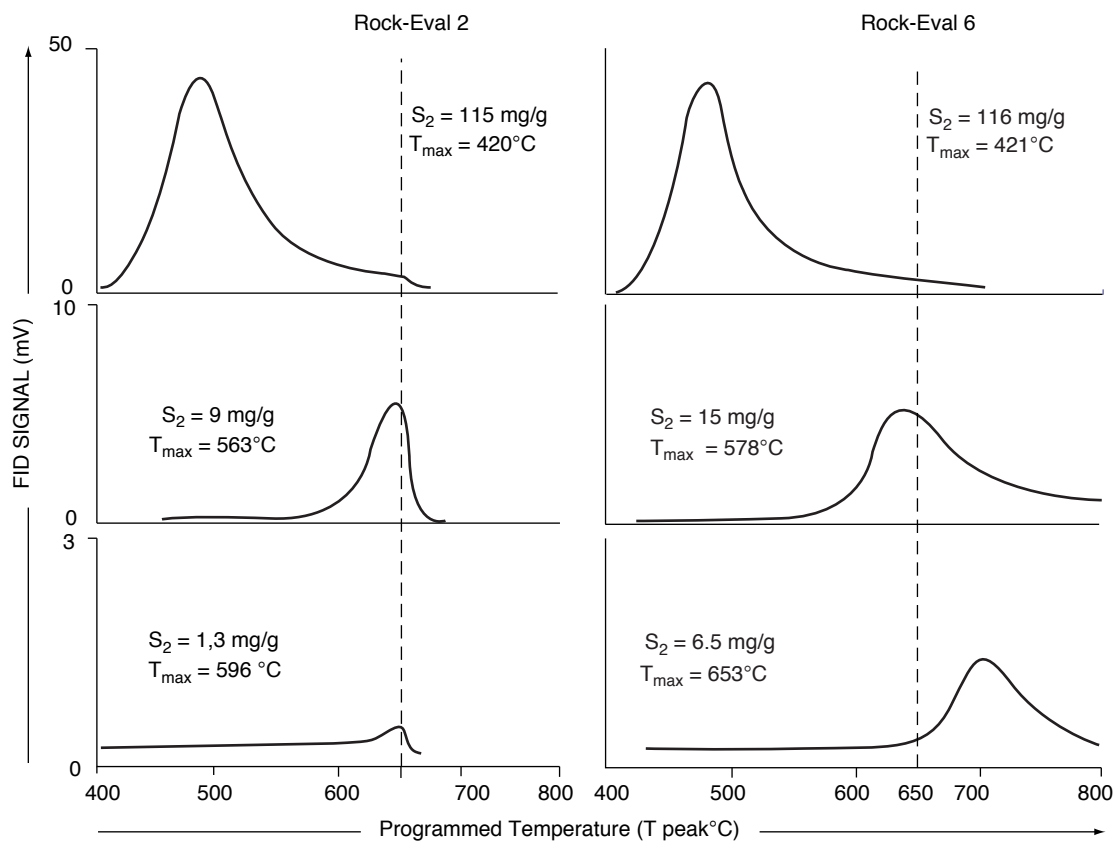


Figure 13

Illustration of the effect of high final pyrolysis temperature with Rock-Eval 6 on the calculation of the residual potential  $S_2$  and on the measurement of  $T_{max}$ .

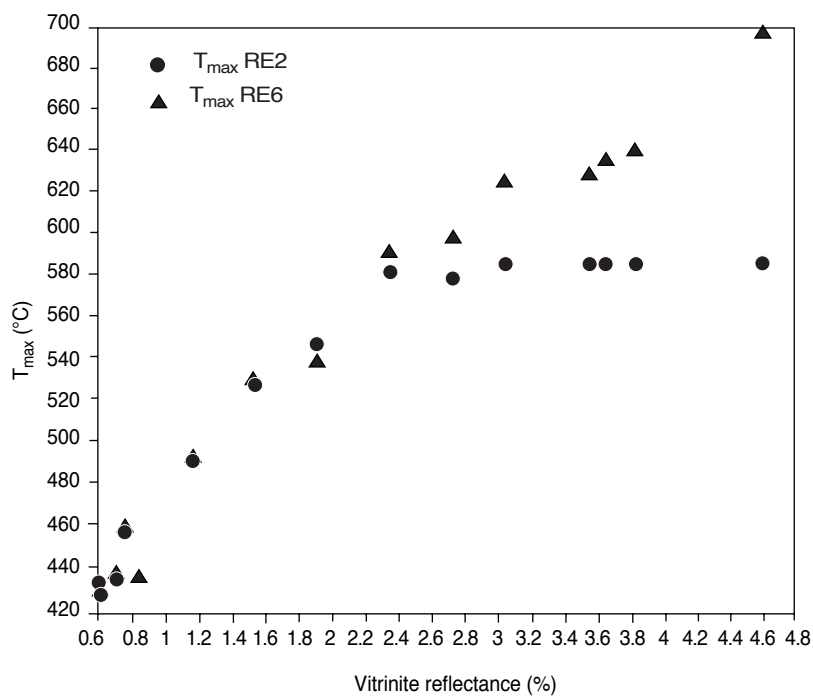


Figure 14

Correlation between  $T_{max}$  and  $R_o$  for Rock-Eval 6 and Rock-Eval 2 on a series of coal samples.

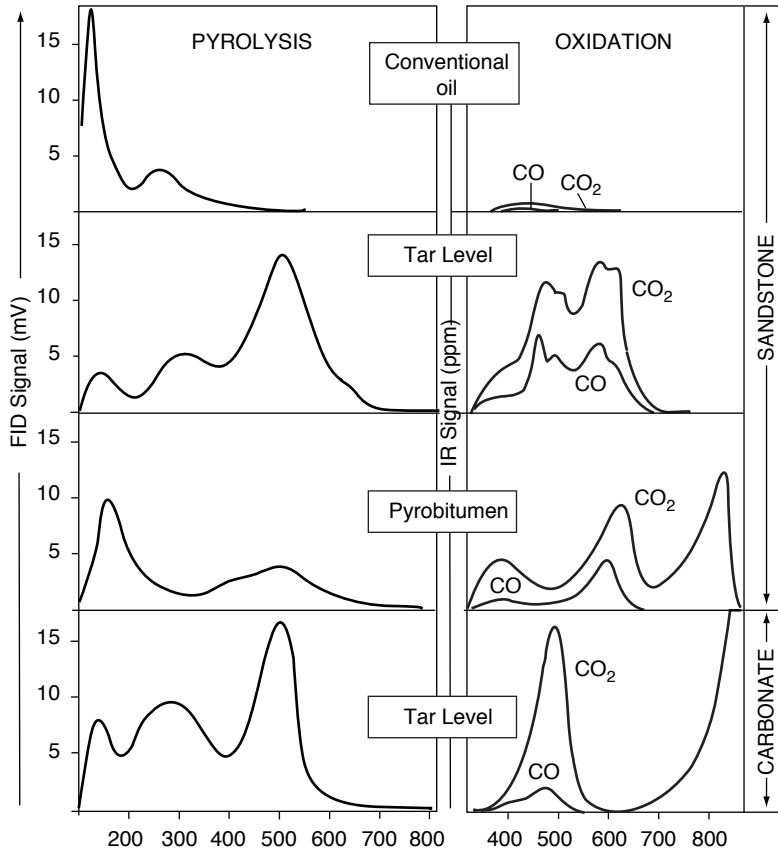


Figure 15  
 Examples of applying Rock-Eval 6 to the study of reservoir rocks.

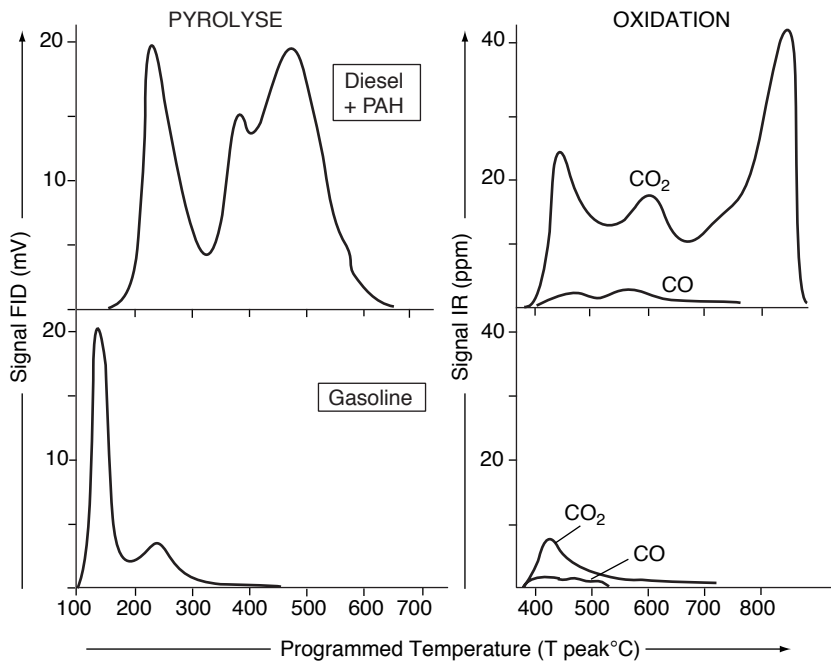


Figure 16  
 Examples of applying Rock-Eval 6 to the study of contaminated soils.



## CONCLUSIONS

The new Rock-Eval 6 pyroanalyser marks an important step in the development of programmed pyrolysis systems. This apparatus provides new functions and parameters that expand applications of the technique in petroleum geoscience. Problems with the older Rock-Eval systems have been reduced. The major improvements and their scientific impact can be summarized as follows:

- Mineral carbon determination:
  - improved characterization of marly/carbonate source rocks;
  - detection of carbonate types (e.g., siderite, calcite, dolomite);
  - enhanced characterization of hydrocarbons in carbonate reservoirs;
  - possible correction of matrix effects.
- Oxygen indices:
  - impact on source rock facies analysis;
  - impact on the knowledge of source rock preservation conditions.
- Improved measurements of TOC and  $T_{max}$ :
  - better analysis of type III source rocks;
  - better analysis of heavy bitumen in reservoirs (tar-mat studies);
  - better characterization of coals.

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