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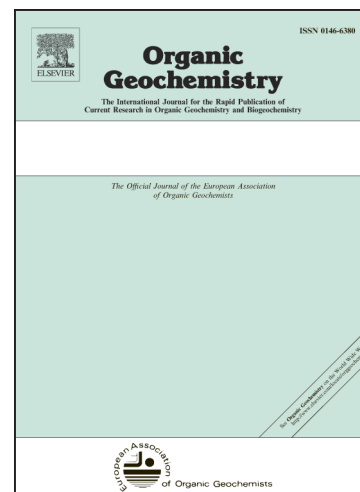
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Guidelines for Rock-Eval analysis of recent marine sediments

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ABSTRACT

Rock-Eval pyrolysis, a widely used petroleum screening technique developed primarily for ancient sedimentary rocks and kerogens, has now been increasingly applied to the characterization of recent lacustrine or marine sediments. However, as illustrated by previous results from various authors and by the analysis of recent sediments from various areas, the thermally labile character of recent organic matter (OM), the presence of poorly crystallized mineral (e.g. carbonate) and the eventual presence of salts (NaCl, sulfate) might perturb the detection of the pyrolysis effluent. The aim here was to outline the problems generated by such perturbation and to demonstrate that specific operating conditions needed for proper analysis of recent marine sediments. A modified Rock-Eval pyrolysis program, starting at lower temperature (180 °C) with a heating rate of 30 °C/min, is proposed as a standard mode for the analysis of recent OM in order to avoid misleading interpretation of Rock-Eval data and make possible the inter-comparison of results whatever the Rock-Eval device used.

Keywords: Rock-Eval, Pyrolysis, Recent sediments, Quaternary, Organic matter, Congo turbiditic system, Timor Sea.

1. Introduction

Rock-Eval pyrolysis was developed primarily for ancient sedimentary rocks and kerogens and became a standard analytical technique in the petroleum industry (Espitalié et al., 1977, 1985a,b, 1986; Peters, 1986; Lafargue et al., 1998; Behar et al., 2001), even for unconventional resources (Romero-Sarmiento et al., 2015). It has been increasingly applied to the characterization of organic matter (OM) in soils (Di Giovanni et al., 2000; Disnar et al., 2003; Hetényi et al., 2005; Sebag et al., 2006; Graz et al., 2012; Saenger et al., 2013; Hétényi and Nyilas, 2014), the detection of black carbon (Copard et al., 2006; Poot et al., 2009) and even the analysis of pure organic products (Carrie et al., 2012). It has also been applied for several decades to the study of recent lacustrine sediments (Campy et al., 1994; Di Giovanni et al., 1998; Meyers and Lallier-Vergès, 1999; Ariztegui et al., 2001; Steinmann et al., 2003; Sanei et al., 2005; Jacob et al., 2004; Boussafir et al., 2012; Zocatelli et al., 2012; Lavrieux et al., 2013; Sebag et al., 2013, amongst others) or recent marine sediments (Peters and Simoneit, 1982; Hussain and Warren, 1991; Calvert et al., 1992; Combourieu et al., 1999; Ganeshram et al., 1999; Ozcelik and Altunsoy, 2000; Holtvoeth et al., 2001, 2003, 2005; Tamburini et al., 2003; Baudin et al., 2007, 2010; Kim et al., 2007; Marchand et al., 2008; Tribouvillard et al., 2008, 2009; Biscara et al., 2011; Riboulleau et al., 2011; Hare et al., 2014; Hatcher et al., 2014, amongst others).

However, the thermally labile character of recent OM might perturb the detection of pyrolysis effluents, especially when the analysis is performed using a mode devoted to ancient sediments. Indeed, the immaturity of recent sediments requires specific analytical

procedures which were not always employed in the above studies. Furthermore, the presence of salts (NaCl, sulfate) and poorly crystallized minerals (e.g. carbonate) might also perturb the detection of pyrolysis effluents from recent marine sediments.

This study examines the above problems and provides guidelines for understanding and interpreting Rock-Eval pyrolysis data from recent marine sediments.

2. Material and methods

The samples were collected from different parts of the deep sea turbiditic system of the Congo River and from a hemipelagic succession in the Timor Sea. Sediments from the Congo deep sea fan are younger than 20 ka and those from the Timor Sea younger than 140 ka. The geological setting of the sites and the characterization of the sedimentary OM are given by Baudin et al. (2010) or Stetten et al. (submitted) for the Congo deep sea turbiditic system and by Moreno et al. (2008) or Liu et al. (2014) for the Timor Sea.

Since the invention of the technique in the middle of the 1970s, various Rock-Eval devices were designed by the Institut Français du Pétrole (IFP) and marketed by different companies. The principles and basic operating conditions of the apparatus were described by Espitalié et al. (1977) for Rock-Eval 1, by Espitalié et al. (1985a, 1985b, 1986) or Espitalié and Bordenave (1993) for Rock-Eval 2 and 3 and finally by Lafargue et al. (1998) and Behar et al. (2001) for Rock-Eval 6. Rock-Eval 2 and Rock-Eval 3, the latter being also termed Oil Show Analyser (OSA), have been traded since the middle of 1990s and some are still operational. The Rock-Eval 6, marketed by Vinci Technologies, is the most recent version and is widely used. Obviously, analysis and interpretation of Rock-Eval data should be considered by each interpreter depending on the particular device in use.

Briefly, the Rock-Eval 6 technique provides several measurements from the successive pyrolysis and oxidation of a sample. First, the splitting of the pyrolysis effluent (under N_2) into two halves at the outlet of the pyrolysis oven, allows the simultaneous detection and quantitation of hydrocarbonaceous effluents with flame ionization detection (FID) and CO and CO_2 with infra red (IR) detection, respectively (Fig. 1). The S1 and S2 signals successively determined with FID, correspond first to the amount of free hydrocarbons (S1, gas and oil) volatilized for 3 min at $300\text{ }^\circ\text{C}$, the second peak (S2) representing the hydrocarbons generated from kerogen cracking between 300 and $650\text{ }^\circ\text{C}$, with a heating rate of $25\text{ }^\circ\text{C}/\text{min}$. The amounts of CO_2 and CO represent the S3 and S3 CO peaks, respectively. All these basic parameters are expressed either in mg of hydrocarbons or CO_2/CO per gram of rock. The temperature at which the hydrocarbons maximum resulting from kerogen cracking occurs is called T_{max} .

The residual organic and inorganic carbon content (in wt %) of the pyrolyzed sample is obtained by combustion in air from 300 to $850\text{ }^\circ\text{C}$, with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. The CO_2 and CO resulting from this combustion are also detected with an IR cell and correspond to peaks S4 and S5 for CO_2 and peak S4 CO for CO (Fig. 1). From these basic parameters, the total organic carbon content (TOC, wt %) is calculated as the sum of pyrolyzed OC and residual OC. The hydrogen index (HI, mg HC/g TOC) corresponds to the quantity of pyrolyzable organic compounds (S2 peak) relative to TOC. The oxygen index (OI, mg CO_2 /g TOC) corresponds to the quantity of CO_2 (S3 peak) relative to TOC. The Rock-Eval 6 device, which measures CO_2 and CO separately, allows three OIs to be defined: one for CO_2 , one for CO and an additional one for CO_2+CO , called OIRE6. The latter is expressed in mg O_2 /g TOC. Finally, the mineral carbon (MinC) is also calculated as $S3'+S3'CO + S5$ peaks (Fig. 1). Note

that only Rock-Eval 6 allows selective detection of residual OC and inorganic carbon. MinC is not a parameter provided by earlier Rock-Eval devices.

The above procedure is called the 'Bulk-rock/basic' method/cycle on the Rock-Eval 6 device (Lafargue et al., 1998; Behar et al., 2001; Sarmiento-Romero et al., 2015) and is well suited for ancient sediments and sedimentary rocks. Another procedure exists for coal and pure OM (i.e. kerogen concentrates) where the final pyrolysis temperature is 800 °C instead of 650 °C (Behar et al., 2001). This 'pure OM' method does not allow determination of the mineral carbon, which is virtually absent from such material.

Some differences exist in the procedure depending of the Rock-Eval device used. The most important differences are listed in Table 1. In particular, the temperature of the splitter located at the outlet of the pyrolysis oven varies from 400 °C for the Rock-Eval 6 to 500 or 550 °C for Rock-Eval 2 and Rock-Eval 3, respectively.

No standard procedure has been agreed for recent sediments, although Rock-Eval pyrolysis is widely used for the characterization of OM in such samples. Espitalié et al. (1985a) suggested using the 'cycle 3' mode on Rock-Eval 2 or 3, with a lower temperature at the beginning of the pyrolysis (180 °C), but few studies followed their advice. Disnar et al. (2003) and Hetényi et al. (2005) proposed a standard procedure for the Rock-Eval analysis of soils, with the pyrolysis starting at 200°C, but all subsequent studies did not follow their recommendation. Recently, Carrie et al. (2012) presented an interesting study showing the Rock-Eval signature of pure organic moieties but did not propose a standard procedure for the analysis of sediments and soil, in contrast to the title of their paper. In fact, they used the 'bulk-rock/basic' method/cycle, which is not appropriate for the Rock-Eval analysis of recent sediments and soils.

This study attempts to define a standard mode for the analysis of recent OM in order to avoid misleading interpretation of Rock-Eval data and to make possible the inter-comparison of results, whatever the Rock-Eval device used.

To this end, and because of some differences in their working principles, three different Rock-Eval devices were used and compared: a Rock-Eval 2, an OSA and a Rock-Eval 6 Turbo. The main differences between them are summarized in Table 1. Another important difference is the inert gas flow used to transport the pyrolysis effluent. Rock-Eval 2 and OSA devices use He as inert gas, whereas Rock-Eval 6 uses N₂. Behar et al. (2001) showed that using He led to a slightly increase in the S₂ value (5 to 10 relative wt %) for samples containing Type I kerogen or Type II kerogen.

3. Experimental procedures for Rock-Eval pyrolysis of recent sediments

3.1. A cycle devoted to 'recent sediment'

As stated by Peters (1986), "an accurate interpretation of Rock-Eval data requires access to the FID (and IR) records", the so-called pyrograms illustrated in Fig. 1. Indeed, pyrograms from very immature samples analyzed with the 'bulk-rock/basic' method/cycle show poorly separated S₁ and S₂ peaks with a trough between them well above the baseline (Fig 2). As the Rock-Eval 6 device allows ready modifying of the heating program, it is recommended that the pyrolysis be started at a lower temperature. For their study of soils, Disnar et al. (2003) started the pyrolysis at 200 °C and used a heating rate of 30 °C/min. However, with some RE devices (e.g. RE 6), it is practically possible to start with a temperature as low as 100 °C, such a low temperature being well-suited for the study of soil contaminated with light hydrocarbons (Ducreux et al., 1997; Lafargue et al., 1998; Haeseler et al., 1999). To keep the duration of the pyrolysis step similar to that of the oxidation step and to be

consistent with the 'cycle 3' existing on Rock-Eval 2 and 3 devices, we chose to start at 180 °C, with a heating rate of 30 °C/min, instead of the 25 °C/min for the 'basic' cycle. This slight modification of the 'Bulk-rock/basic' method/cycle is hereon termed the 'bulk-rock/recent sediment' method/cycle. This 'recent sediment' cycle does not require any change for the oxidation step compared with the 'basic' cycle.

3.2. Results and discussion

Using a heating program such as the one proposed above for the pyrolysis step (i.e. beginning at a temperature as low as 180 °C) offers a better determination of the S1 peak, without any hydrocarbonaceous effluent arising from a beginning of pyrolysis of the OM (Fig. 2). This is particularly important for immature samples in which thermally labile functionalized organic compounds (proteins, carbohydrates, hemicellulose, lipids ...) constitute a significant part of the OM. The "fragility" of these compounds makes starting the pyrolysis at a low temperature an absolute necessity.

Changes in the pyrolysis program induce changes in the FID response and consequently in the determination of the classical Rock-Eval parameters. With a start at a lower temperature, the S1 and S2 peaks are modified primarily as illustrated in Fig. 2, with a smaller S1 peak and its return to baseline before the onset of the S2 peak. T_{max} and pyrolyzable carbon (PC) must also be affected by the use of the 'recent sediment' cycle proposed here.

For a better comparison, we analyzed the IFP 55000 and IFP 160000 standards – recommended for calibration of the Rock-Eval apparatus – using both 'basic' and 'recent sediment' cycles. Due to the difference in heating rate, the S2 peak was narrower and taller using the 'recent sediment' cycle than for the 'basic' cycle (Fig. 2). Nevertheless, the surface of the S2 peak from IFP 55000 and 160000 standards was very similar, with only a small

increase of ± 0.20 mg/g using the 'recent sediment' cycle (Table 2). Such a difference is negligible as the accuracy for S2 of the IFP 160000 standard was ± 0.50 mg/g, and this had absolutely no impact on the PC content. The T_{\max} value for IFP 55000 and 160000 standards increased by 2-3 °C using the 'recent sediment' cycle, which is also in the range of fluctuation for this parameter (Table 2). The integration of S3CO and S3CO₂ was not affected by the use of the 'recent sediment' cycle, so the OI value was not affected.

As the S1 peak intensity was less important with the 'recent sediment' cycle than for the 'basic' cycle in the analysis of recent sediments (Fig. 2), the S2 peak intensity increased proportionally but the sum of the S1 and S2 peaks was similar whatever the cycle used (Table 2). The HI value was, however, different using one or the other cycle, with an increase using the 'recent sediment' cycle (Fig. 2 and Table 2). This increase was expected as the S2 value increased, whereas TOC was similar. T_{\max} also showed a small difference with an increase of 3-4 °C using this cycle. This is probably due to the cracking kinetics of thermally "fragile" compounds, which are slightly different with a heating rate of 25 or 30 °C/min (see Braun and Burnham, 1987 for a further explanation).

We also analyzed two samples of recent sediments using both cycles and different Rock-Eval devices (Table 2). As expected, when using the 'recent sediment' cycle instead of the 'basic' cycle, the decrease in S1 is much more important with the recent sediments because of their richness in a thermally labile fraction, compared to the IFP standards. The S2 value increases proportionally with the 'recent sediment' vs. 'basic' cycle and the sum of S1 and S2 peaks is similar whatever the cycle (Table 2). T_{\max} showed an increase of 5-6 °C using this cycle and, as expected, HI also increased.

To summarize, the 'bulk-rock/recent sediment' method/cycle proposed here simply needed a change in the pyrolysis heating program (without any change in the oxidation program). A start at 180 °C and a heating rate of 30 °C/min seems appropriate for the analysis of recent OM without any noticeable artifacts. This procedure displays TOC and OI values very similar to the classical 'bulk-rock/basic' method/cycle and both S2 and HI values are believed to be better determined using this cycle when applied to recent sediments.

In addition to the temperature program described above, the analysis of recent sediments using Rock-Eval pyrolysis requires some attention as these sediments may contain thermally "fragile" minerals. As developed below, parasitic effects might also be particularly important when salts and/or poorly crystalized carbonate are present, as frequently occurs with recent sediments.

4. Effect of salts during Rock-Eval pyrolysis of recent marine sediments

4.1. An example of erroneous interpretation

Holtvoeth et al. (2005) discussed the abundance and nature of the terrigenous OM supplied to the Atlantic Ocean by the Niger and Congo rivers. According to these authors, the sediments from the Congo deep sea fan contain a thermally stable organic fraction absent from the Niger delta. This unusual fraction was revealed from Rock-Eval analysis, which displayed a bimodal S2 peak under programmed pyrolysis. The twin S2 peaks were respectively named S2_{lm} and S2_{hm}, after their order of appearance (Holtvoeth et al., 2001; Fig. 3). In contrast to the first peak that maximizes at a T_{\max} temperature ≤ 430 °C, as expected from recent immature sediments, the second usually maximizes at values that frequently approach 550 °C (Holtvoeth et al., 2001). The relative intensity of these two peaks, expressed through the so-called lm/hm index, was initially thought to reflect the

respective proportions of low maturity and high maturity OM in Congo deep sea fan sediments (Holtvoeth et al., 2001, 2003). Later, the presence of the apparently highly mature organic fraction in the Congo deep sea fan sediments and their absence from those off the Niger delta was assumed to arise from the nature of the soils in their watersheds, mostly oxisols in the case of the Congo and ultisols for the Niger (Holtvoeth et al., 2005). This assertion seemed to be consistent with the study of Disnar et al. (2003), who presented the results of an analytical survey of soils from various areas of the world, using Rock-Eval pyrolysis. These authors mentioned that ferralsols from tropical areas provide a high temperature signal that is absent from soils from temperate areas.

Nonetheless, the high temperature signal recorded for soil samples reported by Disnar et al. (2003) was only important for the deep soil horizons, the least eroded by runoff. In addition, most of the samples studied by Holtvoeth et al. displayed a T_{max} of ca. 540 °C and still showed a notable HI value of ca. 200 or even higher (up to 400 mg HC/g TOC). Normally, a T_{max} value of 540 °C or higher is indicative of a very high degree of maturity, corresponding to the beginning of the dry gas window for Type III kerogen (such high values are considered to be unrealistic for Type I and Type II kerogens; Espitalié et al., 1985b 1986). At such a high degree of maturity, coaly material can only have a residual oil potential, i.e. an $HI \leq 50$ mg HC/g TOC, much lower than the 200-400 mg HC /g TOC reported by Holtvoeth et al. (2001, 2003, 2005) for the Congo deep sea fan sediments.

The reasons for the anomalous behavior of the S2 peak misinterpreted by Holtvoeth et al. (2001) related to (i) the presence of salts and (ii) the use of a Rock-Eval 2 device. As mentioned by Espitalié et al. (1985a) "in some type of rocks, a more or less appreciable rise in the FID signal may be observed, creating a second S2 peak in the record. This second peak

does not correspond to hydrocarbon compounds but is caused by the ionization of mineral salts (chlorides and sulfates) volatilized during the pyrolysis". This parasitic effect is not only recorded by recent porous sediments enriched in salts precipitated during evaporation of interstitial water, but also by rocks from ancient evaporitic deposits.

From a practical standpoint, a decrease in the temperature of the splitter at the exit of the pyrolysis oven considerably attenuates this phenomenon. This explains the great intensity of the second parasitic S2 peak recorded by Holtvoeth et al. (2001) since they used a Rock-Eval 2 device with a temperature of the splitter of 500 °C (or even 550 °C in Rock-Eval 3 device), whereas this temperature is only 400 °C on the Rock-Eval 6 device (Table 1). The later temperature change was introduced precisely to reduce the parasitic ionization related to salts.

More recently, we analyzed samples from the same Congo deep sea fan (Baudin et al., 2010; Stetten et al., submitted) using both Rock-Eval 3 (OSA) and Rock-Eval 6 apparatus. With the OSA, we obtained the same FID records as those reported by Holtvoeth et al. (2001), with a double S2 peak (Fig. 4). By contrast, the parasitic ionization due to salts decreases using Rock-Eval 6 device and most of the second S2 peak disappears (Fig. 4). Previous washing of rock with deionized water before Rock-Eval analysis may also attenuate this parasitic effect when chlorides are involved. Fig. 4 also shows the FID records obtained with OSA and Rock-Eval 6 from the same sample rinsed with deionized water before re-analysis.

To conclude, the high temperature signal observed by Holtvoeth et al. (2001, 2003, 2005) in Rock-Eval pyrograms of Congo deep sea fan sediments is obviously due to FID perturbation by salts. The effect can be easily eliminated by simply desalting the samples with deionized water prior to analysis. Note that such a treatment has no effect on the high temperature signal observed for some tropical soils (e.g. ferralsols) by Disnar et al. (2003). The discussion

by Holtvoeth et al. (2005) on the difference between soil OM in late Quaternary Niger delta and Congo deep sea fan sediments and between the soils of the corresponding watersheds is therefore irrelevant. The various hypotheses and conclusions inferred from the supposed existence of such a fraction in their previous studies (e.g. Holtvoeth et al., 2001, 2003) should also be scrutinized with care.

4.2. Benefits and inconvenience of washing recent sediment prior to Rock-Eval analysis

To remove salts, the most efficient approach is to shake the powdered sample in deionized water (1/10 v/v) for 5 min. Usually, only one rinsing is enough but the operation could be duplicated if needed (in the case of sediments deposited in evaporitic environments). After centrifugation and drying, the sample is ready for analysis.

The first advantage of rinsing recent sediments is for the Rock-Eval apparatus itself. Indeed, the presence of salts (chlorides and sulfates) causes damage during the oxidation phase, in particular on the piston of the furnace, the thermocouple and the crucibles, which all become corroded.

As stated above, the second benefit of desalting is to determine the real S2 peak.

Consequently, the TOC proportion and HI value are correct, as is T_{max} , as demonstrated by the following case study. A 9 m succession of turbiditic sediments from 4800 m water depth in the distal lobes of the Congo deep sea fan was analyzed with an OSA device using the 'recent sediment' cycle. All the samples were analyzed as bulk sediment and rinsed after being washed with deionized water. A comparison of the vertical evolution of the S2, TOC, HI and T_{max} parameters is shown in Fig. 5. It clearly appears that S2 from the bulk sediments is overestimated due to the parasite peak caused by salts. This overestimation tends to decrease with depth (Fig. 5), from ca. 80% at the top to ca. 40% at the base of the core,

where the porosity of the sediment decreases, reducing the amount of salty porewater. The effect on the TOC proportion (%) is less pronounced since the S2 peak contributes only 8.3% in the calculation of PC (Espitalié et al., 1977, 1985; Behar et al., 2001). In the present case, as the OM is very immature, the pyrolyzable fraction is much more important than the residual carbon. Accordingly, the TOC difference between the bulk and rinsed sediments is 12% on average. The rinsing effect is well expressed in the evolution of HI (Fig. 5). HI values are overestimated by a factor of 3 at the top of the core. The overestimation decreases with depth, to reach values around 125 mg HC/g TOC, which seem characteristic of the OM in these sediments, as HI values fluctuate between 50 and 150 mg HC/g TOC for the rinsed sediments. Finally, the effect of rinsing is remarkable with respect to T_{max} : while this parameter would imply very mature OM in the case of the bulk sediment (T_{max} 488 °C on average, with values up to 600 °C) for rinsed sediment, the T_{max} dramatically decreases to reach values (423 °C on average) consistent with the fresh OM content of the turbiditic sediments of the Congo deep sea fan (Baudin et al., 2010; Stetten et al., submitted). With non-rinsed sediments, the parasitic effect due to salts disappears near the bottom of the core, as shown by the S2, TOC, HI and T_{max} parameters that tend to show similar values for bulk sediments and rinsed sediments (Fig. 5).

If rinsing recent marine sediments provides the beneficial effects described above, it might have, however, the drawback of eliminating a water soluble (or even hydrolysable) portion of the OM. To test this, we analyzed with a Rock-Eval 6 device 84 samples of surficial sediments from the Congo deep sea fan using the 'recent sediment' cycle, with both bulk and rinsed sediments. The dissolved OC (DOC, ppm) in water after rinsing was determined using an OI Analytical Aurora 1030 Bioritech apparatus for 34 of the samples. The accuracy of this

method is ± 2 ppm. The S2 peak from each analysis was deconvoluted as a sum of Gaussian functions using Fityk, free software for nonlinear fitting of analytical functions to data (Wojdyr, 2010 and <http://fityk.nieto.pl/>). We used the auto-add tool without any adjustment. This allows separating the S2 peak into three Gaussian curves as shown in Fig. 6. The first corresponds to labile OM which is partly hydrolysable. The second corresponds to the kerogen or proto-kerogen. Lastly, the third corresponds to the shoulder at the end of the S2 peak due to the parasitic ionization related to salts. The surface of each S2 sub-peak was calculated using Fityk, which allowed determining the proportion (%) of each fraction constituting the entire S2 peak. By comparing the ratio of the different S2 sub-peaks for bulk and rinsed samples, it was possible to estimate on the FID response both the parasitic effect of salts and the hydrolysable effect on the OM.

As shown in Fig.6, washing modified the shape of the S2 peak. The bulge at the end of the peak, due to the parasitic ionization of salts, strongly decreased but did not totally disappear, most probably because some sulfates may still have been present and additionally because thermally resistant organic compounds were also detected at the end of the pyrolysis. The surface of the third Gaussian curve represented between 0.9 and 11.7% (5.5% on average, n=84) of the entire S2 peak for the bulk samples whereas it varied between 0 and 4.3% (1.7% on average, n=84) for rinsed sediments. Another change on the shape of the S2 peak was the smoothing of the early peak, corresponding to the thermally labile OM fraction. The shoulder on this part of the S2 peak for bulk samples almost completely disappeared for rinsed samples. We calculate that this change, on average, represents only 3.7% of the surface of the S2 peak. We believe that the hydrolysable fraction of OM was responsible for this shoulder at the beginning of S2 peak. The DOC concentration measured on the washing water varied from 2.9 to 7.9 ppm or from 0.7 to 1.7 ppm relative

to OC (n= 34). On the basis of these data, we estimate that the hydrolysable fraction corresponded to 3 to 8 wt % of TOC, with an average of 4.2 wt % (n= 34). This value is in the same range as the decrease in the surficial proportion (%) of the S2 peak for rinsed sediments.

This change on the shape of S2 peak had little effect on the TOC and HI values. However, the washing had a more important impact on T_{max} as the thermally labile fraction was removed. An average increase of ca. 5 °C in T_{max} was obtained between the bulk and rinsed samples (Fig. 6). At the same time, the loss of hydrolysable fraction induced a small decrease in the OI values, as this fraction is usually oxygen-rich.

5. Effect of poorly crystallized carbonate in recent sediments

The amount of MinC is calculated with Rock-Eval 6 as the sum of the CO₂ released during the pyrolysis phase, above 400 °C, and the CO₂ released by carbonate decomposition during the oxidation phase, between 650 °C and 850 °C [see Fig. 1 and refer to Behar et al. (2001) for further explanation]. Recently, Pillot et al. (2013) promoted the Rock-Eval analysis as a rapid method for determining the nature and amount of carbonate in sediments based on the CO₂ flux produced during the oxidation phase of the analysis. Depending on the type of carbonate mineral (azurite, malachite, siderite, rhodochrosite, magnesite, dolomite, aragonite or calcite), the thermal destabilization produced a peak characterized by both its shape and the temperature of maximum production of CO₂. It is then possible to deduce the nature of the carbonate from its specific decomposition temperature. Pillot et al. (2013) mention, however, that the size of some carbonate minerals has an effect in terms of thermal destabilization. Although this phenomenon is moderate for most carbonates, small calcite minerals are destabilized more easily than large calcite minerals. For instance, chalk is

destabilized at a lower temperature than marble, but the difference is only 2 to 4 °C, with the destabilization temperature always ≥ 775 °C (see Table 1 in Pillot et al., 2013). It should be noted that these authors used pure carbonate fractions for their experiments and did not show curves for natural samples having a complex mineralogy.

Our own experience in analyzing sedimentary rocks using Rock-Eval pyrolysis led us to modulate the extrapolation made by Pillot et al. (2013). In most sedimentary rocks, the natural mixture of carbonate minerals of different origin does not display the simple and unequivocal series of thermal destabilization obtained with pure products. This is particularly apparent for recent sediments in which the carbonate minerals are usually poorly crystallized and may then show thermal destabilization at a temperature lower than demonstrated by Pillot et al. (2013).

We compared the CaCO_3 fraction (%) of a recent hemipelagic succession from the Timor Sea, determined using a carbonate bomb (Liu et al., 2014) with values determined using Rock-Eval, assuming that all the MinC was in the form of pure calcite or aragonite. This hypothesis was confirmed by means of X-ray diffraction. This technique provides an easy way of distinguishing between the two polymorphs of CaCO_3 . The two have their highest intensity peak at different positions, and the general aspect of the two patterns is different. Aragonite has its greatest peak (111) at relatively small 2θ and has several lesser peaks, whereas calcite has a booming 104 peak slightly to the right of the large aragonite peak, and few and comparatively small other peaks. In the hemipelagic recent sediments from the Timor Sea, most of the CaCO_3 is in the form of calcite, but the width of the 104 peak suggests a poorly crystallized form.

It appears that the determination of MinC using Rock-Eval is overestimated when compared with the % CaCO₃ determined with the bomb technique (Fig. 7). Conversely, TOC is underestimated, as confirmed via C elemental analysis of a decarbonated sample of this hemipelagic succession (Liu, 2011). The discrepancy is due to the simultaneous generation of CO₂ from OM and poorly crystallized CaCO₃ during the oxidation phase of Rock-Eval pyrolysis as shown by the records of the S4CO₂ and S5 peaks (Fig. 8). Samples from the Timor Sea were analyzed both as bulk sediment and as decarbonated samples, after prior acid treatment (HCl, 2N). For bulk sediment, the thermal decomposition of carbonate (S5 peak) occurs at a low temperature, with the maximum in CO₂ generation near 680 °C instead of 780 °C for pure well crystallized calcite (Pillot et al., 2013). If we apply a splitting between S4CO₂ and S5 in the middle of the trough between the two peaks, as recommended by Behar et al. (2001), TOC is underestimated by 50%. In any case, the partition between the two peaks automatically made with the Rock-Eval software is here obviously inaccurate. By contrast, the oxidation of decarbonated samples shows that CO₂ and CO from OM are generated until 680 °C (Fig. 8). Consequently, with bulk samples, it is not possible to distinguish the CO₂ concomitantly produced by the oxidation of OM and the thermal decomposition of poorly crystallized calcite. We forced the software to split the S4CO₂ peak from the S5 peak near 578 °C, a temperature corresponding to the intersection of the curves obtained from bulk and decarbonated samples (Fig. 8). Even with such a correction, the TOC % was a little underestimated compared with C-elemental analysis (Liu, 2011) and, more importantly, the OI values were overestimated, with values as high as 750 mg CO₂/g TOC (Fig. 9). In a modified van Krevelen diagram (HI-OI), the position of recent sediments containing poorly crystallized calcite is clearly out of the area of classical OM types. Despite the fact that recent OM contains a high amount of oxygen compounds, the extremely high

OI values reported for the bulk sediments from the Timor Sea are irrelevant. Consequently, determination of the type of OM using HI and OI values from these bulk samples is unreliable. Only Rock-Eval results from the kerogen concentrates isolated from the same samples allow OM typing (Fig. 9).

6. Miscalculation due to high amount of oxygen compounds in recent marine sediments

Lastly, the richness in oxygen compounds in recent OM may also alter the determination of some Rock-Eval parameters. According to Behar et al. (2001), the total CO signal obtained during pyrolysis is split into two peaks (S3CO and S3'CO; Fig. 1). S3CO corresponds to the release of functionalities linked to OM and the signal is integrated into the calculation of TOC. S3'CO is due to the reaction of CO₂ (released during the thermal decomposition of carbonate) with OM according to the so-called Boudouard reaction. From one mole of CO₂, this thermal reaction produces two moles of CO, one with carbon of organic origin (integrated into the calculation of TOC), and the other with carbon normally of mineral origin (integrated as CO₂ into the calculation of MinC). In the same way, the CO₂ produced during the pyrolysis phase is split into S3, which corresponds to CO₂ with an organic origin (released from the beginning of the S1 peak up to 400 °C) and S3', which is believed to have a mineral origin (recorded between 400 °C and the end of the pyrolysis phase; Fig. 1).

We analyzed recent diatomaceous ooze from the Antarctic Ocean, devoid of any carbonate, using the 'recent sediment' cyclor ecommended here. The resulting pyrograms (Fig.10) show a nice S2 peak as well as S3, S3', S3CO and S3'CO peaks. The splitting between S3CO and S3'CO falls at 522 °C, near the 550 °C limit defined by Behar et al. (2001). More intriguing were the S3 and S3' peaks, which showed a behavior similar to the CO release. We thus postulate that the S3' and S3'CO peaks recorded here are generated only from OM as no

carbonate was present in the sample. Consequently, the surface of these two peaks should be integrated into the calculation of TOC as part of the pyrolyzable carbon (PC). For the diatomaceous ooze, the increase in TOC was 15% and accordingly the HI and OI values decreased slightly (Fig. 10).

In their study of pure biochemical products using Rock-Eval pyrolysis, Carrie et al. (2012) also noted that the S3', S3'CO and even the S5 peaks were detected and they converted them into an OC contribution since their samples did not contain carbonate. Since peaks were observed after the temperature cutoff for MinC, they also manually integrated the IR signals in order to determine the total amount of oxygen-bearing OM and TOC.

7. Conclusions

The Rock-Eval technique, originally designed for the analysis of ancient sediments and kerogens, is now frequently used to characterize recent sediments and soils. However the thermally labile character of recent OM and poorly crystallized minerals (e.g. carbonates) and the eventual presence of inorganic salts (NaCl, sulfates...), that might perturb detection of pyrolysis effluents, requires specific operating conditions. First, starting the pyrolysis at 180 °C or 200 °C (instead of 300°C as for ancient organic material), is of absolute necessity to avoid serious decomposition of the most labile components of the OM with the following main consequences: an erroneously high S1 signal (supposed to account for "free hydrocarbons") and a lowering of S2 and HI, accounting for the hydrogenated part of the OM. In contrast, poorly crystallized carbonate, that might also begin to decompose at lower temperature than expected, might increase S3 and OI, thus providing an indication for an erroneously high oxygen content for the OM. Finally, if not eliminated by way of prior washing, the presence of salts such as NaCl and sulfates, common in the porewater of recent

marine sediments, directly perturbs the FID signal, thereby giving rise, at high pyrolysis temperature, to a second S2 signal that might imprudently be interpreted as due to a mature organic fraction.

As illustrated by various examples mentioned here, some authors still ignore these problems and the way of overcoming them, thereby obtaining data under inadequate conditions and which cannot therefore be compared with other data, or even more important, interpret parasite signals as resulting from particular organic components and from this build a misleading interpretation.

The proposed 'recent sediment' cycle does not require any change for the oxidation step compared with the 'bulk-rock/basic' method/cycle and just needs a change in the pyrolysis heating program. Starting the pyrolysis phase at 180 °C with a heating rate of 30 °C/min seems appropriate. This cycle displays TOC and OI values very similar to the classical 'basic' cycle and both S2 and HI values are believed to be better determined using the cycle when it is applied to recent sediments. Accurate conclusions require access to the pyrograms and an understanding of the pitfalls in the interpretation of Rock-Eval data. For critical samples, interpretation should be verified via other mineralogical or geochemical analyses.

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Caption of Tables and Figures

Table 1

Differences in operating mode and parameters using different Rock-Eval devices.

Table 2

Comparison of selected parameters with different Rock-Eval devices operating with 'basic' or 'recent sediment' cycle on selected samples. IFP 55000 and 160000 standards are ancient sedimentary rocks, whereas samples appearing in the grey-shaded zone of the table correspond to recent marine sediments. Each sample was analyzed at least 10x and some standard deviation values for IFP standards correspond to 100 analyses.

Fig. 1. Analytical procedure and records for the 'basic' cycle on the Rock-Eval 6 device. The straight lines refer to the temperature evolution through time. The surfaces of the different peaks are integrated for the calculation of TOC and MinC. Modified from Behar et al. (2001).

Fig. 2. Comparison of the FID responses (S1+S2 peaks) for a recent marine sediment and for IFP standard 160000 recorded via Rock-Eval 6 using the 'basic' cycle (solid line) and the 'recent sediment' cycle (dotted line). See text for the description of each cycle. The 'recent sediment' cycle allows better determination of the S1 and S2 peaks without any change in $T_{\text{peak}}/T_{\text{max}}$ for recent marine sediment. The straight lines refer to the temperature evolution through time (AU, arbitrary unit).

Fig. 3. Rock-Eval pyrograms of organic-rich (top) and organic-poor (bottom) samples of recent sediments showing distinct fluctuation in the bimodal character of the S2 peak (lm, low maturity; hm, high maturity; redrawn from Fig. 7 in Holtvoeth et al., 2001).

Fig. 4. Comparison of FID response (S1+ S2 peaks) obtained using both OSA (top) and Rock-Eval 6 (bottom) for analysis of a sample of recent marine sediment from the terminal lobes of the Congo deep sea fan, without or after previous rinsing. The straight lines refer to the temperature evolution through time. The second S2 peak (AU, arbitrary unit) during analysis of bulk sediment is a parasitic ionization due to salts that disappears after washing (dotted lines). The parasitic ionization is less important with Rock-Eval 6 because of the lower temperature of the splitter. The Rock-Eval parameters are obviously inaccurate when salts are present.

Fig. 5. Vertical evolution of Rock-Eval parameters (TOC, S2, HI and T_{max}) along a 9 m core of turbiditic sediments from the terminal lobes of the Congo deep sea fan. The data were acquired on bulk (solid line) and rinsed sediments (dotted line) using an OSA device. Note the parasitic effect due to salts, which perturbs all parameters down to 8.5 m.

Fig. 6. Example of deconvolution of S2 peak from bulk (top) and rinsed (bottom) sediment from the terminal lobes of the Congo deep sea fan (AU, arbitrary unit). The three Gaussian curves obtained using the Fityk software (Wojdyr, 2010) are the best fit of analytical functions to data. The first corresponds to labile OM, the second to the (proto)kerogen and the third is partly due to the parasitic ionization by salts. After washing (bottom) the third curve strongly decreases but does not totally disappear as some sulfate may be still present

and because thermally resistant organic compounds are generally detected at the end of the S2 peak.

Fig. 7. Comparison of MinC (%) determined from Rock-Eval pyrolysis and CaCO_3 (%) determined with a carbonate bomb technique for a selection of recent sediment samples from the Timor Sea. MinC is overestimated due to the simultaneous generation of CO_2 by OM and poorly crystalized CaCO_3 during the oxidation phase of Rock-Eval pyrolysis.

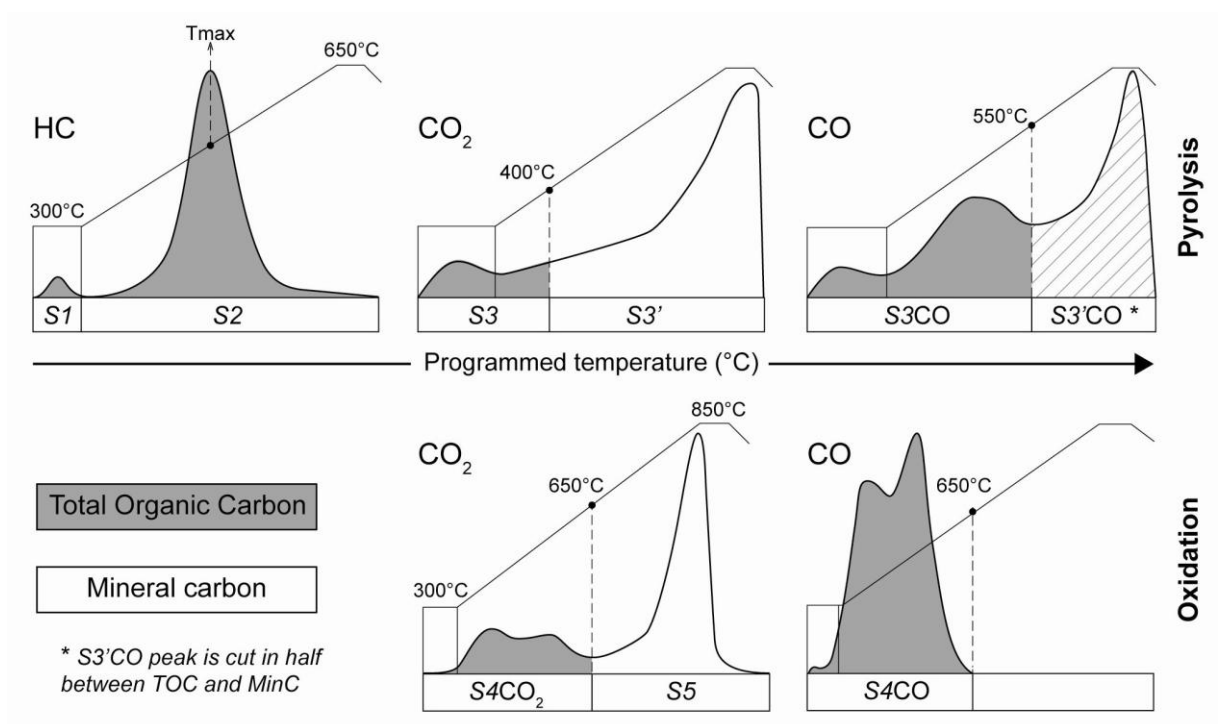
Fig. 8. Infra-red cell response (S4 CO_2 and S5 peaks) from two hemipelagic recent sediment samples from the Timor Sea analyzed using a Rock-Eval 6 device. Each sample was analyzed before and after decarbonation by acid treatment. The thermal decomposition of carbonate (S5 peak) occurs at low temperature because the carbonate fraction is made up of poorly crystalized calcite. The automatic cutoff between S4 CO_2 and S5 peaks usually made by the Rock-Eval software is inaccurate here. The straight lines refer to the temperature evolution through time.

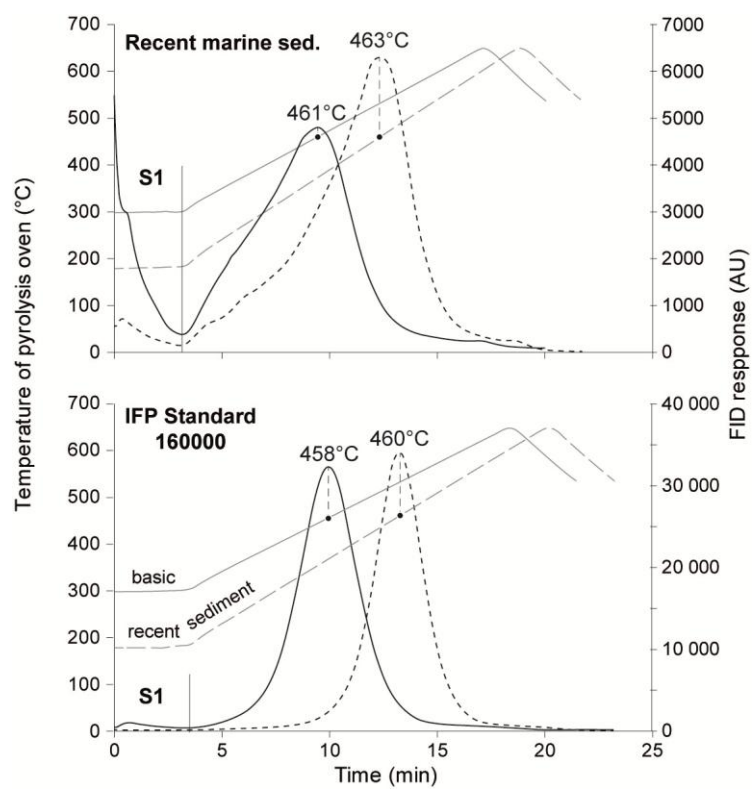
Fig. 9. Comparison of OM typing using a modified van Krevelen diagram (HI-OI) for bulk samples and kerogen concentrates of recent hemipelagic sediments from the Timor Sea. The extremely high OI values for bulk sediments are an artefact due to the cracking at low temperature of poorly crystalized CaCO_3 that interferes with the determination of organic derived CO_2 . Consequently, determination of the type of OM is unreliable. Note that the OI axis on the modified van Krevelen diagram usually does not exceed 200 mg CO_2 /g TOC.

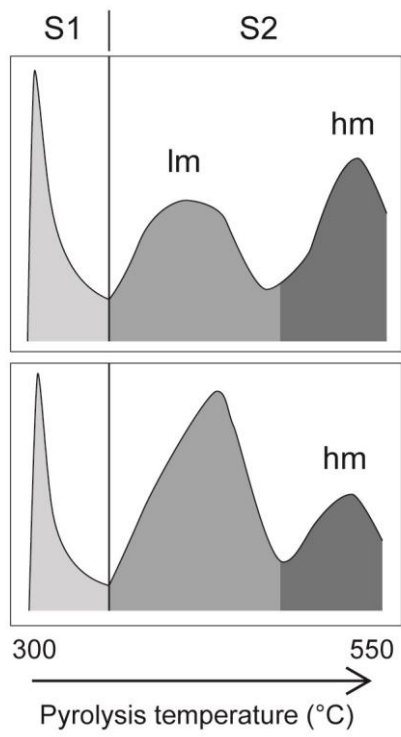
Fig. 10. Records of the different peaks generated by pyrolysis of a recent diatomaceous ooze

from the Antarctic Ocean. The straight line refers to the temperature evolution through time. The cutoff between peaks automatically made by the Rock-Eval software provides the parameters (TOC, MinC, HI and, OI) on the first line of the table. As this sample did not contain any CaCO_3 , the $S3'$ and $S3'CO$ peaks should here be considered within the organic carbon fraction. Accordingly, the Rock-Eval parameters are modified as shown on the second line of the table.

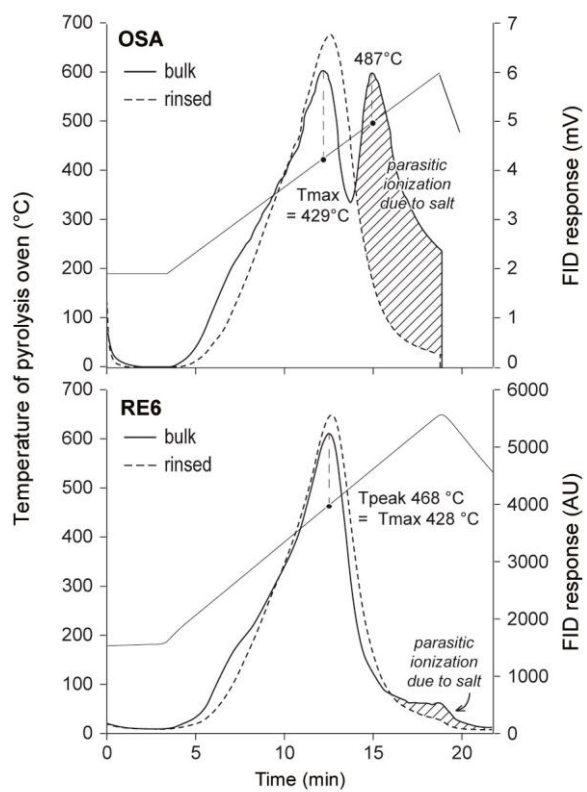
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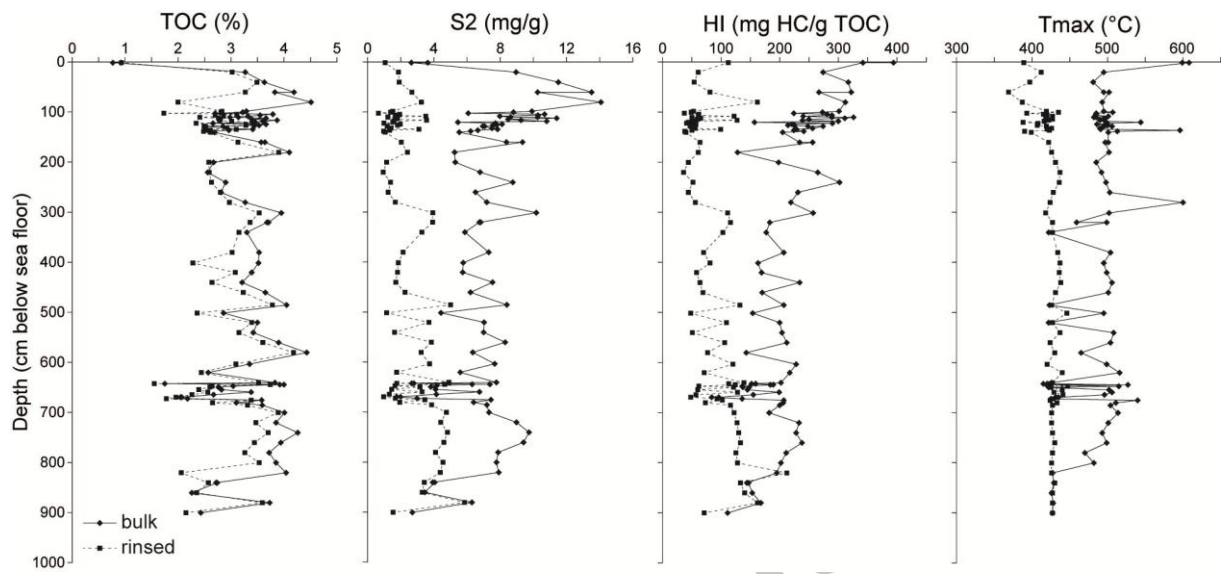




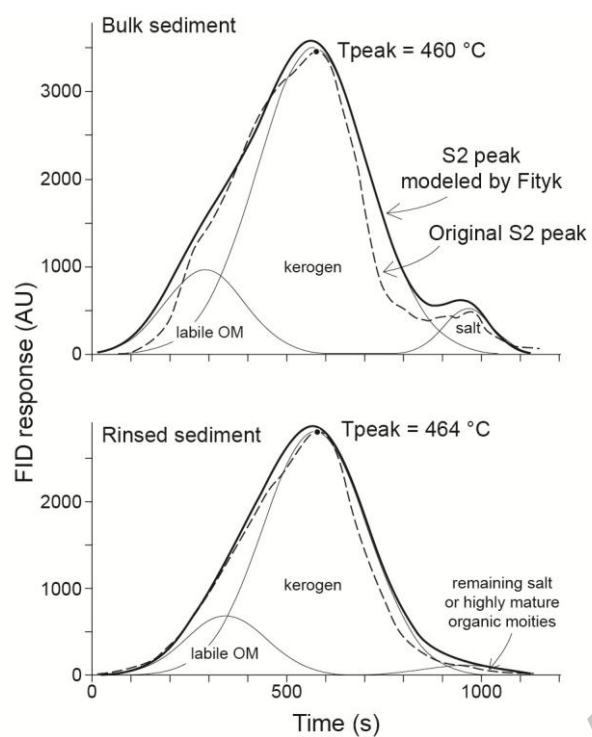


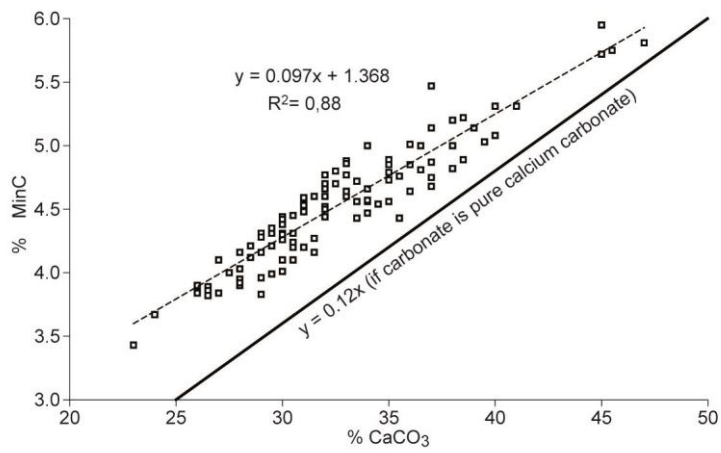
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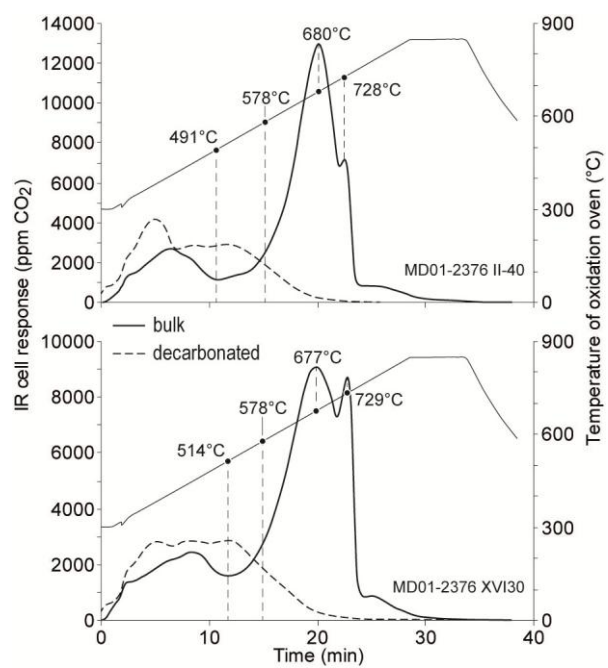


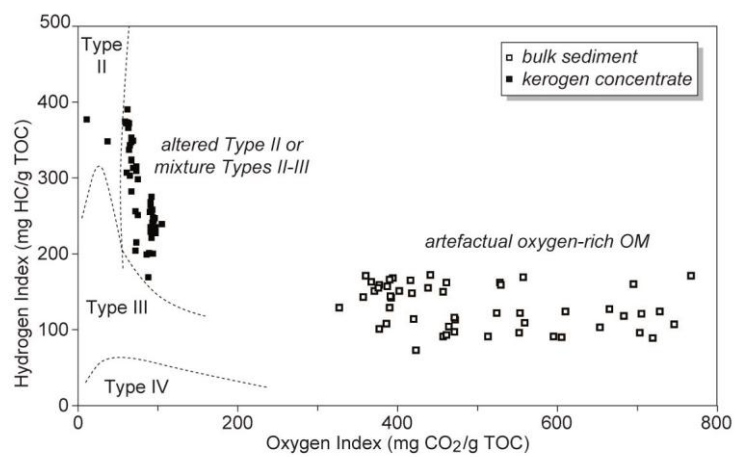
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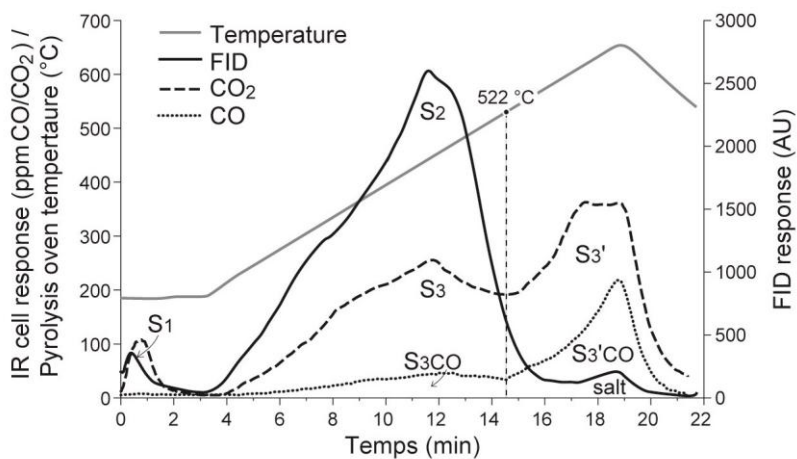


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$TOC = 1.42\%$ $C_{min} = 0.21\%$ $HI = 363\text{ mg/g TOC}$ $OI = 135\text{ mg CO}_2/\text{g TOC}$
 $TOC = 1.63\%$ $C_{min} = 0.0\%$ $HI = 316\text{ mg/g TOC}$ $OI = 118\text{ mg CO}_2/\text{g TOC}$

Device	Inert gas	Splitter temperature	Final pyrolysis temperature	Oxidation temperature	RE parameters
Rock-Eval 2	He	500 or 550 °C	600 °C	600 °C	S1, S2, S3 (< 400 °C), S4, PC, RC, TOC, Tmax, HI, OI
Rock-Eval 3 (OSA)	He	500 or 550 °C	600 °C	600 °C	S1, S2, S4, PC, RC, TOC, T _{max} , HI
Rock-Eval 6	N ₂	400 °C	650 °C	300 to 850 °C	S1, S2, S3, S4, S5, PC, RC, TOC, T _{max} , HI, OI, OICO, OIRE6, MinC

Sample	Device	n		S1 (mg/g)		S2 (mg/g)		T _{max} (°C)		TOC (wt%)		HI (mg/g TOC)	
		Basic	Rec. sed.	Basic	Recent sed.	Basic	Recent sed.	Basic	Recent sed.	Basic	Recent sed.	Basic	Recent sed.
IFP 55000	RE2/OSA	95	50	0.10 ± 0.05	0.02 ± 0.00	8.62 ± 0.22	8.82 ± 0.20	423 ± 3	425 ± 2	2.79 ± 0.07	2.82 ± 0.11	309 ± 6	312 ± 10
IFP 55000 ^a	RE6	43	25	nd	0.01 ± 0.01	8.70 ± 0.20	8.78 ± 0.18	422 ± 1	424 ± 1	2.80 ± 0.04	2.93 ± 0.10	308 ± 6	310 ± 12
IFP 160000b ^b	RE6	600	25	0.14 ± 0.07	0.04 ± 0.04	12.43 ± 0.50	12.64 ± 0.48	416 ± 2	418 ± 2	3.28 ± 0.14	3.30 ± 0.13	379 ± 14	383 ± 15
Timor Sea-230	OSA	10	10	0.21 ± 0.10	0.01 ± 0.01	1.11 ± 0.11	1.35 ± 0.12	412 ± 2	417 ± 3	0.83 ± 0.04	0.81 ± 0.03	132 ± 8	166 ± 6
Timor Sea-230	RE6	10	10	0.23 ± 0.09	0.01 ± 0.02	1.06 ± 0.08	1.31 ± 0.13	413 ± 2	418 ± 2	0.80 ± 0.05	0.81 ± 0.04	133 ± 5	162 ± 6
Congo DSF-MTB06	RE6	8	12	0.52 ± 0.04	0.03 ± 0.01	4.25 ± 0.05	5.40 ± 0.25	412 ± 2	409 ± 3	4.00 ± 0.04	3.71 ± 0.04	106 ± 7	145 ± 4

a Data from Table 7 in Behar et al. (2001); ^b data provided by G. Letort (IFPEN; personal communication).

Highlights

- Several artefacts may occur during Rock-Eval pyrolysis of recent marine sediments.
- A simple standard method is proposed for the analysis of recent organic matter.
- Guidelines are provided for interpreting Rock-Eval data from recent sediments.

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