

# Diagenetic transformation of organic matter in the Holocene sediments of the Black Sea: pyrolysis data

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## Abstract

The article presents the results of pyrolysis (Rock-Eval) and pyrolysis–gas chromatography–mass spectrometry analysis of organic matter (OM) in the Holocene sediments of the Black Sea. The studied samples represent two parts of the sedimentary column: coccolith ooze with 2.8%  $C_{org}$  at the top and sapropels oozes with 8.5%  $C_{org}$  at the bottom. The deposition of Holocene sediments was inferred to take place under euxinic conditions, which are more favorable for organic-matter preservation and sapropel deposition during the Old Black Sea stage. The results show that the modern processes of microbially mediated methane oxidation in the Old Black Sea oozes are interpreted as the main cause of their apparently lower degree of diagenetic transformation as compared to that of coccolith oozes.

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## Introduction

The Black Sea has long been considered as an appropriate test site for modeling and interpretation of ancient marine black shale depositional environments (Calvert, 1990; Demaison and Moore, 1980; Gavshin et al., 1988; Strakhov, 1976). Holocene Black Sea deposits are subdivided into three lithostratigraphic horizons (from top to bottom): I—New Black Sea deposits (coccolith oozes), II—Old Black Sea deposits, Middle Holocene (sapropel oozes, and III—Neouxine deposits, Holocene–Late Pleistocene boundary. The Old Black Sea beds are characterized by a relatively high organic carbon content ( $C_{org}$ ). The generally low  $C_{org}$  value in the recent Black Sea and Neoeuxine beds and bitumen extracts was found to be three times as low as in the Old Black Sea beds (Gavshin et al., 1988).

A drastic change of the sedimentation environment and a transition from Neoeuxine to Old Black Sea deposits was associated with an inflow of Mediterranean salt water through the Bosphorus into the Black Sea's freshwater lake at ca. 7000 years ago (Degens, 1973; Strakhov, 1976). The system evolved from a freshwater oxygenated lake (Neoeuxinian time) to a brackish sea basin (Middle–Upper Holocene), with

permanent water stratification, prolonged anoxia and hydrogen sulfide formation.

Sapropel deposition caused by the inflows of saltwater was followed by a second major lithologic event marking the onset of colonization of the Black Sea by haptophyte microalgae, including the coccolithorid *Emiliania huxleyi* (*E. huxleyi*), which first appears approximately 3500 years ago (Degens, 1973). The occurrence of *E. huxleyi* was reported both in shelf and offshore regions (Belogorskaya and Kondrat'eva, 1965).

Apart from phytoplankton and terrigenous material, the organic matter in recent sediments contains a large amount of bacterial biomass. The importance of the bacterial processes gave rise to the description of the Black Sea as a “bacterial sea” (Sorokin, 1982).

During deposition of bottom sediments, organic matter derived from plants and animals becomes involved in a large number of biochemical and chemical reactions. Proteins, carbohydrates, nucleic acids undergo enzymatic hydrolysis under the action of microorganisms (fungi, bacteria, etc.) and break down into soluble monomers of nucleic acids and polysaccharides. Subsequently, these metabolic products are converted by polycondensation to humic (acid-insoluble), fulvic (acid-soluble) acids, and protokerogen, an organic material insoluble in organic solvents. The content of humic and fulvic decreases while the content of humins (protokerogen) increases with increasing burial depth. The diagenetic

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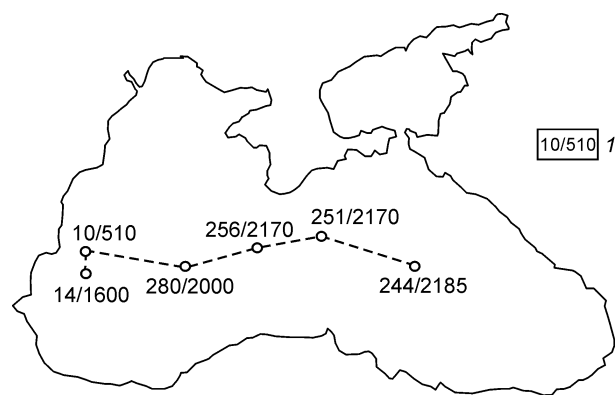


Fig. 1. Map showing bottom sediment sampling locations. 1, station number/water depth (m).

stage of organic matter transformation occurs to a depth of about 0.5–1 km (Tissot and Welte, 1978) at which kerogen becomes the main constituent of organic matter.

Conventional analytical methods, widely used for a study of recent sediments, including sample pretreatment (decarbonatization, extraction, purification, etc.) are usually time-consuming and labor-intensive, considering the object of the study (Poirier et al., 2003). The Rock-Eval pyrolysis (RE pyrolysis) technique was designed for source rock screening and because of its simplicity, it has now been increasingly applied to a variety of other materials such as immature organic matter in soils and recent lacustrine and marine sediments (Disnar et al., 2003) to characterize the degree of their diagenetic transformation. Pyrolysis of organic matter in recent sediments is a complex process consisting of a series of successive steps of thermal degradation of the components of organic matter having different nature, thermal stability, and temperatures of degradation. During diagenesis, thermally labile compounds decompose first in the temperature range 200–400 °C. Protokerogen starts to crack at temperatures above 380 °C. Analysis of pyrograms from samples provides parameters that semiquantitatively describe the degree of diagenetic transformation of organic matter in recent sediments: a high proportion of the low-temperature fraction on the pyrogram of the pyrolyzed sample (HC released at a temperature below 400 °C) is indicative of a high degree of diagenetic transformation.

This study aimed to analyze a series of samples of Holocene sediments (coccolith oozes and Old Black Sea sapropel oozes, CO and SO, respectively) by Rock-Eval and flash pyrolysis chromatography-mass spectrometry (Py-GS/MS) of pyrolysates to evaluate the degree of diagenetic transformation of organic matter.

## Materials and methods

Samples were collected in 1982–1986 during the international geological-geochemical expeditions aboard the R/V *Evpatoria* organized jointly by the Institute of Geology and Geophysics, Siberian Branch, Russian Academy of Sciences

jointly with the National Academy of Sciences and the National Committee of Geology of the republic of Bulgaria (Gavshin et al., 1988; Vyshemirskii et al., 1991).

Samples used in this study were collected at several stations (Fig. 1) located in different facies zones. For example, stations 280, 244 (2000, 2185 m water depths) correspond to areas with very low rates of biogenic sedimentation (Gavshin et al., 1988; Saraev et al., 1986), stations 14, 256 (1600, 2170 m water depths) are located in areas with biogenic sedimentation with occasional turbidite layers, station 251 (2170 m water depth) is located in the area covered by biogenic oozes with multiple turbidite layers, stations 10 (510 m water depth) is situated on the continental slope in the area of biogenic-terigenous sedimentation.

Rock-Eval pyrolysis was performed on a SR Analyzer (Humble Instr. Inc.<sup>TM</sup>). To compare the Rock Eval pyrolysis data for recent sediments with literature data obtained by other analytical methods, the actual temperature near the crucible is used; correspondingly, the temperature of the maximum rate of hydrocarbon (HC) release is marked as  $T_{\text{peak}}$  on the pyrograms (Disnar et al., 2003).

The organic carbon content in decarbonated samples (IR, the insoluble residue after acid treatment) was analyzed on an AN-7529 carbon analyzer. The bitumens were extracted from samples with chloroform at room temperature with a subsequent chromatographic analysis. The molecular composition of saturated hydrocarbons was determined by gas chromatography–mass spectrometry (GC–MS) with a HP 6890 gas chromatograph coupled to a MSD 5975C mass selective detector. A 30 m HP-5MS column was employed. The carrier gas was helium. The temperature was set initially at 40 °C for 2 min, then raised to 290 °C with a heating rate of 5 °C/min and held for 20 min. The Py–GC–MS procedure was previously described by Melenevskii et al. (2009). The samples were analyzed in an increment heating mode: first, thermodesorption of lipids and labile components at 250 °C and 380 °C, respectively (Jocteur-Montrozier and Robin, 1988), followed by cracking of protokerogen at 610 °C.

Compounds were identified using the reference data base (NIST) of mass spectra and retention times (Stankiewicz et al., 1997). The relative abundance of pyrolysable organic compounds (or sum of compounds) was calculated by dividing integrated peak areas of the relevant ion chromatograms by the integrated peaks of *n*-alkanes in the C<sub>10</sub>–C<sub>30</sub> range; the relative mean square deviation calculated from parallel runs was 15%. A detailed flash-pyrolysis analysis was performed on two samples (st. 280) of coccolith (sample 8) and sapropel ooze (sample 18) (Table 1).

## Results

**Pyrolysis data.** Rock-Eval pyrolysis data for the Black Sea sediments are shown in Table 1 and Figs. 2, 3.

As seen on the C<sub>org</sub> = *f*(IR) plot, all data for CO and SO samples (Fig. 2a) form two arrays, one with the carbonate content (100 – IR) of >70% and C<sub>org</sub> of <4%, and the other

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