Electronic Supplementary Materials

Early–Middle Miocene paleoenvironmental and paleoclimate changes in the Toplica Basin (Serbia) inferred from plant biomarkers, biochemical and elemental geochemical proxies

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Supplement 1: Samples and analytical methods

X-Ray Fluorescence (XRF)

The ARL PERFORM'X Sequential X-Ray Fluorescence Spectrometer (Thermo Fisher Scientific, Switzerland) was equipped with a 4200W Rh Xray tube, goniometer, seven optical crystals (AX03, AX09, AX16C, PET, GE111, LiF200, LiF220), and two detectors (flow proportional counter—FPC and scintillation detector—SC). For semi-quantitative and qualitative analyses, the stream sediment STSD-3 was used as a standard (Burazer et al. 2020). The spectrometer was bale to detect all elements from Be to Am. However, only the measurements of Na and heavier elements were considered (O and C concentrations were obtained computationally and from the loss on ignition) for semi-quantitative analysis. The ARL software UniQuant specialized for the standardless analysis (Burazer et al. 2020) was applied for semi-quantitative analysis. The qualitative analysis was perfromed in order to eliminate any doubts about measurements of the elements close to the detection limit and possible interferences emerged as a consequence of line overlaps.

Rock-Eval pyrolysis

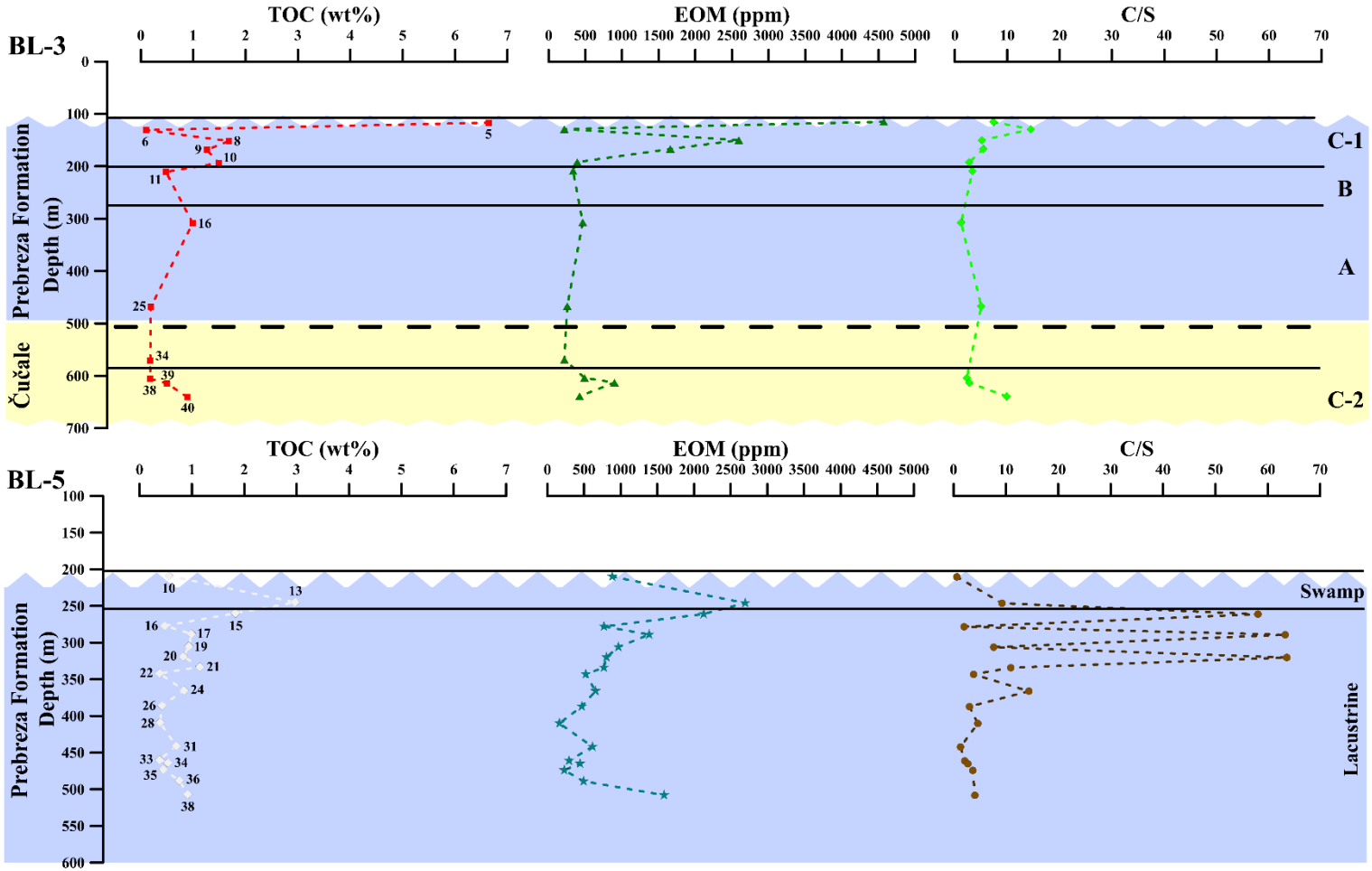
The sample preparation of the sampled for the Rock-Eval pyrolysis included drying, cleaning form contaminants, and homogenization. The initialization process involved the evaporation of free hydrocarbons from the samples by heating them at 300 °C for 3 min. The next step was controlled pyrolysis, which was performed by heating the samples from 300 °C to 650

°C at a rate of 25 °C/min, and in the presence of N_2. Subsequently, samples were transferred to the oxidation oven, where the remaining OM was heated from 300 °C to 850 °C at a rate of 20 °C/min, in the presence of pure air (Burazer et al. 2020).

Organic geochemical analysis

A gas chromatograph Agilent 7890A GC (HP5-MS capillary column, 30 m × 0.25 mm, 0.25 μm film thickness, Helium carrier gas 1.5 cm3/min) coupled to Agilent 5975C mass selective detector (70eV) was used for the analysis of saturated and aromatic fractions. The column was heated from 80 to 300 °C, at a rate of 2 °C/min, and the temperature of 300 °C was maintained for an additional 20 min. Afterward, the temperature of 300 °C was rapidly increased to 310 °C, at a rate of 10 °C/min, and the final temperature of 310 °C was maintained for 1 min. The individual peaks were determined by comparison with literature data and based on the mass spectra (library: NIST5a). For the calculation of parameters, the quantification of the compounds was performed by the integration of peak areas (software GCMS Data Analysis) in the appropriate mass chromatograms (Burazer et al. 2020).

Supplement 2: Variation of TOC (wt%), EOM (ppm), and C/S with depth in the BL3 and BL5 wells.



Supplement 3: Variation of Hydrogen Index (HI) (**left**) and C/N (**right**) with depth in the BL3 and BL5 wells. Individual sedimentary facies are indicated. Only reliable data (TOC > 0.5 wt%—in case of HI and C/N plots), and S2 > 0.2 mgHC/gTOC—in case of HI plots) are used in the plots. C/N categorization are according to Meyers and Ishiwatari, (1993).