

NEW DATA ON THE EXPRESSION OF THE EARLY
EOCENE HYPERTHERMALS IN NORTHERN BULGARIA:
RIBEN SECTION REVISITED

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Abstract

We present new lithologic, nannofossil biostratigraphic and benthic carbon and oxygen isotope records for a marly-rich, 11 m thick Paleocene-Eocene section, now exposed at an old quarry at Riben Village, northern Bulgaria. The occurrence of NP9, NP10 and NP11 nannofossil zones is evidenced by detailed high resolution nannofossil biostratigraphy. The carbon dissolution interval is marked by the abrupt drop of CaCO₃ content and deposition of a clay interval at the onset of the Paleocene-Eocene Thermal Maximum (PETM). Stable isotope analyses of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ were performed on benthic-foraminiferal tests. An unusual two-fold carbon isotope excursion (CIE) in the PETM interval is documented (total negative shift of 2.89‰). Moreover, three paired negative excursions: two in the Paleocene within the PETM interval, upper NP9 zone, and one within the early Eocene, NP11 zone are identified. The most prominent negative carbon isotope excursion (4.90‰ negative shift) is related with ETM3 (or “X” event), 52.84 Ma ago.

Integration of nannofossil biostratigraphy, benthic stable isotope data sets and lithology unravel two separate early Eocene hyperthermal events: the PETM (= ETM1) and the ETM3 (= “X” event), recorded at Riben section.

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Introduction. Fifty-six million years ago, at the boundary between the Paleocene and the Eocene Epoch, the Earth underwent one of its most prominent warming episodes – the Paleocene – Eocene Thermal Maximum (PETM). This event is marked by a rapid negative carbon isotope excursion (CIE) of about -2‰ to -5‰ and characteristic clay interval – carbon dissolution interval (CDI) in the oceanic sections worldwide [1–4]. The PETM duration is estimated at ~ 200 kyr for the carbon isotope excursion and ~ 120 kyr for the associated pelagic clay layer [2]. According to some recent calculations, the global mean surface temperature anomaly for the PETM warming event is within the range of 4 to 5°C [1]. The impact of the abrupt global warming reflects on the entire biosphere. It affected the marine planktonic and benthic communities and the ecosystems onshore. The deep ocean benthic foraminifera were one of the most affected group by the warming, while calcareous nannoplankton also experienced major changes in abundance of certain taxa [3]. In addition of the PETM (at ~ 55.93 Ma), multiple transient global warming events with carbon cycle perturbations have been recognized in the early Eocene, termed “hyperthermals”, prior to the Early Eocene Climatic Optimum (EECO). They include Eocene Thermal Maximum 2 (ETM2, “Elmo” event) at ~ 54.05 Ma and the ETM3 (“X” event) at ~ 52.84 Ma [2]. The most important characteristic used to identify hyperthermal events is a paired negative excursion in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope data of preferably benthic foraminifera associated with more clay-rich sediments, indicating dissolution of carbonate [2].

The occurrence of the PETM in Bulgaria was evidenced in 2005, based on calcareous nannofossil and bulk rock isotope data from three sections in northern Bulgaria – Kladorub, Riben and Bozhuritsa [5]. Since then, the studies have continued in order to investigate the composition of the nannofossil assemblages and biotic response of the nannoplankton communities to the extreme global warming during the PETM, as well as to document the essential changes in the isotope composition of the carbon and oxygen isotopes across the Paleocene-Eocene boundary interval [3,6,7].

In the last two years, significant new data were accumulated from the newly acquainted isotopic, sedimentological, biostratigraphic and quantitative microfossil studies of the PETM section near the village of Riben, Pleven District (central North Bulgaria). Their interpretation sheds new light on the expression of the PETM and possibly a new early Eocene hyperthermal event at this locality such as new data on the carbonate content of the sediments, C and O isotope excursions, sea surface water temperature, quantitative changes and species diversity of calcareous nannoplankton, etc.

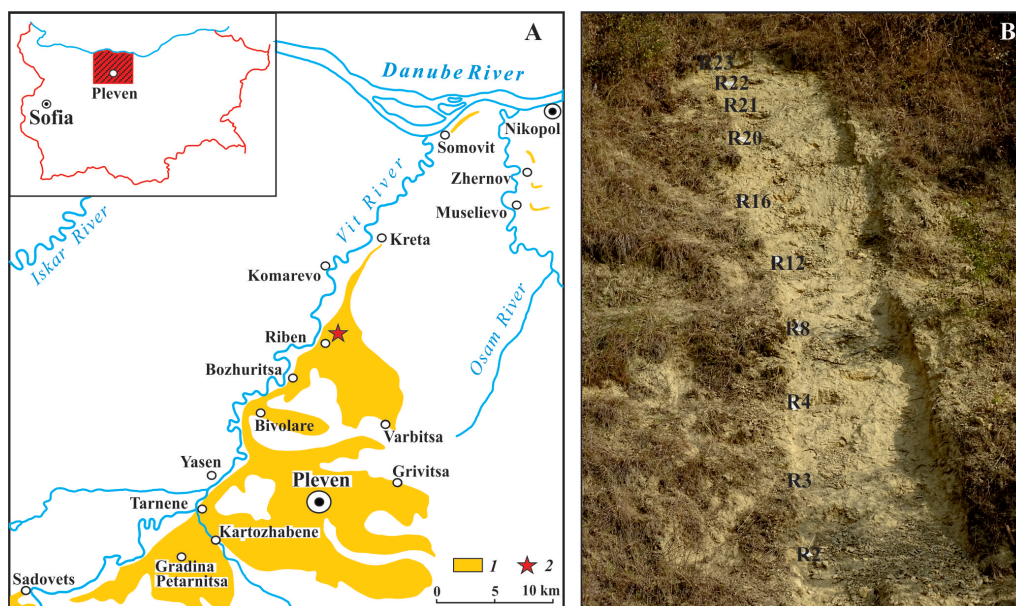


Fig. 1. A – outcrops of the Paleocene-Eocene sediments and location of the studied section Riben; B – Field photo of the trench with position of the samples analyzed

Geological settings. The Riben section is situated on the right bank of the River Vit valley, where Paleocene-Eocene sedimentary rocks are cropping out (Fig. 1A). It is located in an old clay quarry, at 150 m north-east of the centre of Riben village, Pleven District (Fig. 1A, N43°32'04"; E24°37'32"). The stratigraphic succession is traced from the entry point of the quarry along its right slope, where a new trench was unearthed across the Paleocene-Eocene transition interval (Fig. 1B). The sediments of Bozhuritsa Fm (Uppermost Paleocene) and “Beloslav” Fm (Lower Eocene) are exposed, consisting of marls, clays, sandy marls and glauconitic marls (Fig. 1B, Fig. 2). The uppermost parts of Bozhuritsa Fm are represented by silty-clayey rocks. They are beige, light-grey to rusty-brown and orange, coloured by the abundant ferruginous oxides and hydroxide concretions (Fig. 1B, Fig. 2). These are topped by relatively compact, more calcareous marlstone bed, approximately 10–15 cm thick. The latter is overlain (via sharp contact) by sandstones of high glauconite content and silty marls, dark-green in colour (“Beloslav” Fm). The highest glauconite saturation is noted in the basal 15–20 cm, gradually decreasing upwards. Abundant remains of nummulitids, shell debris and well preserved bivalve shells are commonly encountered at the base of these sediments. Up section, beige to grey, weakly glauconitic marls, 2–2.5 m-thick are deposited. The second high glauconitic level is recorded between samples R23–R26 (+3.25 ÷ +4.00 m). The uppermost portions of the section are composed of beige to grey marls (Avren Fm), > 2 m thick [3].

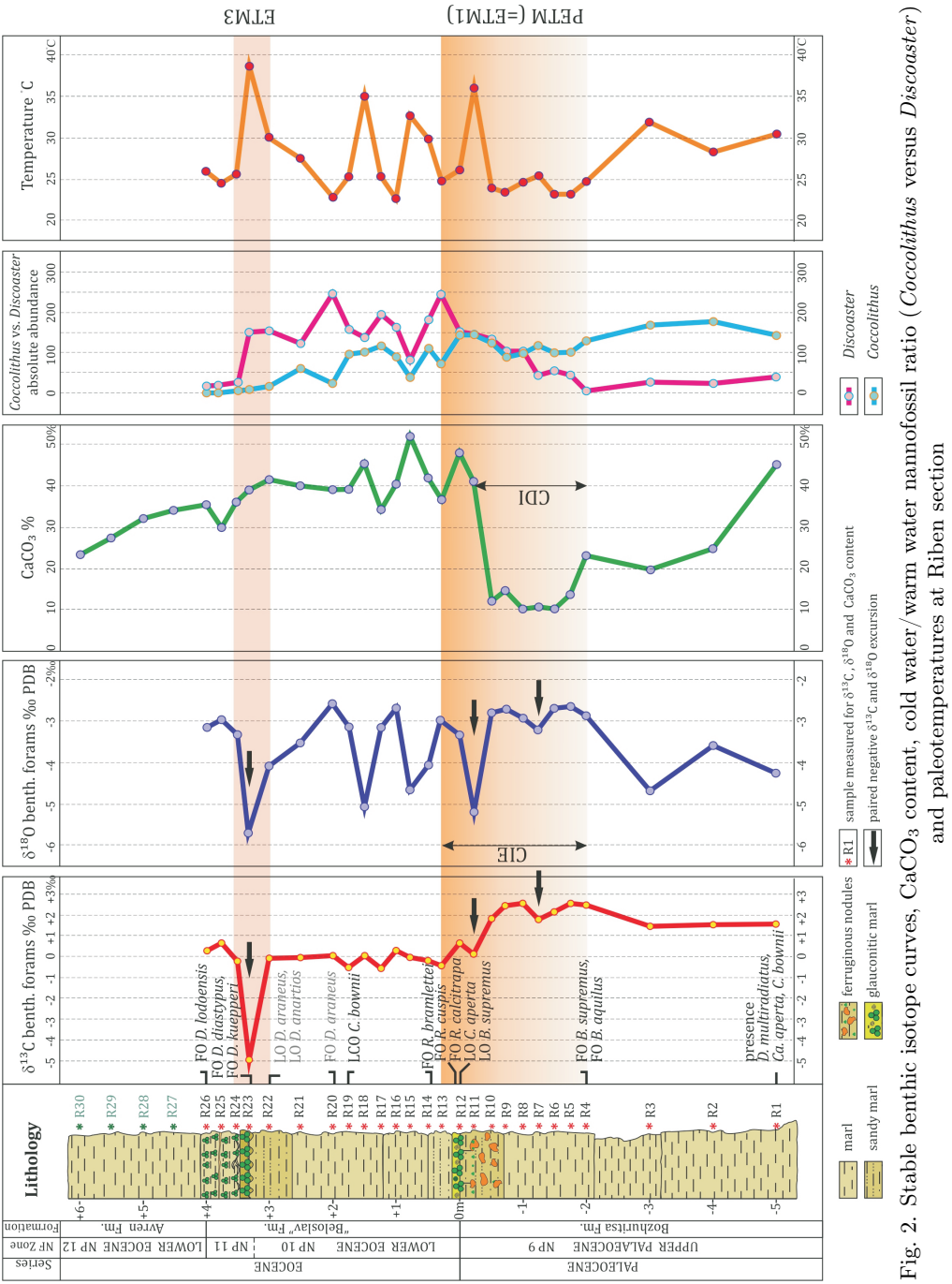


Fig. 2. Stable benthic isotope curves, CaCO₃ content, cold water/warm water nanofossil ratio (*Coccolithus* versus *Discoaster*) and paleotemperatures at Riben section

The section is considered to be continuous across the late Paleocene to the early Eocene, however, a short depositional break spanning the middle and upper part of NP 10 nannofossil zone is suggested [3]. The total thickness of the measured section is 11 m (Fig. 2).

Materials and methods. The PETM interval was sampled for different type of analyses – nannofossil biostratigraphy, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analysis and carbonate content at various resolutions – 1 m in the lower part, 0.25 m in the middle part, 0.10–0.05 m 1 m below and 1 m above the Paleocene-Eocene (P/E) boundary and 0.5 m in the upper part (Fig. 1B, Fig. 2). The P/E boundary is denoted by 0 m in the lithology column, and the position of each sample was considered with respect of this marker level. The samples' position is shown in Fig. 2.

Calcareous nannofossil analysis. Thirty samples, from R1 to R30, were analyzed for their nannofossil and carbonate content. Calcareous nannofossils were observed in simple smear-slides, prepared following a standard methodology [8]. They were logged at $1250\times$ magnification, using an immersion oil objective ($\times 100$) on a *Zeiss Axioskop 40* microscope. Calcareous nannofossil biostratigraphy is mostly based on standard zonation of MARTINI [9]. The latter was used for biostratigraphic subdivision of the PETM interval and detection of stratigraphically significant biohorizons (bioevents) – first occurrence (FO, the lowest stratigraphically occurrence or Base) and last occurrence (LO, the stratigraphically highest occurrence or Top). All smear-slides are stored at the Department of Paleontology, Stratigraphy and Sedimentology, Geological Institute of the Bulgarian Academy of Sciences.

Carbonate content determination was performed using carbonate analysis by treatment with HCl acid. From each sample, 5 g were measured and ground to powder in an agate mortar. The samples were flooded with 2% HCl acid until they stopped reacting. Then they were washed several times with distilled water. The samples were dried and the insoluble residue (insoluble components) was weighed. The quantity of the insoluble residue was subtracted from the initial 5 g and the amount of soluble components was calculated, which represents the carbonate content of the sample (in %).

Carbon and oxygen stable isotope analyses. Twenty-six samples, from R1 to R26 were measured for carbon and oxygen isotopes (Fig. 2). Stable isotope analyses were performed on benthic-foraminiferal tests (genus *Cibicidoides*), retrieved from the sediments, following the classical methodology for foraminifera extraction [10]. The analyses were done at the Stable Isotope Laboratory of the Faculty of Geosciences and the Environment, University of Lausanne, Dorigny, Switzerland. Measurements were performed using a GasBench II linked to a Delta V mass spectrometer. Analytical precision based on replicate analysis of in-house standards averaged 0.03‰ for $\delta^{13}\text{C}$ and 0.05‰ for $\delta^{18}\text{O}$. All isotopic values are reported in the δ -notation in per mil (‰), relative to Vienna Pee Dee Belemnite

standard (V-PDB).

To calculate the paleotemperature, based on data from the measured $\delta^{18}\text{O}$ values, the formula of CRAIG [11], modified by ANDERSON and ARTHUR [12], was applied:

$$T\ (^{\circ}\text{C}) = 16.0 - 4.14 (\delta_{\text{cal}} - \delta_w) + 0.13(\delta_{\text{cal}} - \delta_w)^2,$$

where $\delta_{\text{cal}} = \delta^{18}\text{O}$ value of the analyzed calcite of samples with respect to the PDB standard; $\delta_w = \delta^{18}\text{O}$ ratio of the water from which the calcite precipitated with respect to the SMOW standard and $\delta_w = -1.0\text{‰}$ for “non-glacial ocean” [13].

Results. Nannofossil biostratigraphy. The lower part of the section (−5.00 to 0 m) is assigned to NP9 zone [9] (Fig. 2) due to the presence of *D. multiradiatus* (Fig. 3, 4) from the lowermost sample, as well as *Coccolithus bowni* and *Calcisolenia aperta* (Fig. 3, 6) and the absence of *Rhomboaster*’ representatives. The interval comprised between +0.05 m to +3.25 m is dated NP10 zone (Fig. 2), because of the FOs of *Rhomboaster calcitraba* (Fig. 3, 1–2) and *R. cuspis* at +0.05 m, shortly followed by the FO of *Rhomboaster bramlettei* at +0.40 m. Neither *Tribrachiatus contortus* & *T. digitalis*, nor *T. orthostylus* were recorded

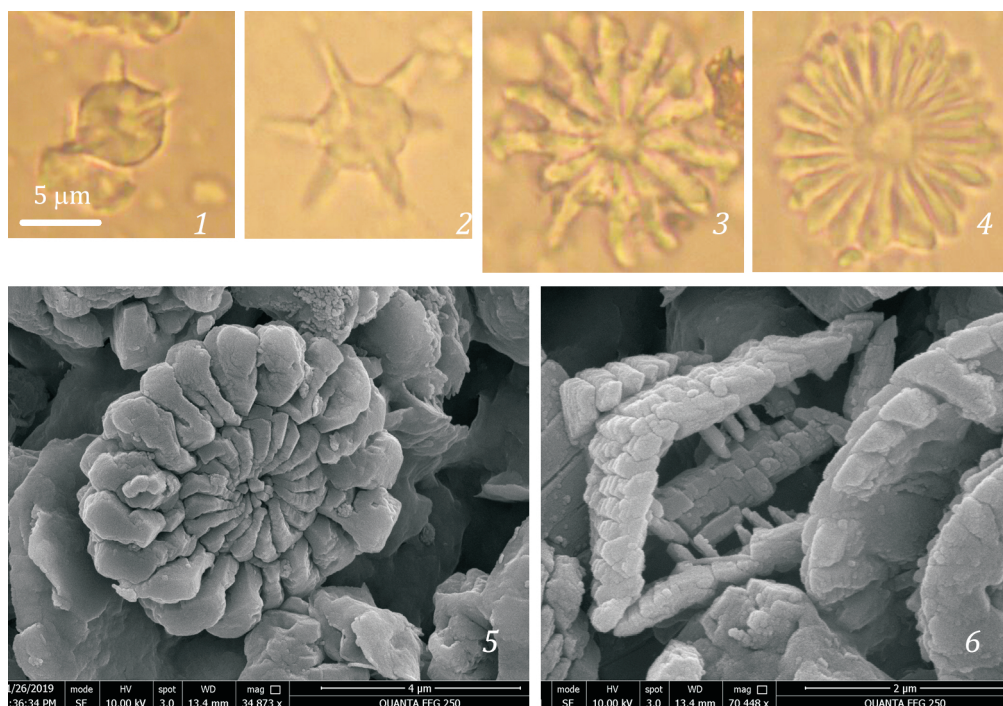


Fig. 3. Microphotos and SEM photos of calcareous nannofossil species from the Riben section. 1–2 – *Rhomboaster calcitraba*, +0.05 m, plane polarized light (PPL); 3 – *Discoaster anartios*, +3.25 m, PPL; 4 – *Discoaster multiradiatus*, +0.05 m, PPL. Scale bar for all PPL photos is 5 μm. 5 – *Bomolithus supremus*, −0.10 m, SEM; 6 – *Calcisolenia aperta*, −0.60 m, SEM

in Riben. However, the FOs of *Discoaster diastypus* and *D. kuepperi* at +3.25 m (R23) could serve as an approximation to trace the base of NP11 zone. The FO of *Discoaster lodoensis* at +4.00 m (R26) marks the base of NP12 zone. Several important bioevents were documented spanning the Paleocene-Eocene transition, they are plotted against $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope curves and CaCO_3 content curve (Fig. 2). The FOs of *Bomolithis supremus* (Fig. 3, 5) and *B. aquilus* lies at –2.00 m, just at the base of the CDI and the negative carbon excursion (CIE), marking the onset of PETM (Fig. 2). The LOs of *Calcisolenia aperta* and *Bomolithus supremus* at –0.10 m is followed by the FOs of *Rhomboaster calcitrata* (Fig. 3, 1–2) and *R. cuspidis* at +0.05 m. These events were recorded in the interval, where the $\delta^{13}\text{C}$ curve reaches its lowest values of PETM CIE negative excursion. The FOs and LOs of *Discoaster araneus* and *D. anartios* (Fig. 3, 3) – species considered worldwide as “CIE excursion taxa”, occurred at +2.00 m and at +3.00 m, respectively, higher up beyond the PETM interval, probably as a result of reworking (Fig. 2). The *Rhomboaster-Discoaster* assemblage is well-known to be characteristic of the PETM interval, but according to MENINI et al. [14], they can both be sporadically present well after the PETM.

In the upper part of the section, the successive FOs of *Discoaster diastypus*, *D. kuepperi* at +3.25 m and *D. lodoensis* at +4.00 m were recorded. Hidden hiatuses at the topmost NP9 and upper NP10 zones could not be excluded. In summary, the nannofossil biostratigraphy of the Riben section is broadly consistent with published shallow marine localities worldwide [14,15]. It is worth emphasizing that, when plotted against the isotope curves, nannofossil bioevents from different localities and settings show a certain degree of diachroneity, as evidenced by Menini et al. [14].

Lithology. The onset of the climatic event is lithologically marked by a drop of the carbonate content worldwide and deposition of Carbonate Dissolution Interval (CDI). In this study we document the first accurate carbonate content record, i.e. the variations of the carbonate content of the sediments across the PETM interval and within the Lower Eocene (Fig. 2). The obtained values (in %) for Riben section, samples R1-R30 are presented in Table 1 (numerically) and in Fig. 2 (graphically).

The CaCO_3 depletion starts in sample R4 (22.60% carbonate content) and is back to the pre-PETM values in sample R12 (48.6% carbonate content), reaching its lowest values between samples R6 to R8 (10.20% to 10.40%). That implies the PETM CDI in Riben section is evidenced between the samples R4 to R11, roughly from –2 m to –0.25 m just below the Paleocene-Eocene boundary (Fig. 2). Up section (R12-R22), the carbonate content fluctuates around 40% (between 51.4% and 34%). In the upper parts of the section (R23-R30) it declines again, with a minimum of 23.40% in sample R30.

The precise localization of the CDI, as well as the thorough revision of the existing and newly obtained nannofossil data proved to be of key importance for

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$\delta^{13}\text{C}$, $\delta^{18}\text{O}$ benth. forams, paleotemperature and carbonate content of the samples studied

# of sample	$\delta^{13}\text{C}$ benth. forams [‰]	$\delta^{18}\text{O}$ benth. forams [‰]	Paleotemperature of sea water [C]	Carbonate content [%]
R1	1.54	−4.26	30.88	45.60
R2	1.50	−3.59	27.59	24.20
R3	1.44	−4.70	33.10	9.80
R4	2.46	−2.87	24.20	22.60
R5	2.56	−2.65	23.18	13.00
R6	2.15	−2.72	23.50	10.20
R7	1.77	−3.21	25.78	10.80
R8	2.56	−2.95	24.57	10.40
R9	2.41	−2.73	23.55	14.00
R10	1.82	−2.81	23.92	12.00
R11	0.11	−5.21	35.73	41.20
R12	0.63	−3.35	26.45	48.60
R13	−0.43	−3.02	24.89	37.00
R14	−0.20	−4.06	29.88	41.80
R15	−0.05	−4.68	32.99	51.40
R16	0.28	−2.67	23.28	40.60
R17	−0.55	−3.16	25.55	34.00
R18	0.03	−5.07	35.00	45.00
R19	−0.51	−3.15	25.50	39.00
R20	0.06	−2.60	22.96	38.80
R21	−0.05	−3.54	27.35	40.00
R22	−0.08	−4.11	30.13	41.20
R23	−4.95	−5.72	38.43	39.40
R24	−0.23	−3.29	26.16	36.40
R25	0.65	−2.96	24.61	30.00
R26	0.27	−3.14	25.45	35.50
R27	—	—		33.20
R28	—	—		31.40
R29	—	—		27.60
R30	—	—		23.40

the reliable interpretation of the isotope curves and the correct identification of the hyperthermal events.

Benthic foraminifera stable isotope results. To definitely identify hyperthermal events in the early Eocene, paired high-resolution benthic stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are needed, since the most important characteristic of the hyperthermals is a paired negative excursion in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values [2]. Following this approach, we identified at least 3 paired negative excursions: two in the Paleocene within the PETM interval, upper NP9 zone, and one within the early Eocene, NP11 zone (Fig. 2, black arrows). Our new benthic $\delta^{13}\text{C}$ record shows an unusual two-fold negative excursion across the interval, corresponding to PETM: first, R4 to R7 (magnitude of 0.69‰), and, after quick returning to the initial values, a second – R8 to R13 (magnitude of 2.99‰). This means that the warming at Riben took place in two steps during the latest Paleocene (Fig. 2, Table 1).

The third paired negative excursion ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) is the most prominent one. It occurred at sample R23 (4.90‰ negative shift for $\delta^{13}\text{C}$ and 1.61‰ negative shift for $\delta^{18}\text{O}$, Fig. 2, Table 1). Nannofossil biostratigraphy anchors this excursion within NP11 zone, aged 53.67 to 52.64 Ma [17]. Therefore, given the currently available astronomically tuned ages of the early Eocene hyperthermals, and specifically the age of the ETM3 at 52.84 Ma [2], we suppose this prominent event corresponds to the Eocene Thermal Maximum 3 event (ETM3) or “X” event [18].

The surface seawater temperature [$^{\circ}\text{C}$] was calculated using $\delta^{18}\text{O}$ data. It ranges between 23.18 $^{\circ}\text{C}$ and 35.73 $^{\circ}\text{C}$ during the PETM event, reaching its highest values of 38.43 $^{\circ}\text{C}$ during the ETM3 (Table 1, Fig. 2).

We conclude that, given currently available benthic isotope record and nannofossil biostratigraphy, as well as specific shape of the $\delta^{13}\text{C}$ benthic isotope curve, hidden hiatuses at the topmost NP9 and upper NP10 zones could not be excluded. Thus, the newly obtained benthic stable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data and nannofossil biostratigraphy evidenced the expression of two separate early Eocene hyperthermal events: the PETM (= ETM1) and the ETM3 (= “X” event), recorded at Riben section.

Conclusions. These are the first lithologic, nannofossil biostratigraphic and benthic stable isotope records from the revisited Riben section, Bulgaria, providing a detailed framework on the expression of the early Eocene hyperthermal events, preceding the EECO. Our findings reveal the occurrence of NP9, NP10 and NP11 nannofossil zones, as well as the CIE and CDI in the latest Paleocene. The CDI, detected by the abrupt drop of CaCO_3 content and deposition of a clay interval, is closely related to the PETM global warming. Moreover, an unusual two-fold CIE in the PETM interval is documented (total negative shift of 2.89‰). Regional geological settings and sedimentation in shallow water environment favouring the hidden hiatuses, could explain this unusual CIE curve.

The most prominent CIE (negative shift of 4.90‰) is registered at the base

of NP11 zone. We hypothesize it may reflect the ETM3 or “X” event (52.84 Ma), as a paired negative $\delta^{18}\text{O}$ excursion occurs at the same level, too.

The seawater temperature fluctuates between 23.18 °C and 35.73 °C during the PETM, and reaches up to 38.43 °C during the ETM3, as inferred from the $\delta^{18}\text{O}$ records.

Our approach of integrating nannofossil biostratigraphy, benthic stable isotope data sets and lithology, unravel two separate early Eocene hyperthermal events: the PETM (= ETM1) and the ETM3 (= “X” event), recorded at Riben section.

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