



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 been increasingly applied to the characterization of recent lacustrine or marine sediments. However, as illustrated by 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 detection of the pyrolysis effluent. The aim here was to outline the problems generated by such perturbation and to demonstrate that specific operating conditions are 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.

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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; Jacob et al., 2004; Sanei et al., 2005; Boussafir et al., 2012; Zocattelli 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-Nebout 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; Tribovillard

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. (unpublished results) 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

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du Pétrole (IFP) and marketed by different companies. The principles and basic operating conditions of the apparatus are described by Espitalié et al. (1977) for Rock-Eval 1, by Espitalié et al. (1985a,b, 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 °C, the second peak (S2) representing the hydrocarbons generated from kerogen cracking between 300 and 650 °C, with a heating rate of 25 °C/min. The amounts of CO_2 and CO represent the S3 and S3CO peaks, respectively. All basic parameters are expressed either in mg of hydrocarbons or CO_2/CO per gram of rock. T_{max} is the temperature at which the maximum hydrocarbon yield resulting from kerogen cracking occurs.

The residual organic and inorganic carbon content (in wt%) of the pyrolyzed sample is obtained by combustion in air from 300 to 850 °C, with a heating rate of 20 °C/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 S4CO 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 the $S3' + S3'CO + S5$ 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; Romero-Sarmiento 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-

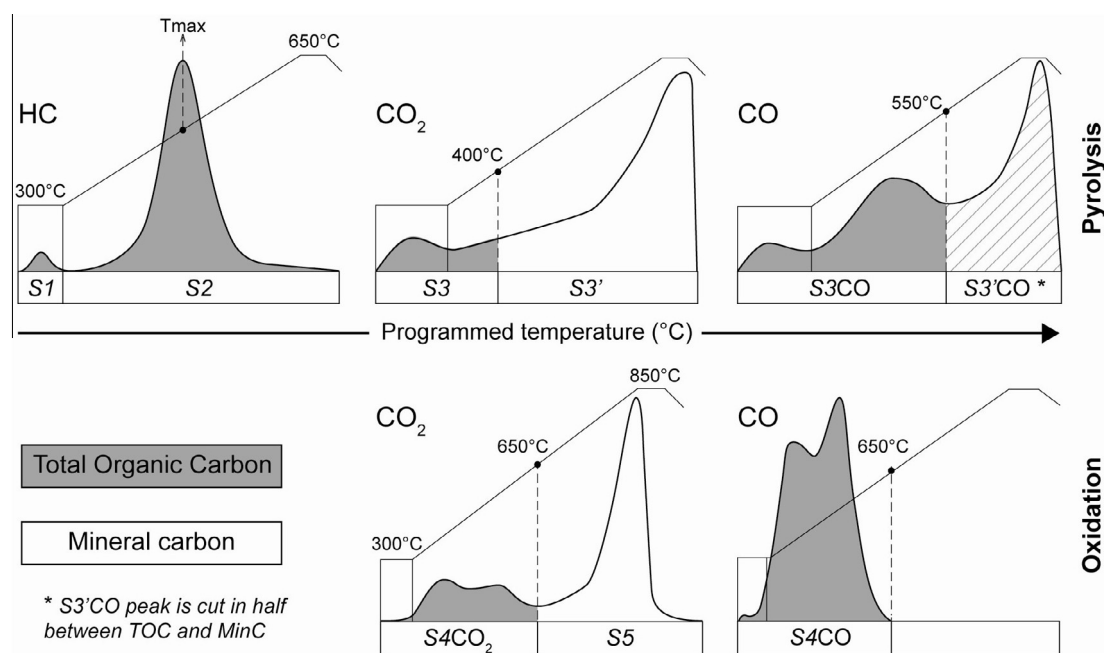


Fig. 1. Analytical procedure and records for the 'basic' cycle on the Rock-Eval 6 device. The straight lines refer to the temperature evolution through time. The surfaces of the different peaks are integrated for the calculation of TOC and MinC. Modified from Behar et al. (2001).

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