

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

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E. Lafargue, J. Espitalié, F. Marquis and D. Pillot



Institut Français du Pétrole, 1-4 Av. de Bois Préau, 92852 Rueil-Malmaison, France

The RockEval 6 is marketed by VINCI TECHNOLOGIES - 14, rue Auguste Neveu - BP 91 - 92503 Rueil-Malmaison cedex - France
Tel: +33 (0)1 41 39 00 20 - Fax: +33 (0)1 47 08 38 99 - E.Mail: vincinet@vinci-technologies.com

Abstracts

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 is 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 functionalities of the latest version of Rock-Eval apparatus (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.

Keywords: Rock-Eval ; source rock characterization ; reservoir geochemistry ; soil contamination

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1. INTRODUCTION

The characterization of 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 consists in the temperature programmed heating of a small amount of rock (100mg) in an inert atmosphere (Helium or Nitrogen) so as to determine (Fig. 1): the quantity of free hydrocarbons present in the sample (S1 peak) and the amount of hydrocarbons and oxygen containing compounds (CO₂) that are produced during the thermal cracking of the insoluble organic matter (kerogen) in the rock (S2 and S3 peaks respectively peak). 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 (S4 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 the Rock-Eval methodology, while others are mainly improvements of the existing method. In this respect, we will first present the Rock-Eval 6 functionalities 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 Tmax (temperature measured at the top of the S2 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.

2. METHODOLOGY: ROCK EVAL 6 NEW FUNCTIONALITIES

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

2.1. 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 high 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 S2 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 = S2/TOC) is more accurate and the range of validity of Tmax is extended to higher values.

Another important outcome of this new functionality is a better kinetic parameters determination for type III organic matter. For such samples, we commonly 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 temperature of oxidation 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 the 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 numerous contaminants are 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 driving 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 (TC1). The second thermocouple (TC2) 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.

2.2. CONTINUOUS ON-LINE DETECTION OF CO AND CO₂ WITH INFRA-RED DETECTORS

For earlier versions of the Rock-Eval instrument, the CO₂ released during pyrolysis was trapped and quantified using a catharometer. Although the S3 peak quantifies the total CO₂ yield, it does not reflect its temperature programmed release during kerogen cracking. This limits interpretation of the S3 response. Similarly during oxidation, the CO₂ 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 introduce sensitive infrared detectors into the Rock-Eval 6, that are capable of continuous on-line recording of the amount of both CO and CO₂ 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 S1 and S2 peaks), (2-3) CO and CO₂ produced during



pyrolysis (CO and CO₂ pyrolysis curves), (4-5) CO and CO₂ produced during oxidation (CO and CO₂ oxidation curves). The sixth curve in Figure 3 is the superposition of CO and CO₂ curves and is very useful for a rapid visualization of the presence or absence of carbonate in the sample.

As we will see in the results that follow, the continuous recording of both CO and CO₂ has brought a number of new useful parameters. For instance, the character of CO and CO₂ 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 was successfully used earlier 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.

2.3. 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 machine 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 S1 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).

3. RESULTS

3.1. MINERAL CARBON DETERMINATION

The amount of mineral carbon is calculated by addition of the CO₂ released during pyrolysis above 400°C and the CO₂ from carbonate decomposition during the oxidation phase from 650°C to 850°C (Fig. 4). Carbonate minerals such as magnesite and siderite start to be decomposed when the pyrolysis temperature approaches 400°C whereas dolomite and calcite (the most important minerals in carbonate sequences) decompose during oxidation (Fig. 5). On this figure, we see that dolomite oxidative decomposition gives two characteristic peaks corresponding to the following reactions:

- (1) $\text{CaMg}(\text{CO}_3)_2 \text{ ----> CaCO}_3 + \text{MgO} + \text{CO}_2$
- (2) $\text{CaCO}_3 \text{ ----> CaO} + \text{CO}_2$ at higher temperature

Calcite decomposition occurs at about 800°C and is recorded 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.

Even though 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 CO₂ released by the oxygenated functions in the organic matter. In Rock-Eval 6, thanks to the continuous on-line recording of CO and CO₂ released during pyrolysis, it seems that the combination of S3CO, S3CO₂ values and Tpeak CO₂ (temperature at the maximum of CO₂ pyrolysis curve; "Tmax CO₂") on bulk rocks can point out very rapidly when and where siderite is occurring. Samples with siderite present S3CO values greater than 5mgCO/g rock; S3CO₂ greater than 10mgCO₂/g rock and Tpeak CO₂ in the 485-520°C temperature range. As a result, we get access to 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 is occurring only under specific environment). Furthermore, the comparison of a series of bulk rocks and acid-treated rocks indicated that, when there is a lot of siderite, we can observe the production of CO during pyrolysis according to the following set of chemical reactions:

- (1) $\text{FeCO}_3 \text{ ----> FeO} + \text{CO}_2$
- (2) $3 \text{FeO} + \text{CO}_2 \text{ ----> Fe}_3\text{O}_4 + \text{CO}$

Once siderite is removed by acid treatment, the CO production stops which results in small values of S3CO (organic CO alone).

Mineral carbon content based on Rock-Eval 6 analysis correlates well with that obtained by routine chemical attack technique 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.

3.2. ORGANIC CARBON DETERMINATION

Like previous Rock-Eval systems, RockEval 6 determines the amount of organic carbon by adding pyrolyzed carbon (PC) and residual carbon (RC). Nevertheless, the continuous CO and CO₂ detection has improved PC and RC quantifications (Fig. 7).

The pyrolyzed carbon is computed from: (1) the hydrocarbon compounds released in peaks S1 and S2, assuming that they contain about 83% of organic carbon, (2) the CO released during pyrolysis up to 500°C (S3CO peak) and (3) the CO₂ released during pyrolysis up to 400°C (S3CO₂a peak). To avoid interference by release of pyrolytic CO₂ from carbonate minerals such as siderite, only the first part of the CO₂ pyrolysis curve is taken into account. Likewise, in order to avoid possible interference caused by Boudouard's reaction, where the CO₂ released early during carbonate decomposition can react with the residual carbon to produce CO (CO₂ + C --> 2 CO), we limit 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 (S4CO peak)



and CO₂ up to 650°C (S4CO₂ peak). At higher temperatures, there is no more CO production and the CO₂ comes generally from the decomposition of carbonates.

The progresses made in organic carbon determination have brought higher performances 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 measured now for mature coal samples (Vitrinite Reflectance (Ro) > 2%) is drastically improved since high temperature oxidation allows a complete combustion of the organic matter, thus providing the true residual carbon in the sample (Fig. 9).

3.3. OXYGEN INDEX DETERMINATION

In the previous Rock-Eval apparatus, the Oxygen Index (OI in mgCO₂/g TOC) is calculated from the amount of CO₂ released and trapped over the 300°C to 390°C pyrolysis range. For the Rock-Eval 6 instrument, both CO and CO₂ are continuously monitored during the programmed pyrolysis of a rock sample. From these curves, Oxygen Indices specific to CO₂ (OI_{CO₂}) and for CO (OI_{CO}) can be defined (Fig. 10). The combination of these two values gives the true Oxygen Index (OI_{RE6}).

This improvement in the calculation of the Oxygen Index allows the use of the OI_{CO₂}/OI_{CO} ratio and the OI_{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

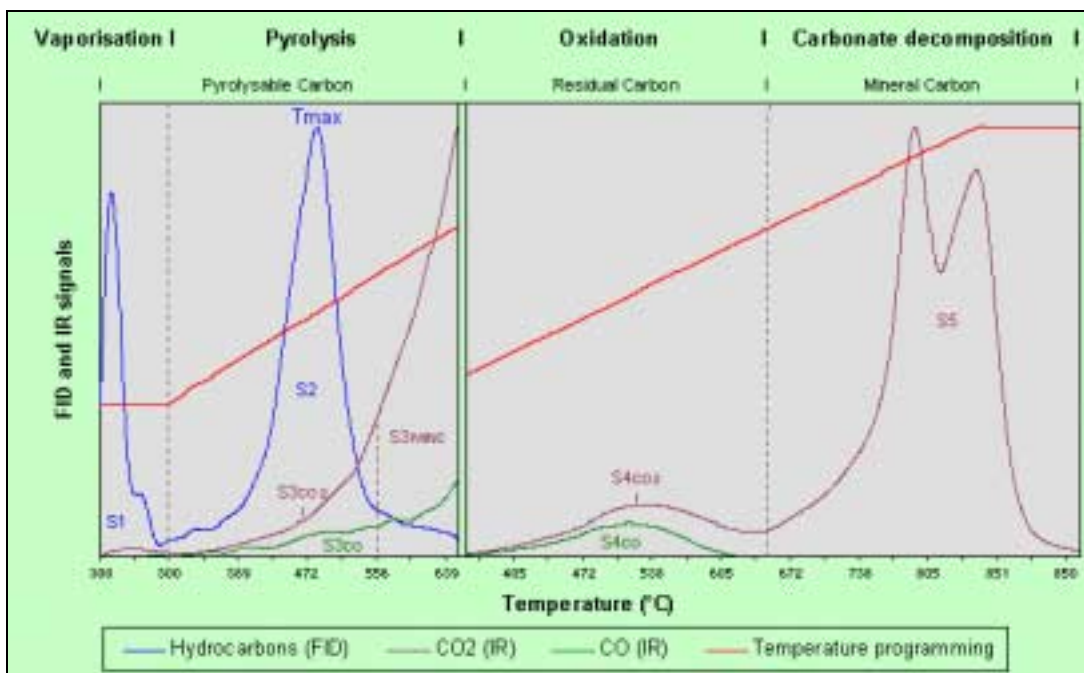
upon paleoenvironment of deposition (Lafargue and Burwood, 1997). These differences were also illustrated by the CO and CO₂ pyrolysis curves that vary from one depositional environment to the other thus indicating variations in the chemical composition of the organic matter (Fig. 12).

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

3.4. RESIDUAL PETROLEUM POTENTIAL (S2) AND HIGH TEMPERATURE TMAX

For Rock-Eval 6, the final pyrolysis temperature is 850°C instead of 600°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 Tmax values for type III samples with vitrinite reflectance values (Ro) greater than 2%. Figure 13 shows differences between the S2 peaks obtained by Rock-Eval 2 and Rock-Eval 6 for coal samples with a large range of maturities. The figure shows that the value of S2 changes significantly and that Tmax values over 600°C are significant and are not an artifact of the measurement caused by very small S2 peaks. The correlation between Tmax and Ro (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 S2 makes it difficult to know whether there is still 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 kinematics of deformation of the basin. This reconstruction requires maturity measurements that were difficult to obtain with previous Rock-Eval apparatus 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).



Example of a complete Rock-Eval 6 analysis of crude rock.

The pyrolysable carbon is computed from S1, S2, S3co and S3co2 residual carbon (RC) from S4co and S4co2 and mineral carbon (MINC) from S5 and S3MINC.

The TOC is calculated by taking the sum of the Pyrolysable carbon (PC) and the residual carbon (RC).

4. ROCK EVAL 6 ENLARGED APPLICATIONS

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

4.1. RESERVOIR GEOCHEMISTRY

Geochemistry of reservoirs is an area of growing interest with a 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., Kauffman, 1990; England 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 advantages of Rock-Eval 6 are the 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 S1 peak and a smaller S2 peak. Almost no CO and CO₂ are generated during oxidation.

The second sample shows a small S1 peak, a bimodal S2 peak (small S2a and large S2b) and significant amounts of CO and CO₂ released during the 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 S1, S2a and S2b peaks but we also observe an important CO₂ peak produced during 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

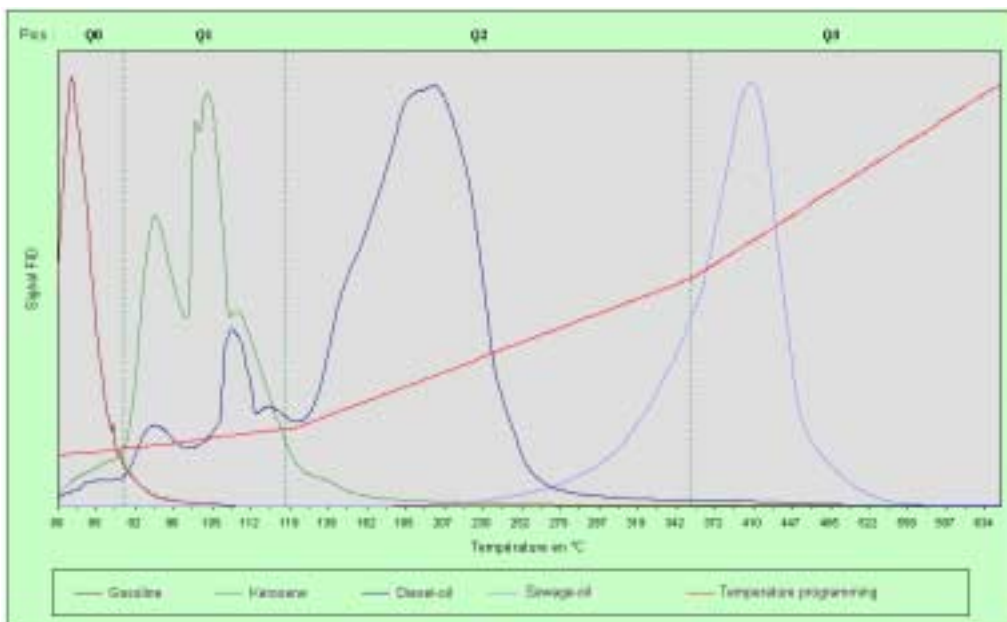
pyrobitumen produced by in-place secondary cracking of an oil accumulation. This distinction is very important since it can guide exploration and production strategies in oil fields with tar-mats.

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 high amounts of resins and asphaltenes present in the rock. During the oxidation phase of the sample, the strong CO₂ production at about 500°C and the CO production correspond to the residual organic carbon, whereas the very high amount of CO₂ produced at higher temperature corresponds to the decomposition of the carbonate matrix.

4.2. 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 due to the possibility of starting 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). For this application a specific pyrolyser called Pollut-Eval with cooled autosampler has been developed in order to reduce the loss of light compounds. 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 and CO₂ by the infrared detectors.

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



This pyrogram shows the superposition of curves obtained with the Pollut-Eval for gasoline, kerosene, diesel-oil and sewage-oil.

To identify the pollutant, we use the relative value (identified by the letter R and numbered from 0 to 3) of the hydrocarbon amount measured in each pre-defined integration area.

The relative values corresponding to each pyrogram are :

- Gasoline : R0 = 93%
- Kerosene : R1 = 81%
- Diesel-oil : R2 = 74%
- Sewage-oil : R3 = 75%



Pollut-Eval data can be correlated to standard environmental data such as infrared response. Pollut-Eval data are complementary to infrared or gas chromatographic analyses because they allow rapid screening of a large number of samples, thus helping to identify the samples 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 CO₂ 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 CO₂ are recorded during oxidation.

5. CONCLUSIONS

The new Rock-Eval 6 pyroanalyzer marks an important step in the development of programmed pyrolysis systems. This apparatus provides new functionalities and parameters that expand applications of the technique in petroleum geoscience. Problems related to the older Rock-Eval systems have been ameliorated. 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 rocks facies analysis
 - > impact on the knowledge of source rocks preservation conditions
- Improved measurements of TOC and Tmax:
 - > 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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6. REFERENCES

- BARKER, C. 1974. Pyrolysis techniques for source rock evaluation. *Amer. Assoc. Pet. Geol. Bull.*, **58**, 2349-2361.
- BERNER, R.A. 1981. A new geochemical classification of sedimentary environments. *J. Sed. Petrol.* **51**, 359-365.
- CLAYPOOL, G.E. and REED, P.R. 1976. Thermal analysis technique for source rock evaluation: Quantitative estimate of organic richness and effects of lithologic variation. *Amer. Assoc. Pet. Geol. Bull.*, **60**, 608-626.
- CLEMENTZ, D.M., DEMAISON G.J. and DALY A.R., 1979. Well site geochemistry by programmed pyrolysis. *Proceedings of the 11th Annual Offshore Technology Conference*, Houston, OTC 3410, v.1, 465-470
- CURTIS, C.D. 1977. Sedimentary geochemistry: environments and processes dominated by involvement of an aqueous phase. *Phil. Trans. R. Soc. London. A.*, **286**, 353-372.
- DALY, A.R. and PETERS K.E. 1982. Continuous detection of pyrolytic carbon monoxide: A rapid method for determining sedimentary organic facies. *Amer. Assoc. Pet. Geol. Bull.*, **66**, 2672-2681.
- DUCREUX, J., LAFARGUE E., MARQUIS, F., PILLOT, D. and BOCARD, C. 1997. Use of Rock-Eval method for the evaluation of soils contaminated by hydrocarbons. *Analisis*, **25**, n° 9-10, 40-44.
- ENGLAND, W. and CUBITT, J. 1995. The Geochemistry of Reservoirs. *Geol. Soc. Sp. Publ.*, 86.
- ESPITALIE, J., LAPORTE, J.L., MADEC, M., MARQUIS, F., LEPLAT, P. and PAULET, J. 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Petr.*, **32**, 23-45.
- ESPITALIE, J., MARQUIS, F., and BARSONY, I. 1984. Geochemical logging. In: *Analytical pyrolysis- Techniques and applications*, K.J. Voorhees ed., Boston, Butterworth, 276-304.
- HORSFIELD, B. 1985. Pyrolysis studies in petroleum exploration. In: *Advances in Petroleum Geochemistry* (eds J. Brooks and D. Welte), Vol. 1, 247-298, Academic Press, New York.
- KAUFFMAN, R., AHMED, A., and ELSINGER, R.J. 1990. Gas chromatography as a development and production tool for fingerprints in oils from individual reservoirs: Application in the Gulf of Mexico. In: *GC-SSEPM Foundation Ninth Annual Research Conference Proceedings*, October 1, 1990, 263-282.
- LAFARGUE, E. and BURWOOD, R. 1997. Improved source rock characterisation utilizing Rock-Eval 6 derived Oxygen Indices. In: *18th Int. Meeting on Org. Geoch. Sept. 22-26, 1997, Maastricht*, pp. 727-728, *Book of abstracts*.
- LARTER, S.R. and DOUGLAS, A.G. 1982. Pyrolysis methods in organic geochemistry: An overview. *J. Anal. Appl. Pyrol.*, **4**, 1-19.
- PETERS, K.E., 1986. Guidelines for evaluating petroleum source rocks using programmed pyrolysis. *AAPG Bull.*, **70**, 329.
- PETERS, K.E. and SIMONEIT, B.R.T., 1982. Rock-Eval pyrolysis of Quaternary sediments from Leg 64, sites 479 and 480, Gulf of California. *Initial Report of the Deep Sea Drilling Project*, **64**, 925-931.
- SCOTT, A.R., KAISER, W.R. and AYERS Jr, W.B., 1994. Thermal maturity of Fruitland coal and composition of Fruitland Formation and Pictured Cliffs sandstone. In: *Coal Bed Methane in the Upper Cretaceous Fruitland Formation, San Juan Basin, New Mexico and Colorado*, New Mexico and Colorado, Bull., 146, 165-185.
- TRABELSI, K., ESPITALIE, J. and HUC, A.Y. 1994. Characterisation of extra heavy oils and tar deposits by modified pyrolysis methods. In: *European symposium on Heavy Oil Technologies in a Wider Europe, Proceedings*, June 7&8, 1994, 30-40.
- van BUCHEM, F.S.P., EBERLI, G.P., WHALEN M.T., MOUNTJOY, E.W. and HOMEWOOD, P., 1996. The basinal geochemical signature and platform margin geometries in the Upper Devonian mixed carbonate-siliciclastic system of western Canada. *Bull. Soc. Geol. France*, **167**, 685-699.



FIGURES CAPTIONS

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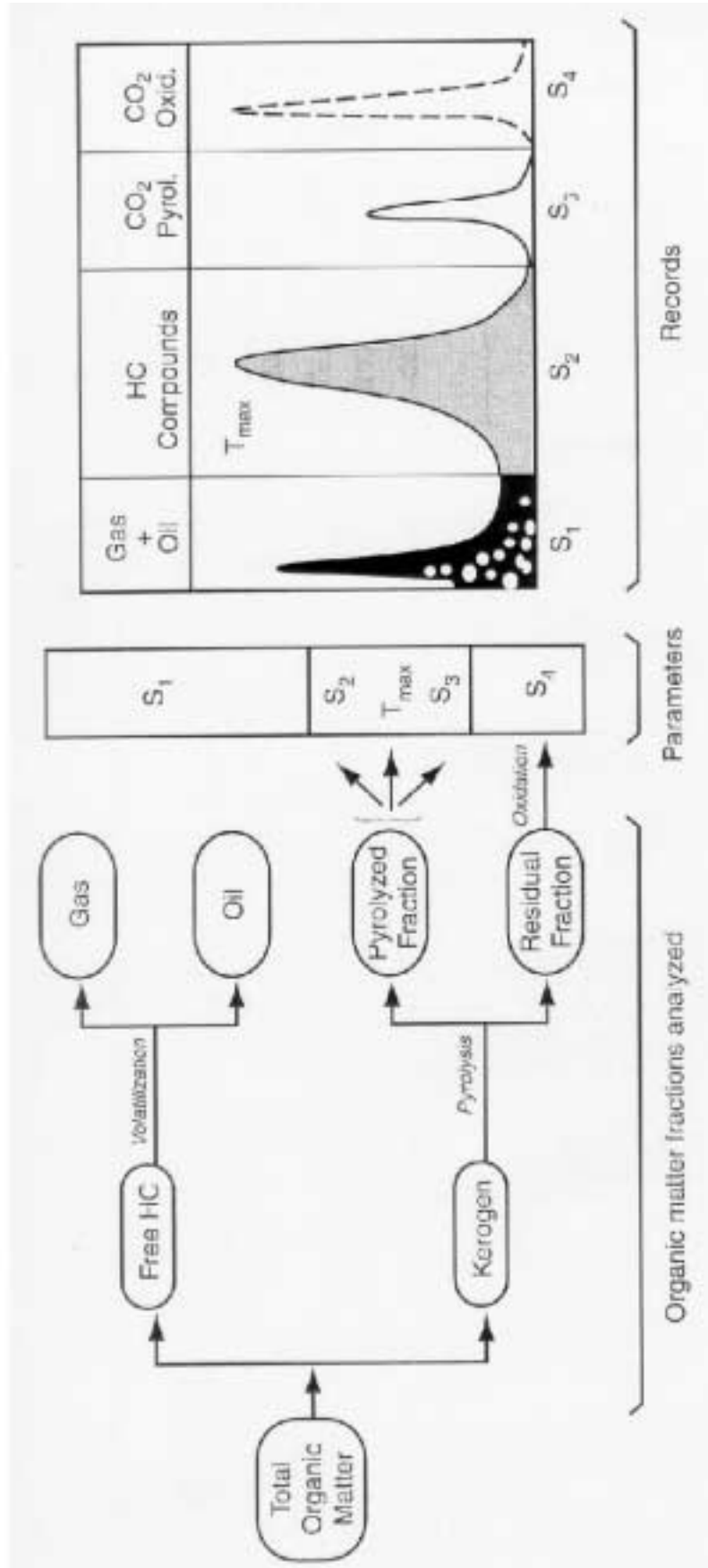


Figure 1: General diagram showing the different fractions of the total organic matter of rocks analyzed, the corresponding parameters and their recordings.

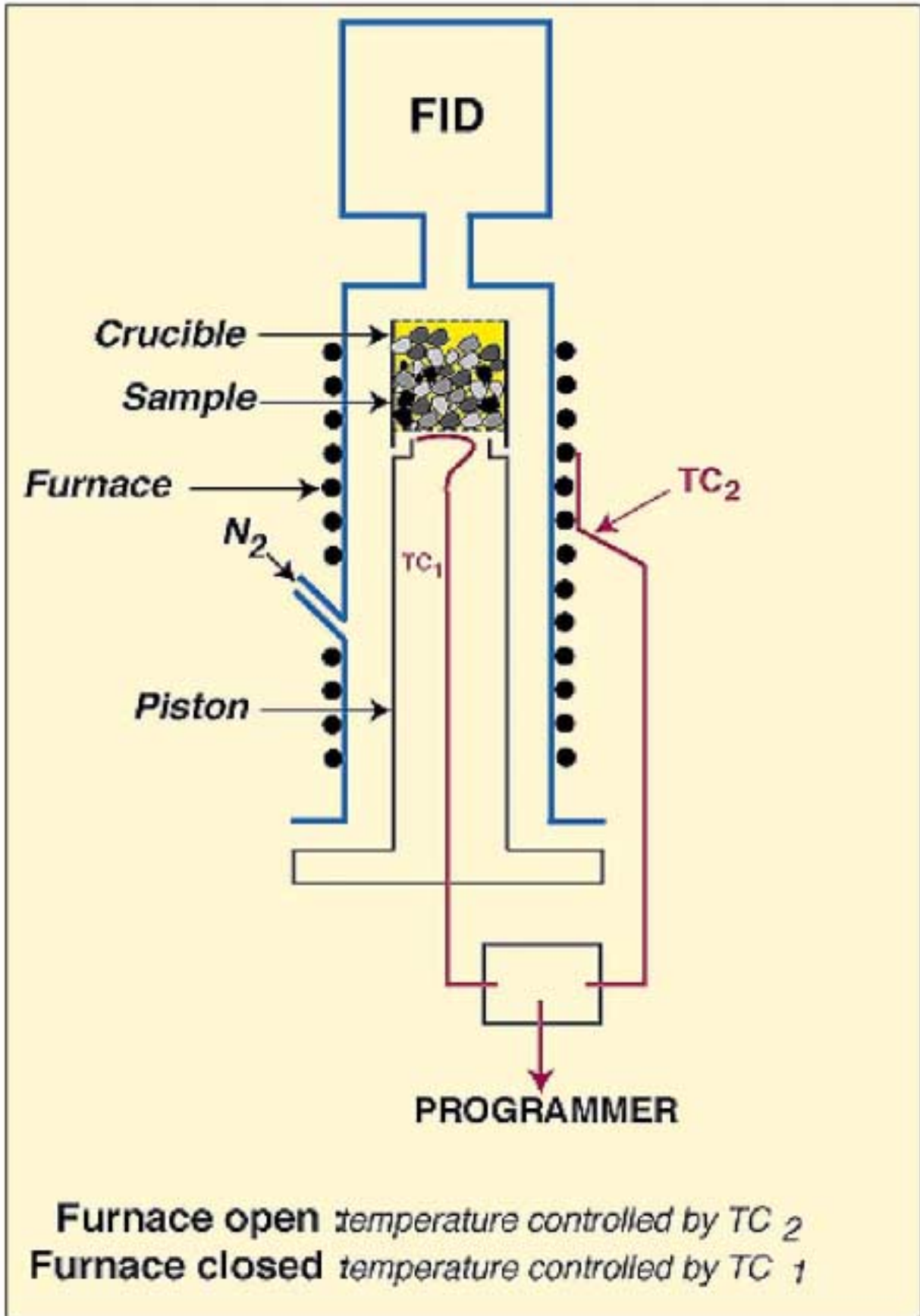


Figure 2: Schematic diagram indicating the location of the thermocouple for temperature regulation in the pyrolysis oven.

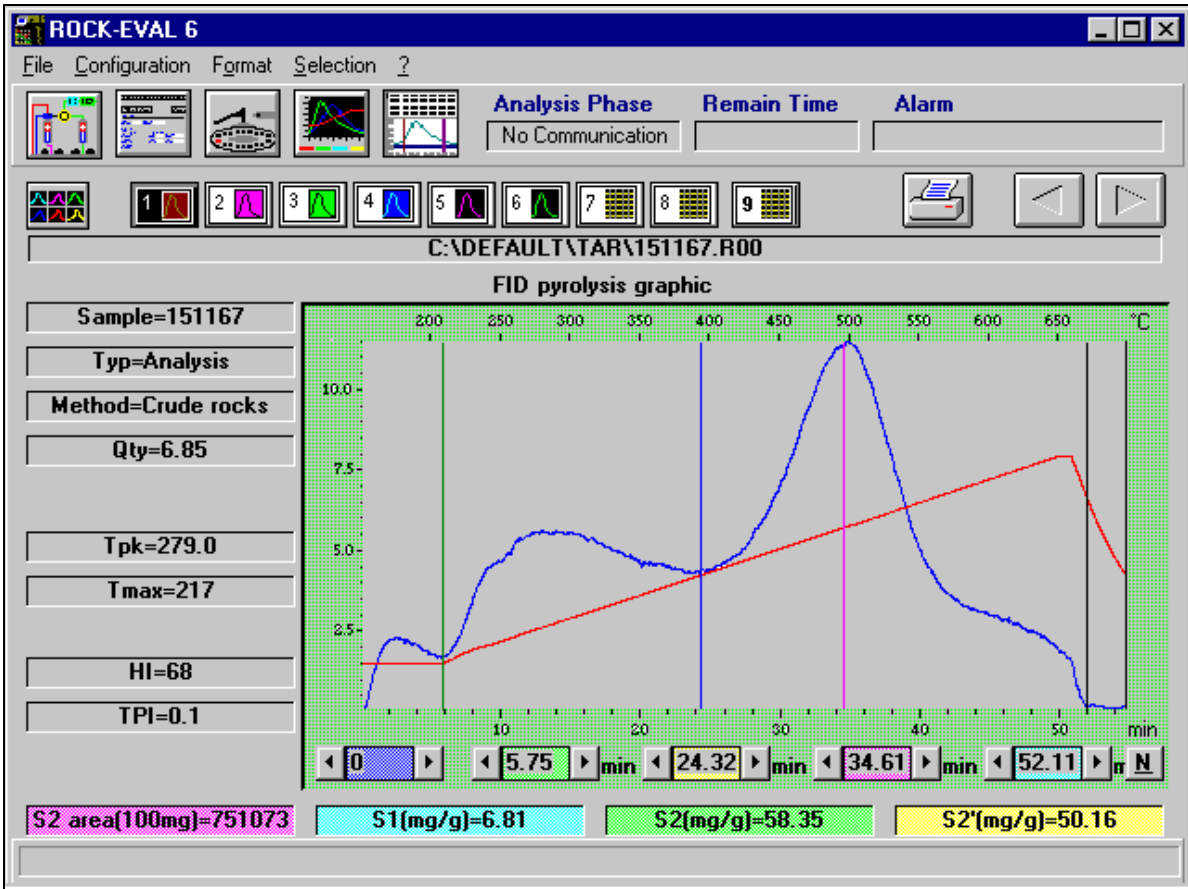
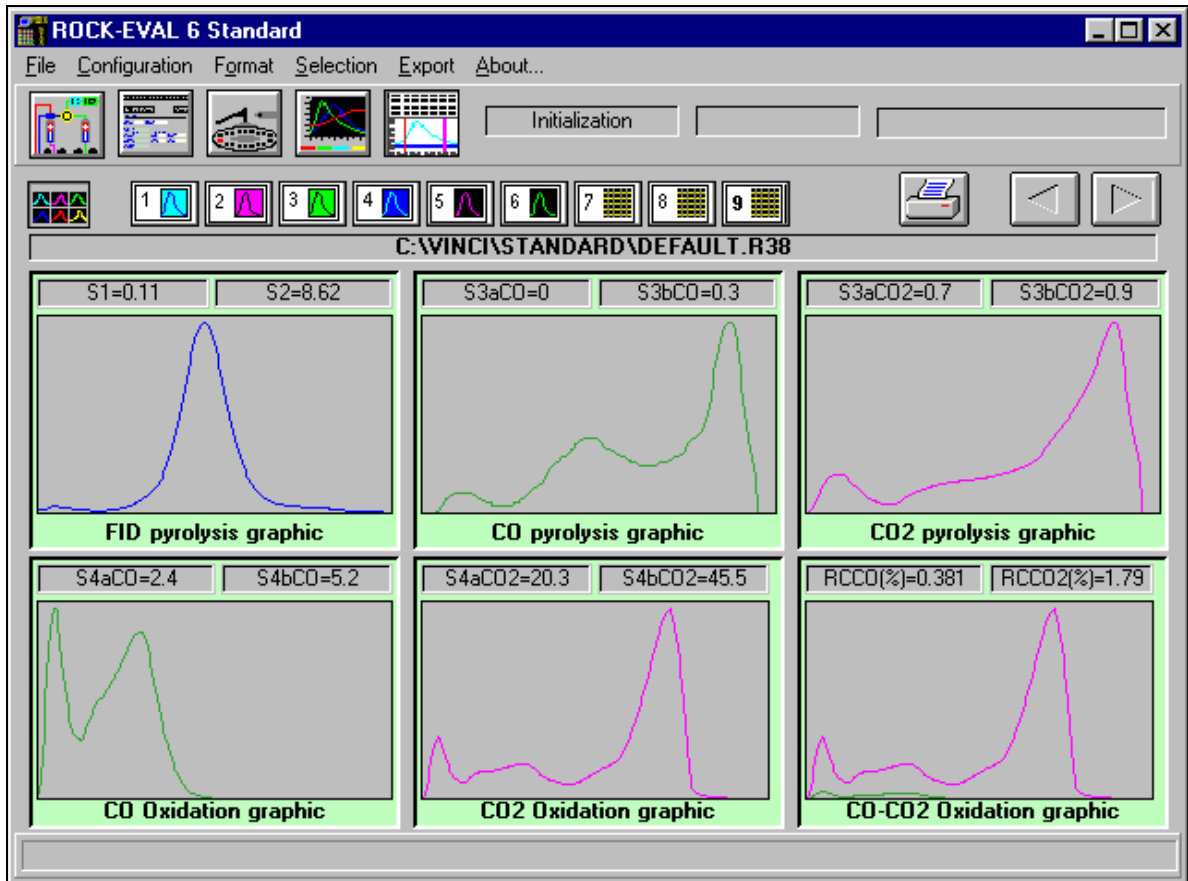


Figure 3: Illustration of Rock-Eval 6 standard recordings for hydrocarbons, CO and CO₂ during the pyrolysis and oxidation phases.

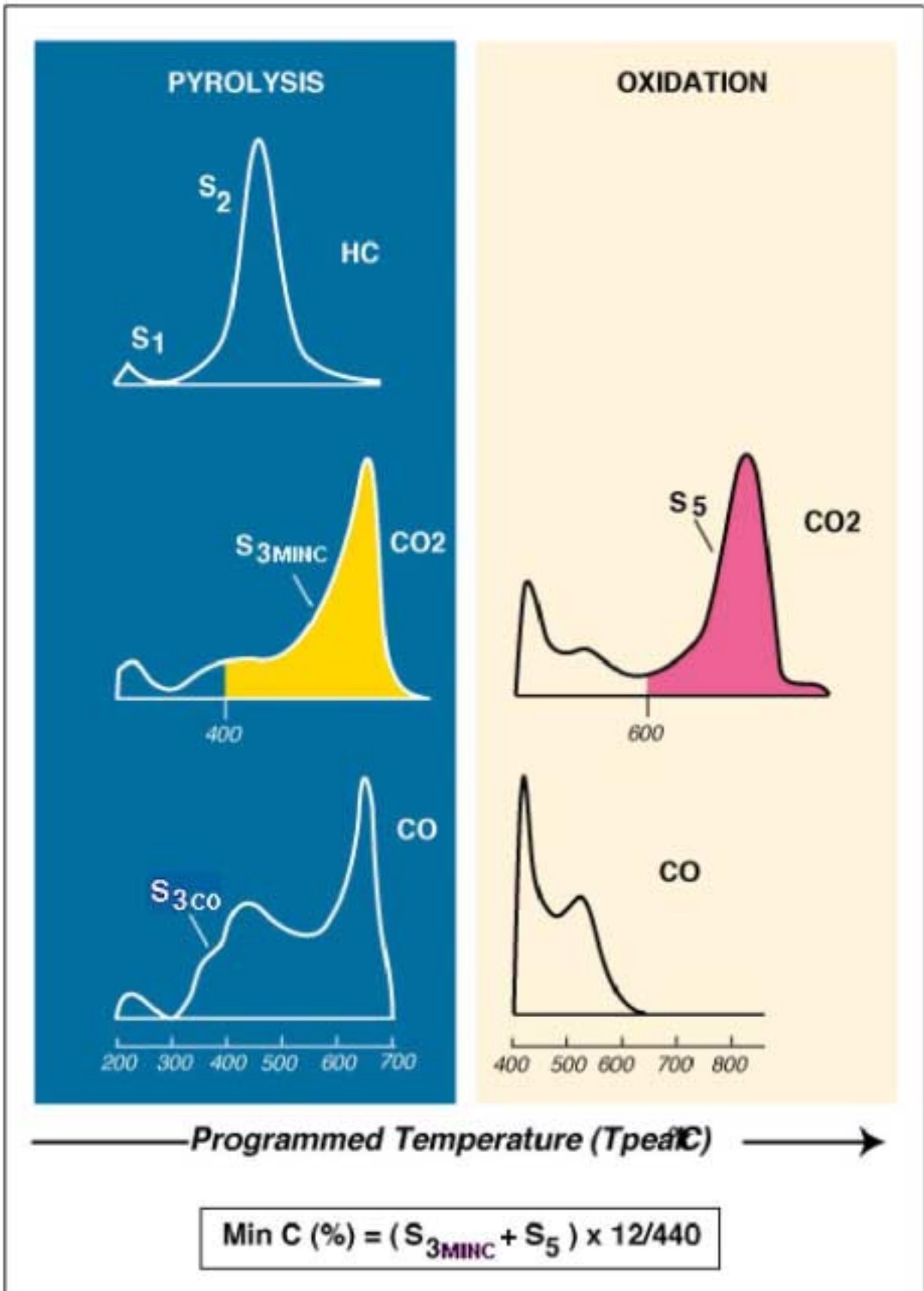


Figure 4: Principle of determination of mineral carbon (MINC; %) using CO₂ pyrolysis and oxidation curves.

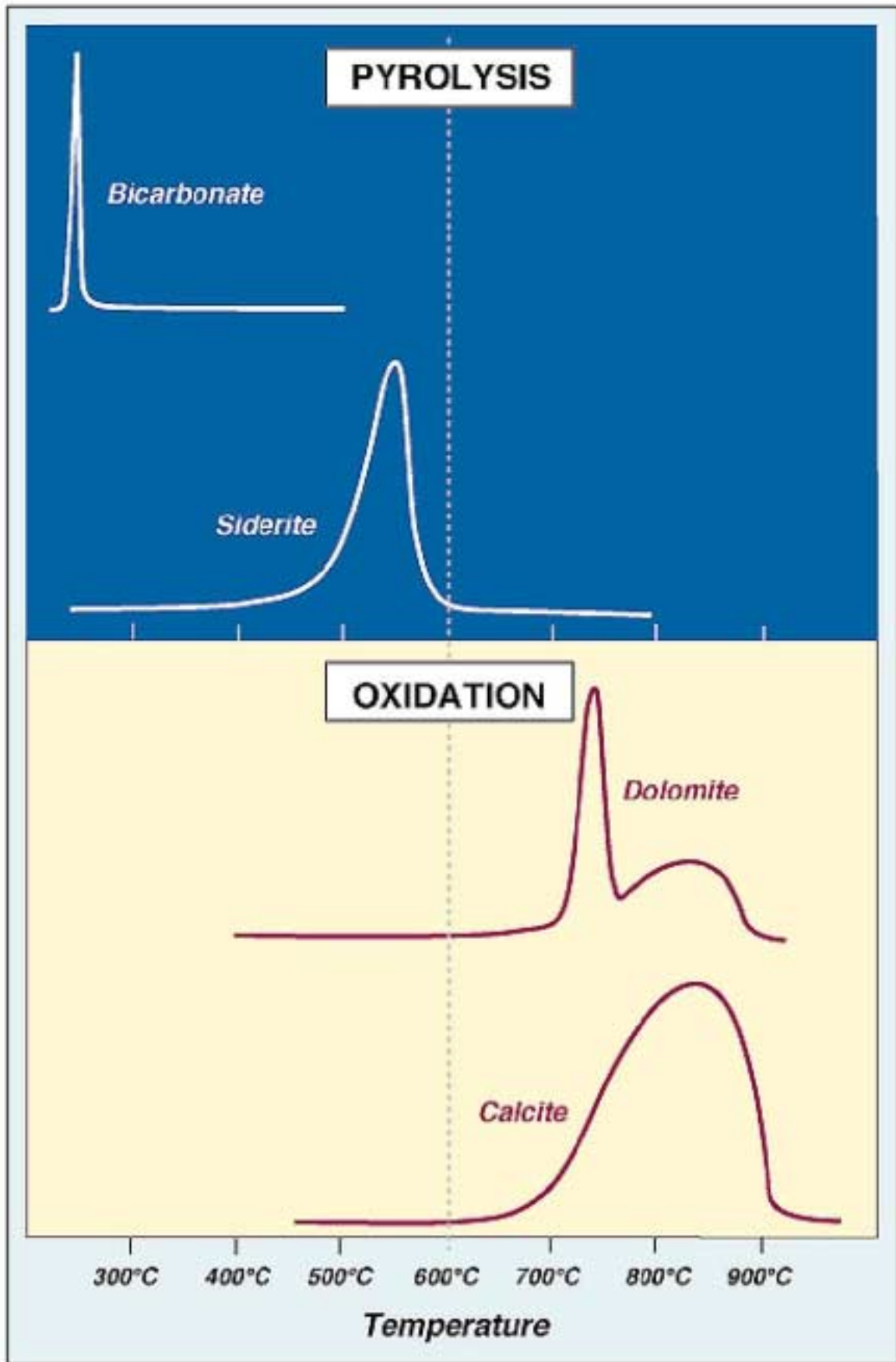


Figure 5: Rock-Eval 6 response of different types of carbonate minerals illustrating their progressive decomposition with increasing temperature.

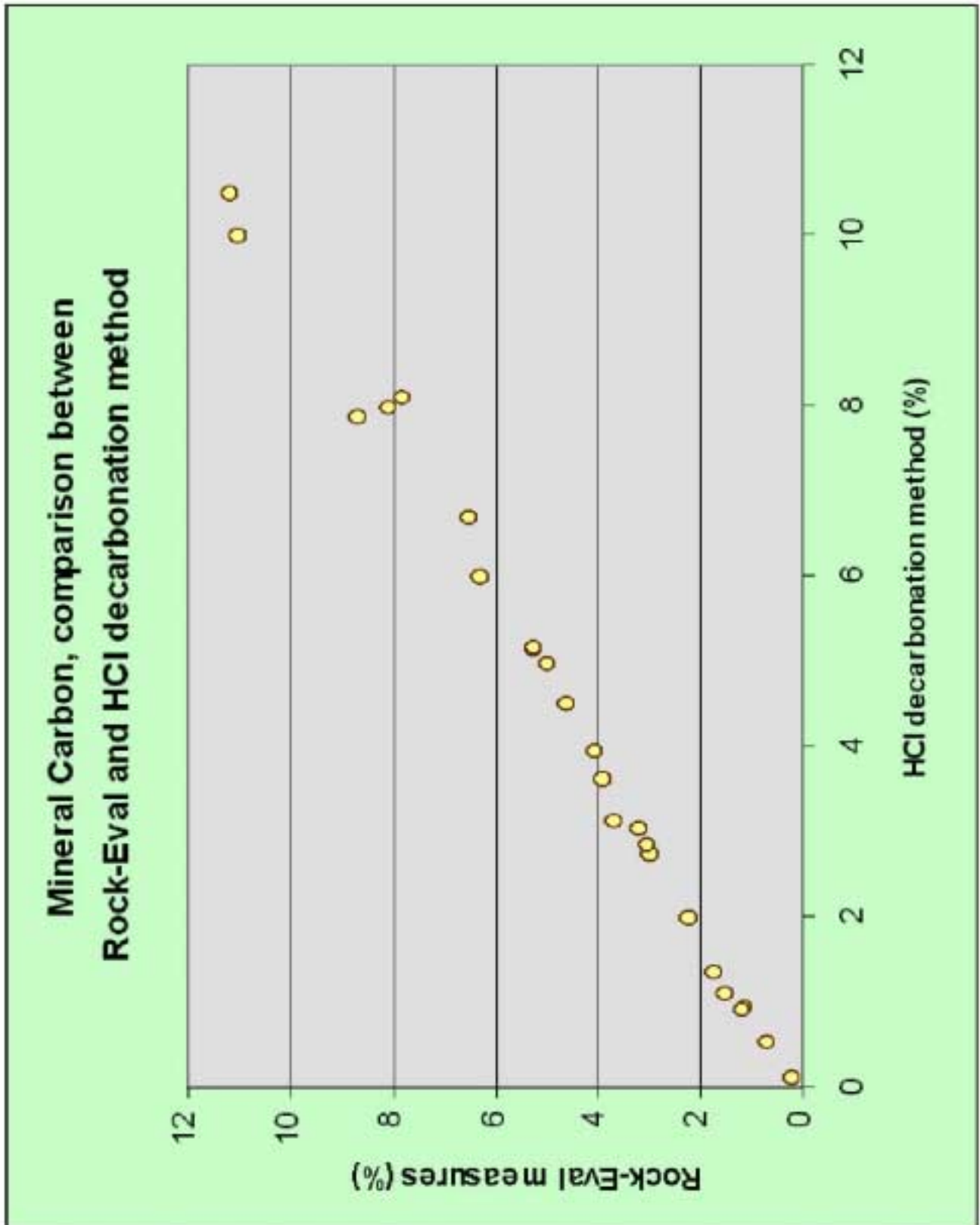


Figure 6: Comparison of mineral carbon determination using Rock-Eval 6 and acid attack.

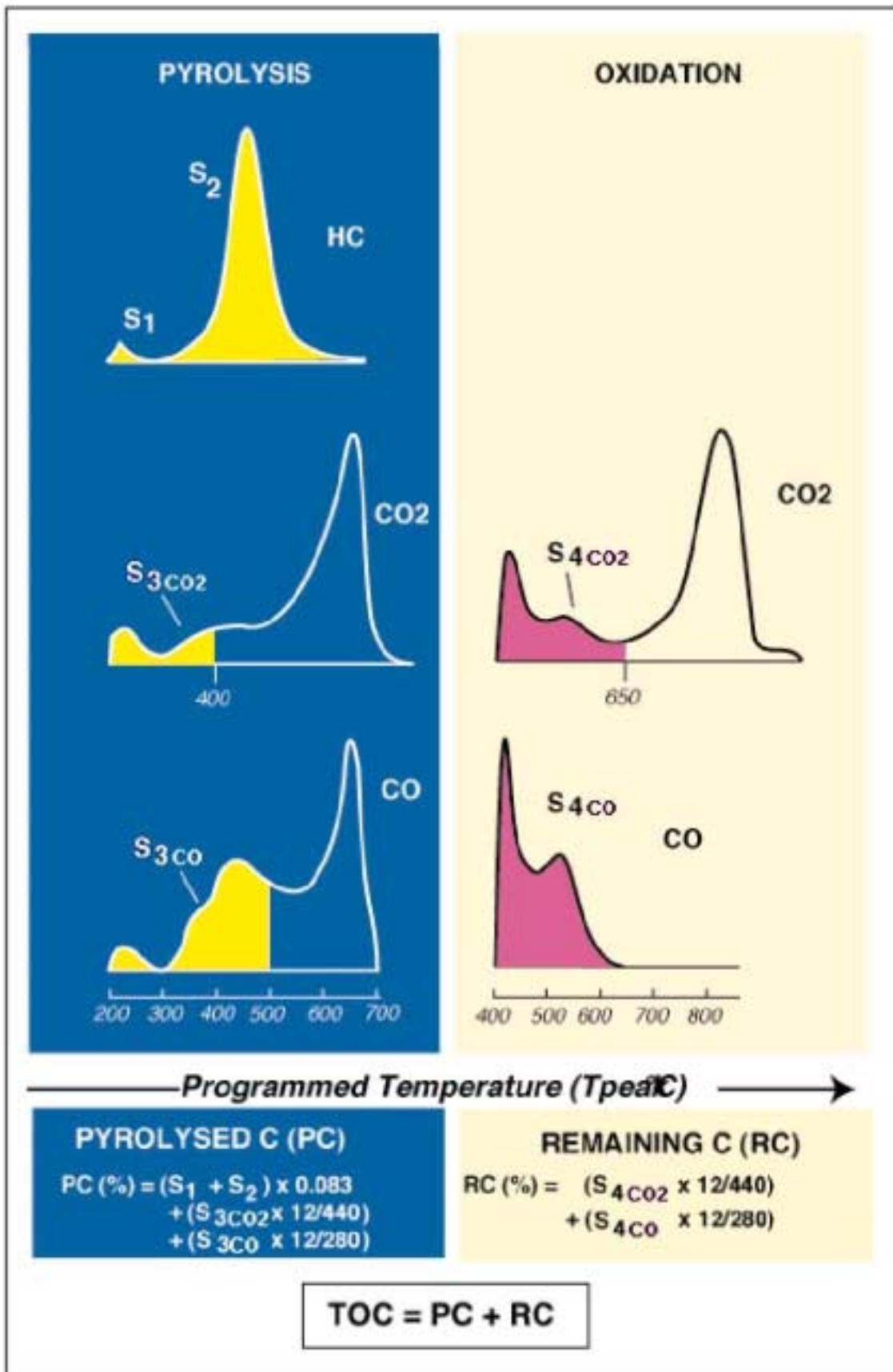


Figure 7: Principle of determination of the total organic carbon (TOC; %) using FID, CO₂ pyrolysis and oxidation curves to calculate the amounts of Pyrolyzed Carbon (PC) and Residual Carbon (RC).

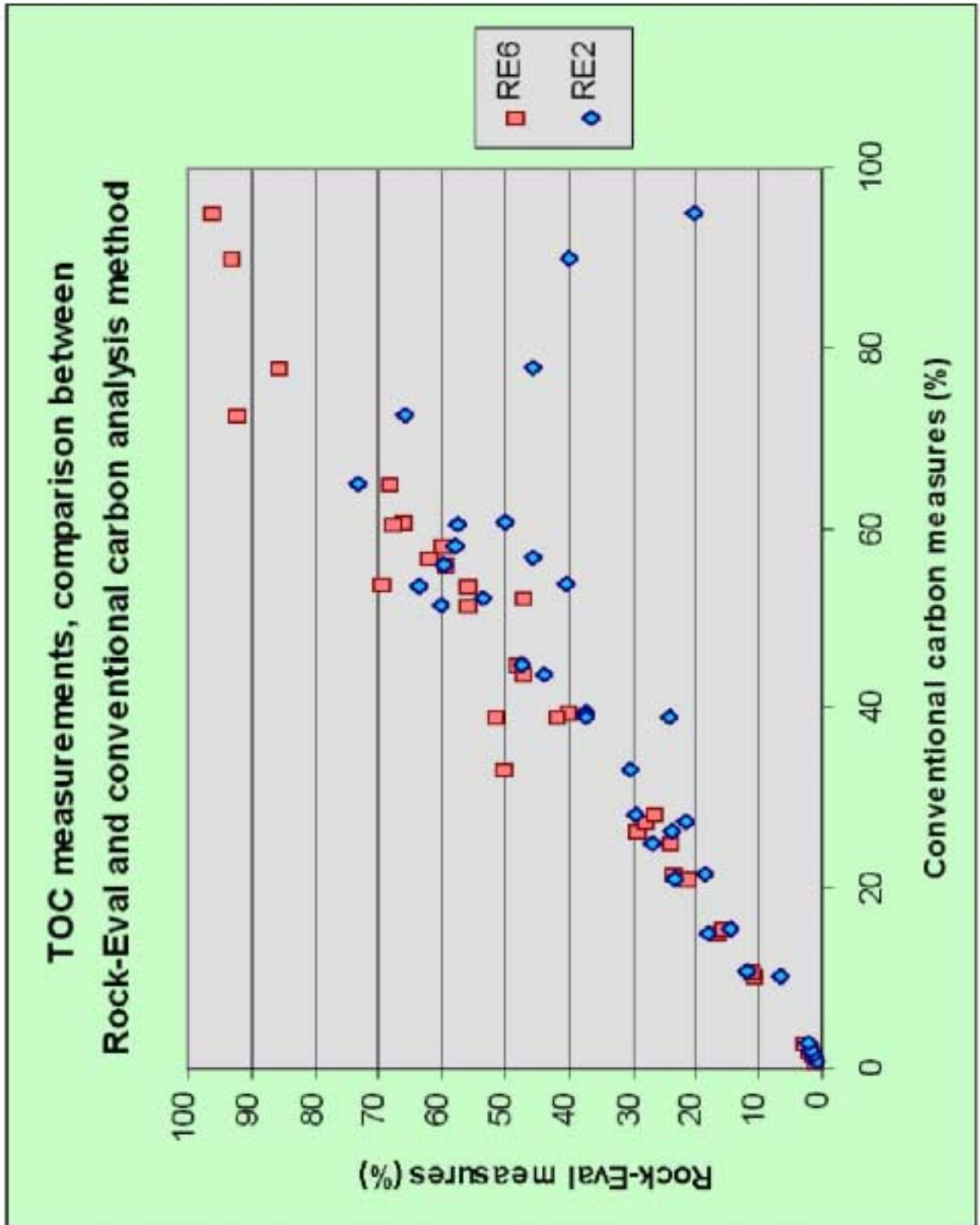


Figure 8: Comparison of organic carbon determination using Rock-Eval 6 and conventional carbon analysis method.

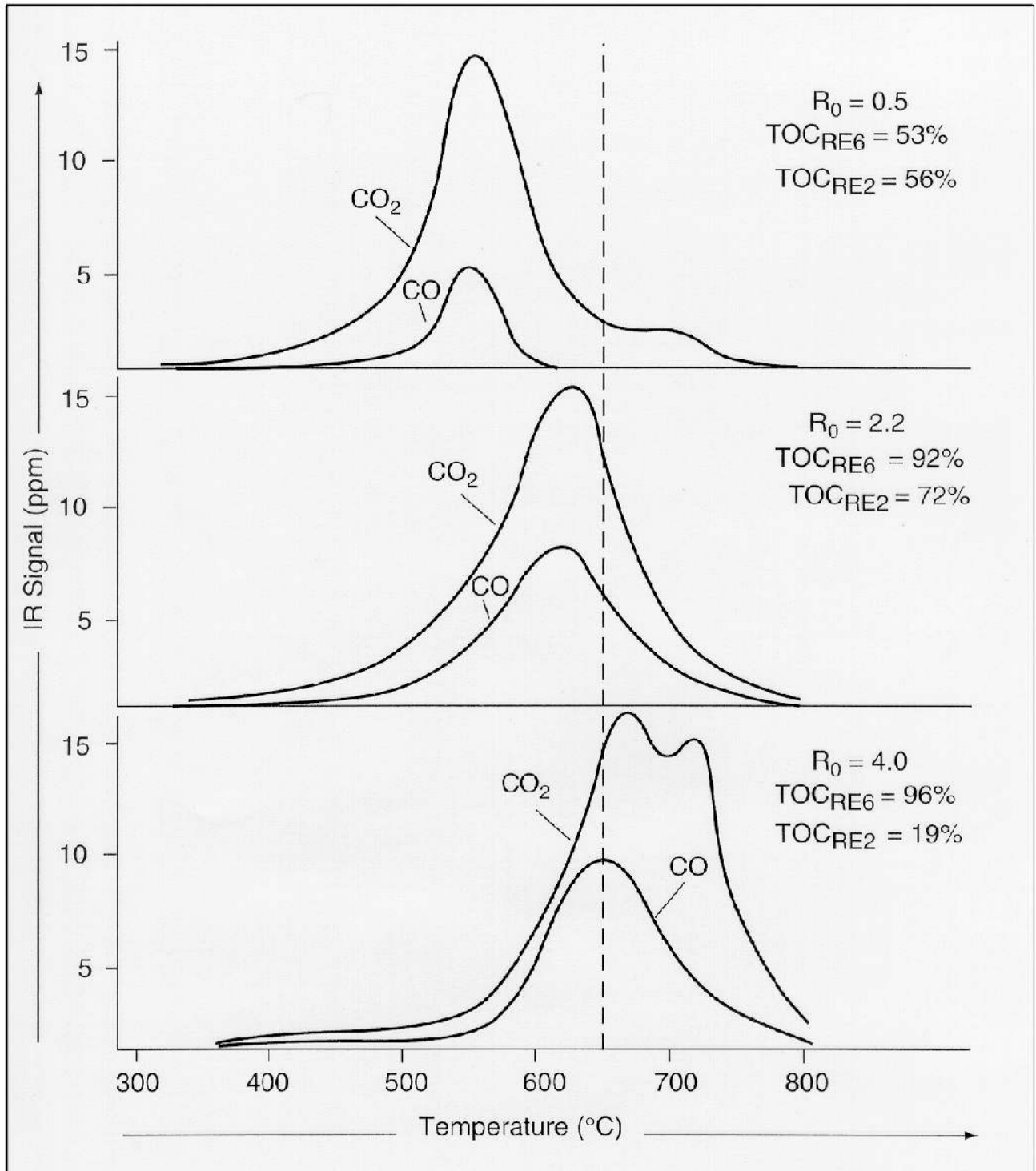


Figure 9: Examples of oxidation curves for a series of coal samples at increasing maturity. The resulting TOC calculation shows the differences between Rock-Eval 6 and Rock-Eval 2 measurements.

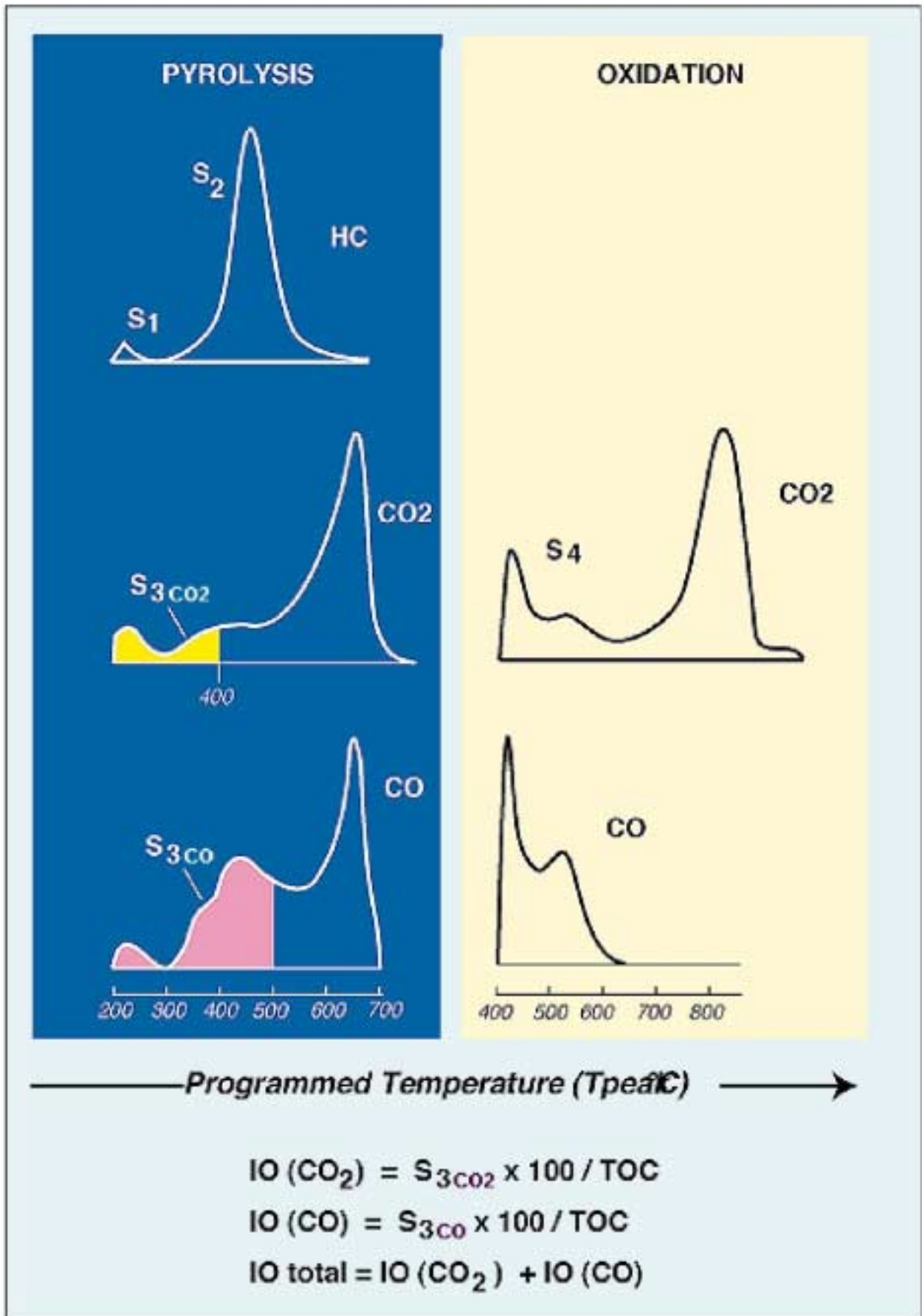


Figure 10: Principle of determination of the Oxygen Indices using CO₂ and CO pyrolysis curves.

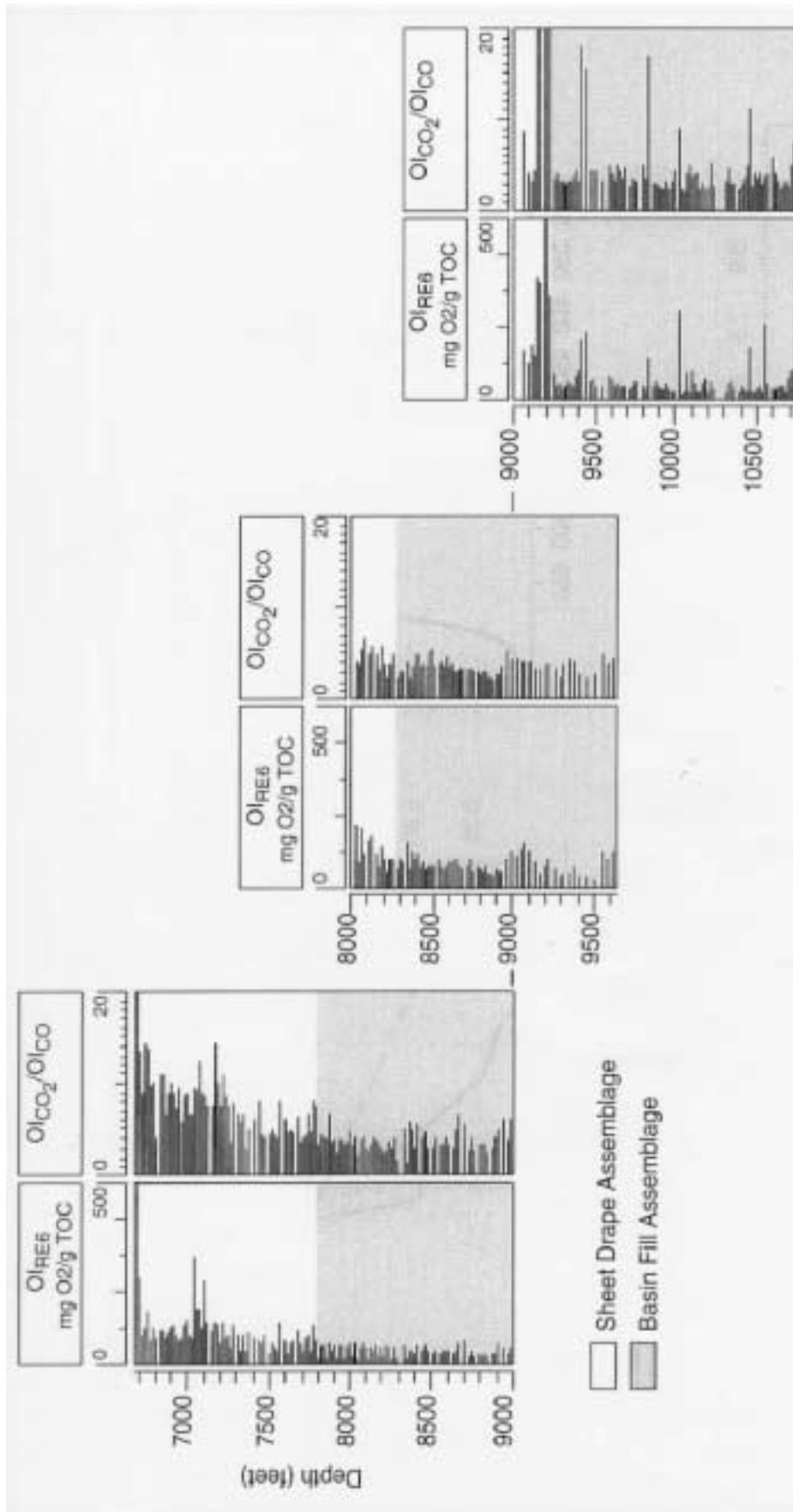


Figure 11: Correlation of Rock-Eval 6 Oxygen Indices across different wells of Lower Congo Basin illustrating the transition from basin fill to sheet drape assemblages.

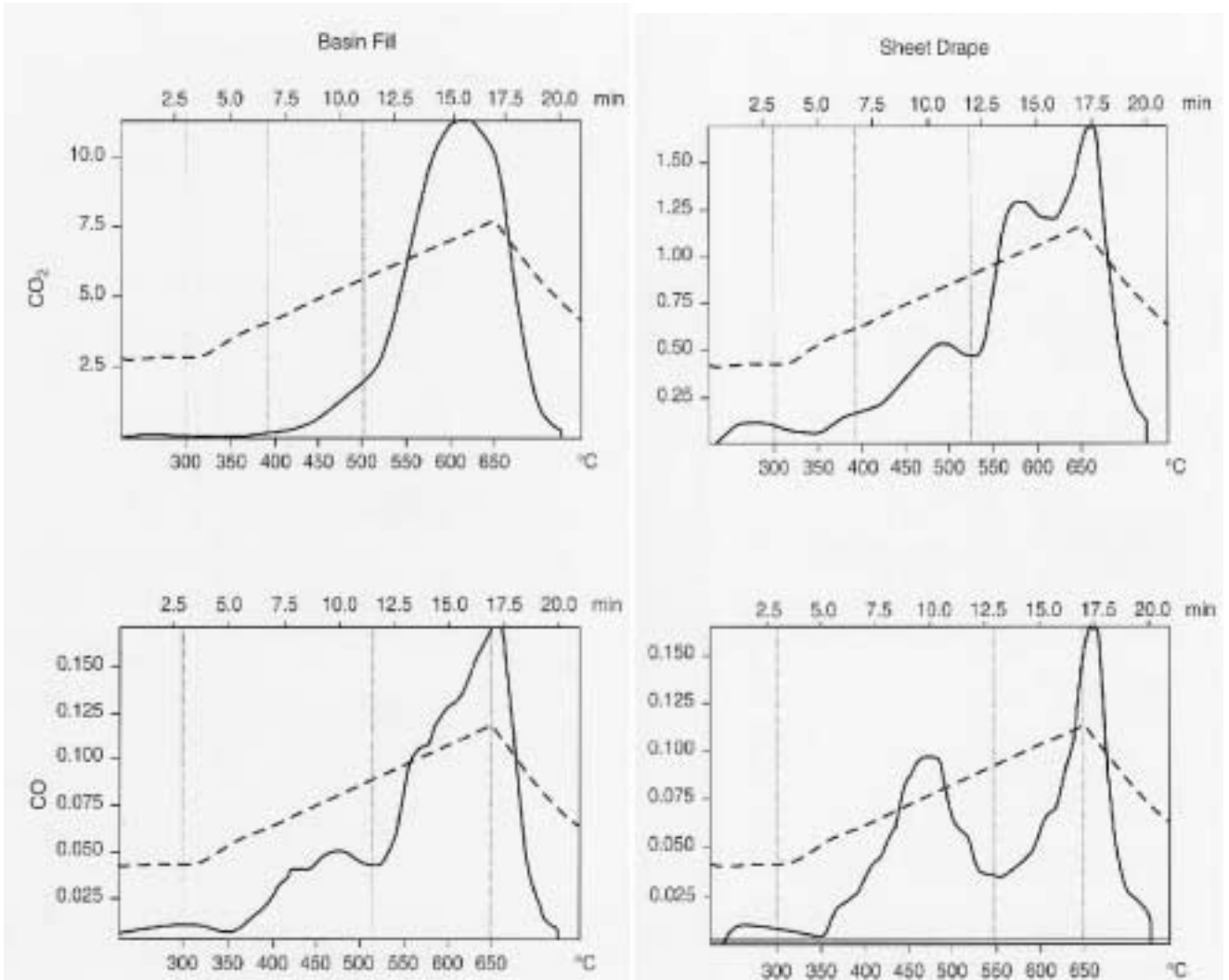


Figure 12: CO₂ and CO pyrolysis curves illustrating the differences of the composition of the organic matter in the basin fill and sheet drape organo-facies.

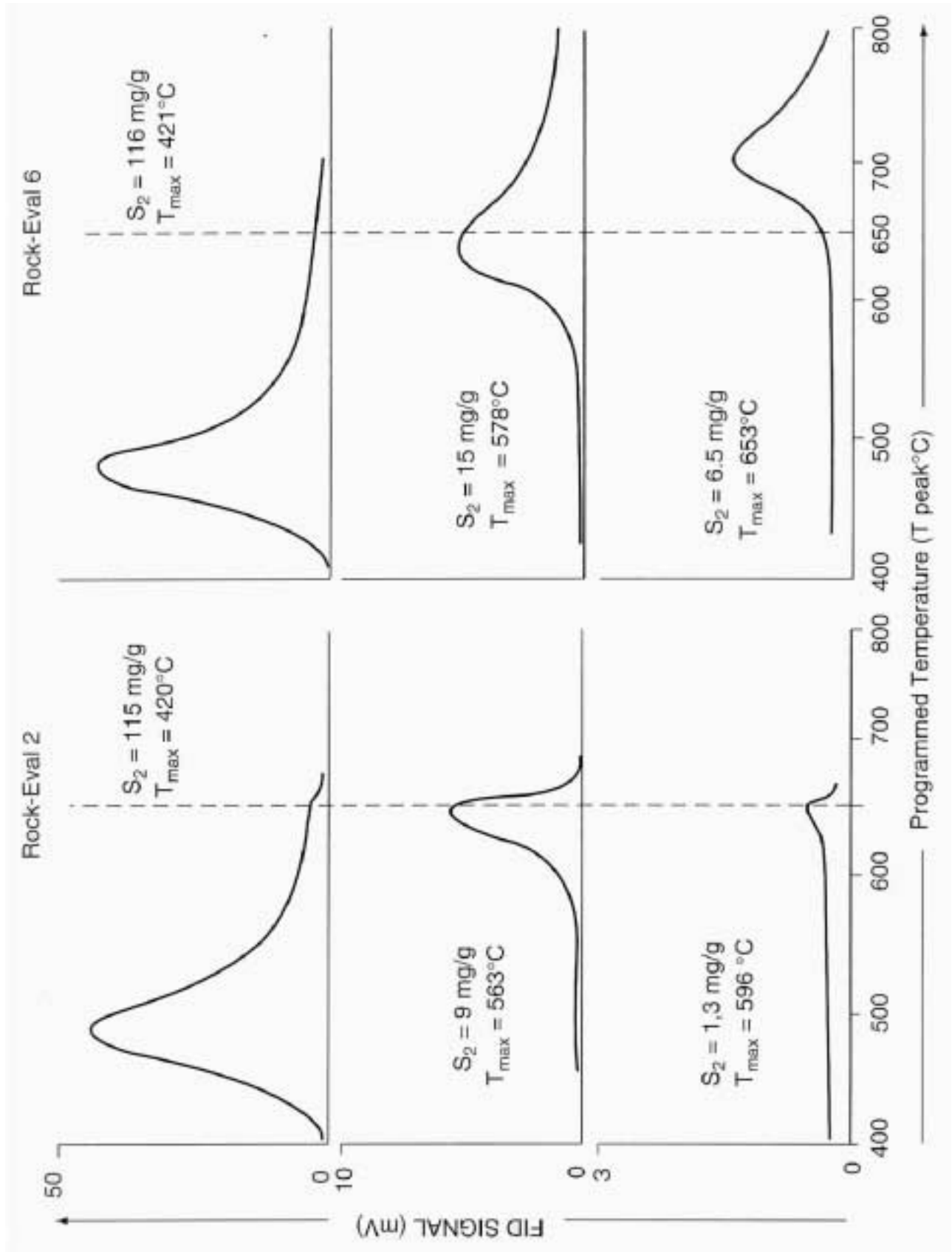


Figure 13: Illustration of the effect of high final pyrolysis temperature with Rock-Eval 6, on the calculation of the residual potential S_2 and on the measurement of T_{max} .

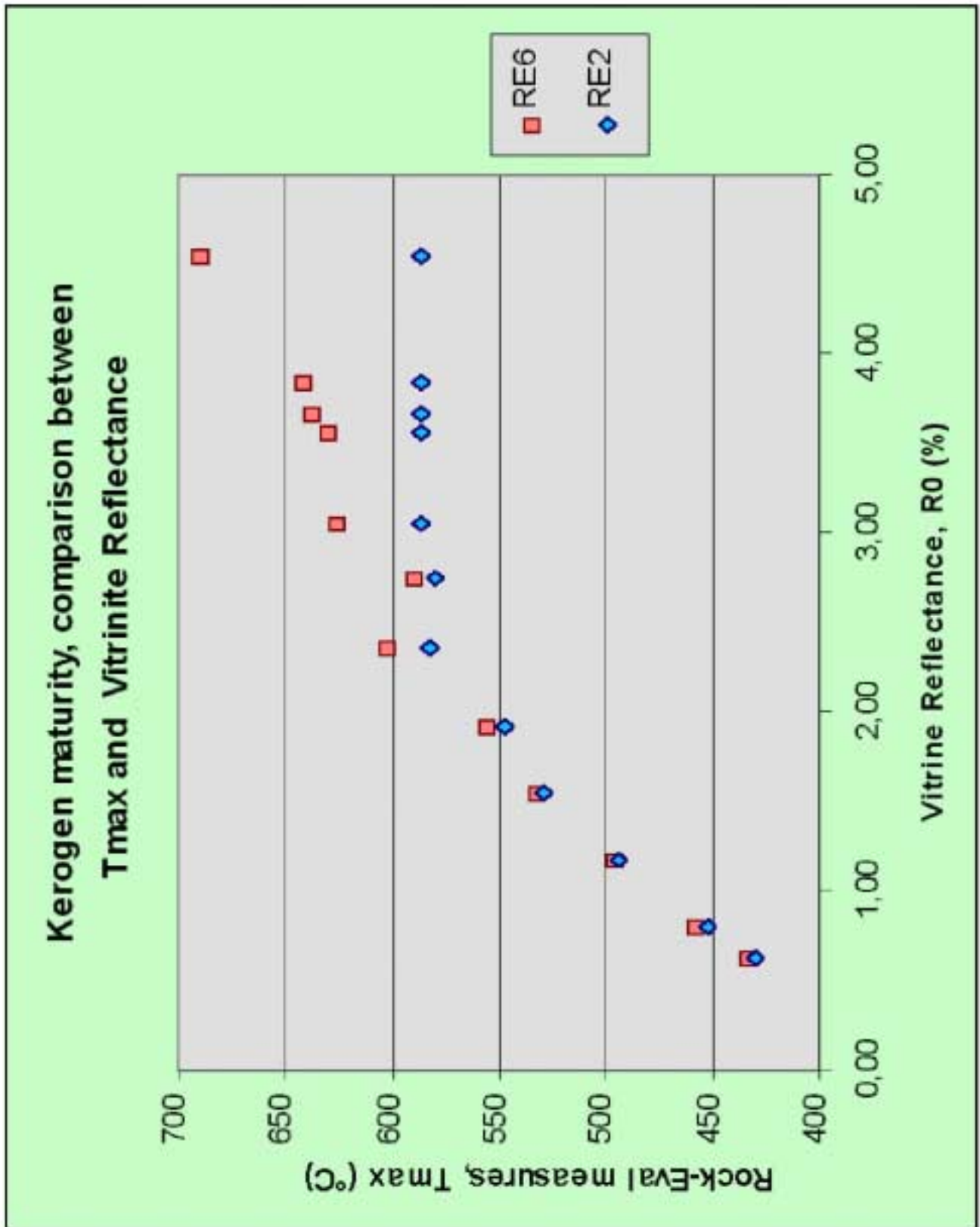


Figure 14: Correlation between Tmax and Ro for Rock-Eval 6 and Rock-Eval 2 on a series of coal samples.

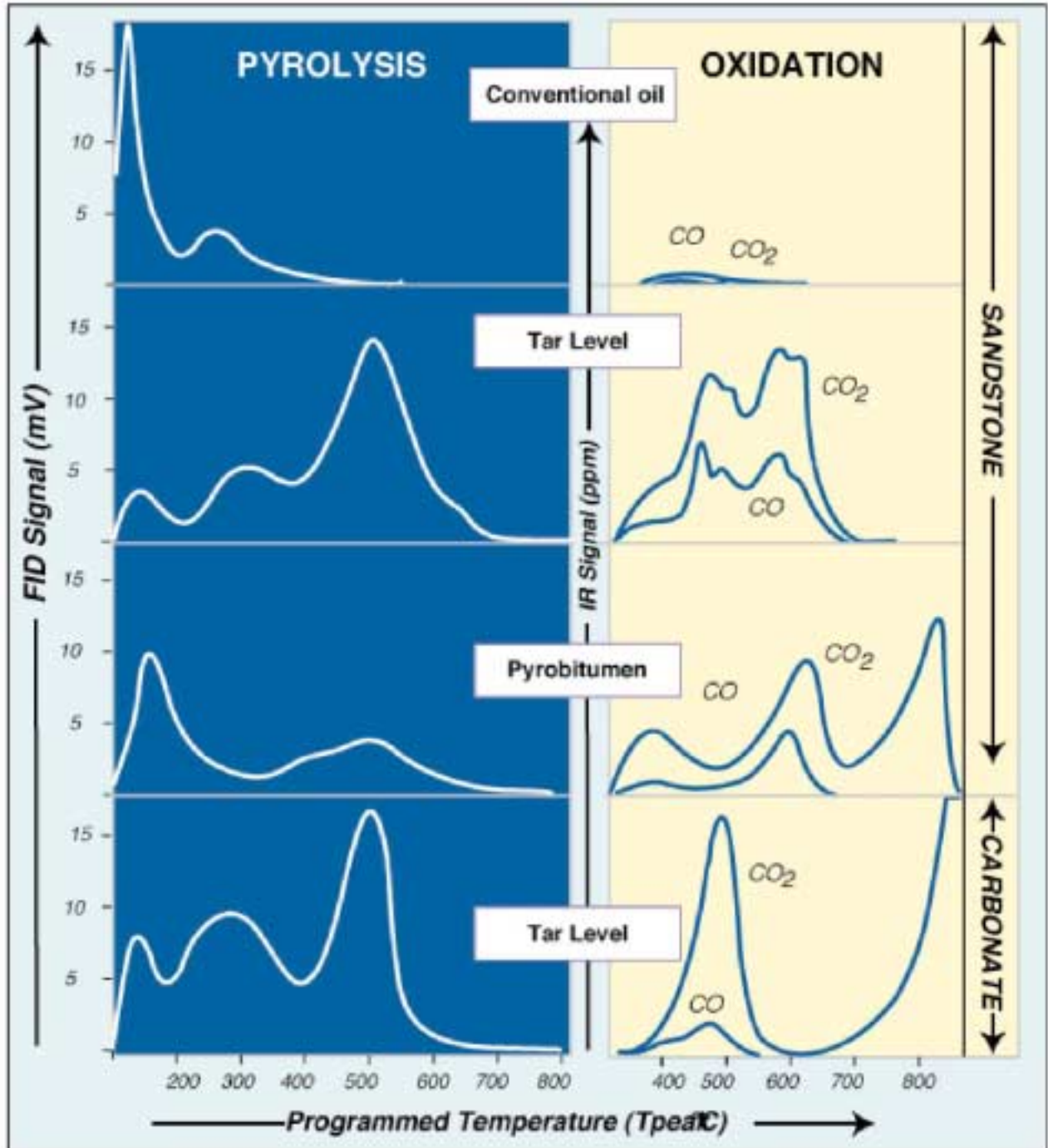


Figure 15: Examples of application of Rock-Eval 6 to the study of reservoir rocks.

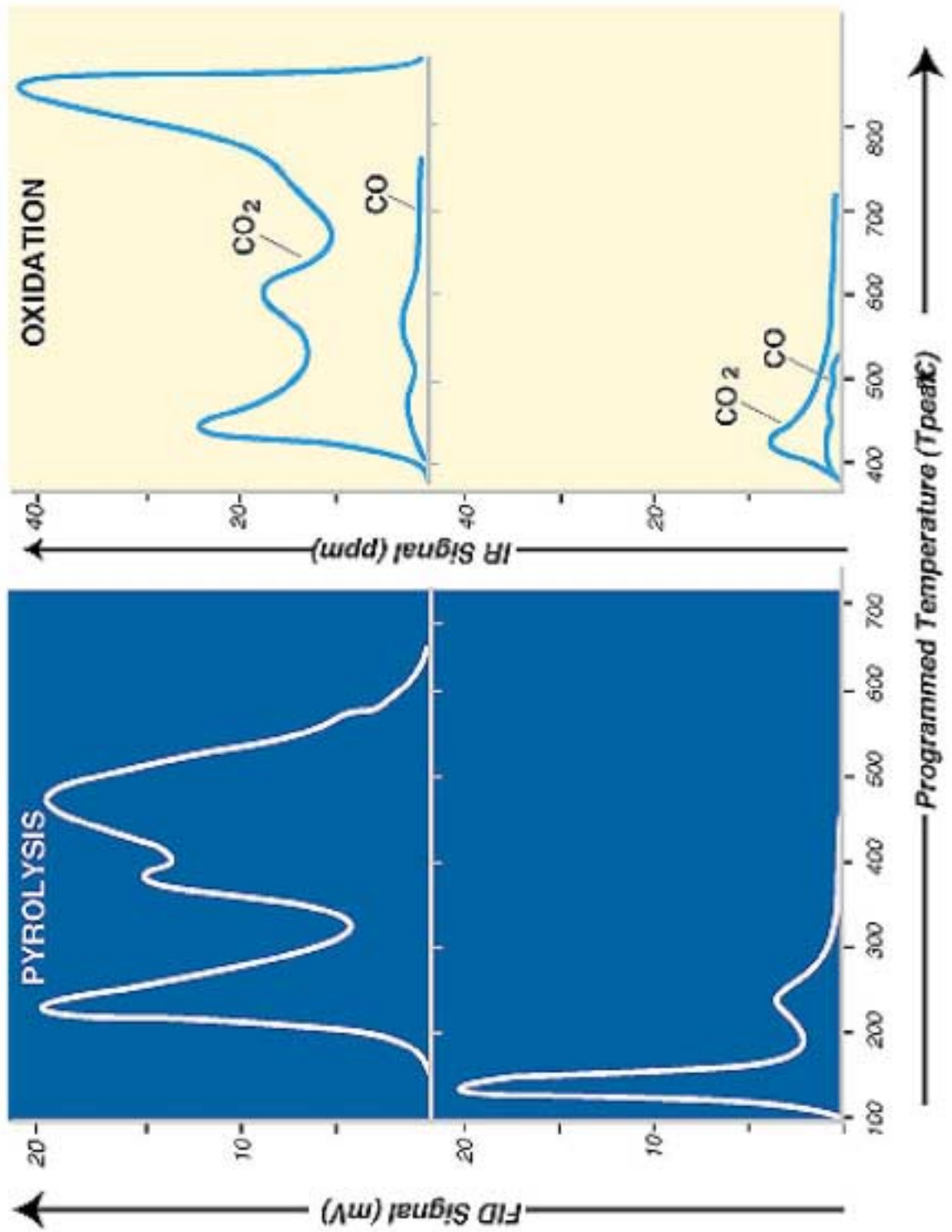


Figure 16: Examples of application of Rock-Eval 6 to the study of contaminated soils.