Доклади на Българската академия на науките
Comptes rendus de l'Académie bulgare des Sciences

Tome 73, No 12, 2020

GEOLOGY
Event stratigraphy

FIRST DATA ON THE EXPRESSION OF THE CAMPANIAN-MAASTRICHTIAN BOUNDARY EVENT IN BULGARIA: CALCAREOUS NANNOFOSSIL AND CARBON ISOTOPE RECORD

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(*Submitted by Academician T. Nikolov on September 23, 2020*)

Abstract

We present the first combined calcareous nannofossil and stable isotope data (δ^{13}C and δ^{18}O) from the Kladorub section, NW Bulgaria, to study the local expression of the globally recognized Campanian-Maastrichtian Boundary Event (CMBE). Calcareous nannofossil study proves the completeness of the sedimentary succession, with zones UC15e^{TP} through UC20d^{TP} evidenced. The isotope data, derived from benthic foraminifera, show that the carbon isotope excursion (CIE) curve displays the well-known superimposed detailed structure of five small positive peaks (CMBE1 to CMBE5). The CMBE-CIE in the Bulgarian locality is characterized by a significant magnitude of 1.97‰, reaching its maximum value in CMBE1 (1.90‰), while the minimum value (–0.07‰) is in CMBE2. The Campanian-Maastrichtian boundary, drawn at the LO of the nannofossil species *Uniplanarius trifidus,* lies at the top of CMBE3. Two more neighbouring events, bracketing the CMBE – namely the Late Campanian (LCE) and the Middle Maastrichtian events (MME), are possibly also recorded in Bulgaria.

Key words: Campanian-Maastrichtian Boundary Event, calcareous nannofossils, carbon isotopes, NW Bulgaria

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This work has been carried out in the framework of the National Science Programme "Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters", supported by the Bulgarian Ministry of Education and Science (Agreements No D01-230/06.12.2018, D01-322/18.12.2019).

DOI:10.7546/CRABS.2020.12.11

Introduction. Much of the Late Cretaceous Epoch was characterized by an extreme greenhouse climate, followed by cooling in the latest Cretaceous ([1] and references therein). The transition of the Earth's system from the mid-Cretaceous greenhouse to the cooler Cenozoic climate happened stepwise, marked by a range of clear, globally expressed cooling events ([1] and references therein). The first of these events commenced in the late Campanian and lasted until the early Maastrichtian: the so-called Campanian-Maastrichtian Boundary Event (CMBE) [1].

The CMBE is a globally recognized, prominent negative carbon-isotope excursion that lasted ~ 2.5 Ma [1]. It has been recorded in shelf-sea settings and oceanic sites in the Pacific, Southern and south Atlantic oceans (e.g., [1–4]). This event is believed to reflect changes in the global carbon cycle and, respectively, to mark the most significant cooling of the Earth's climate at the end of the Cretaceous Period. The magnitude of the CMBE carbon-isotope excursion (CMBE-CIE) is highly variable and ranges from 0.3‰ to 0.5‰ (at Gubbio, Italy; Tercis-les-Bain, France; and Shahneshin, Iran) to values up to 1.0‰ at Kronsmoor (Germany), Stevns-1 (Denmark) and in the bottom-waters of Holes 690C (Maud Rise) and 525A (Walvis Ridge) [1–4]. Moreover, the CMBE-CIE displays a superimposed detailed structure consisting of five small-scale positive excursions, successively numbered as CMBE1 to CMBE5 [1]. Two of them, CMBE1 and CMBE4, are prominent peaks, whereas the peaks of CMBE2 and CMBE3 are not always distinctly developed in all sections and could be suppressed [1,4].

Late Cretaceous climate changes have not yet been studied in Bulgaria. The idea to focus on the CMBE and search for its expression in Bulgarian sections was prompted by the authors' knowledge [6,7] of the existence of a suitable continuous, relatively well-exposed upper Campanian–lower Eocene sedimentary succession near the village of Kladorub, NW Bulgaria (Fig. 1). At this locality, many global events have already been recorded, such as the K/T Boundary Event, Mid-Paleocene Biotic Event and the Paleocene-Eocene Thermal Maximum [5–7]. Thus, it represents a unique and complete geological archive of late Campanian–early Eocene times on Bulgarian territory. Also, the Kladorub section has recently been a subject of a thorough biostratigraphic study based on calcareous nannofossils [8] in the frame of a successfully completed PhD thesis and young researcher's project of GG.

In this study, we present an initial interpretation of our newly acquired geochemical data, obtained in the course of a targeted investigation of the variations of $\delta^{13}C$ and $\delta^{18}O$ values across the Campanian-Maastrichtian boundary at Kladorub. In terms of the biostratigraphic framework, we rely on the new detailed high-resolution calcareous nannofossil subdivision of the Kladorub section [8]. GG was responsible for applying the entire protocol of laboratory processing of samples for isotope geochemistry, as well as for elaborating a modern calcareous nannofossil biostratigraphy of the section. KS and GG were responsible for complex interpretation of the isotope curves and delineation of the carbon isotope events

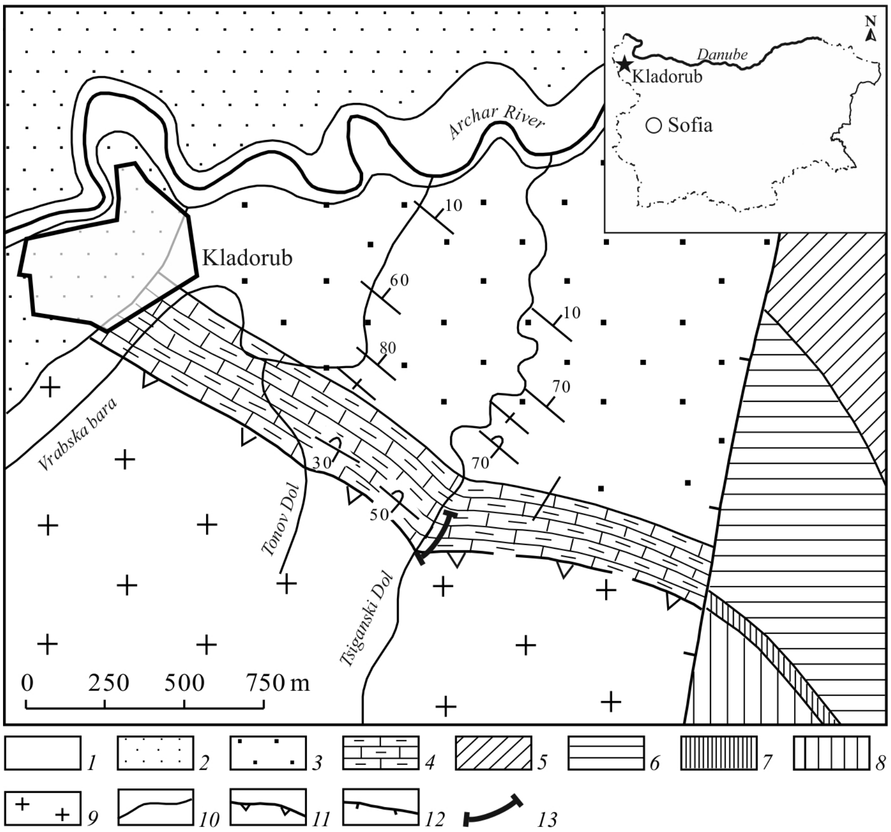

Fig. 1. Geological sketch map of the studied area (after [5]): 1 – Quaternary; 2 – Dimovo Fm.; 3 – Staropatitsa Fm.; 4 – Kladorub Fm.; 5 – Simeonovo Fm.; 6 – West Balkan Carbonate Group; 7 – Polaten Fm.; 8 – Kiper Fm.; 9 – Paleozoic granitoids; 10 – lithostratigraphic boundary; 11 – reverse fault; 12 – normal fault; 13 – studied section

in relation to the recorded nannofossil bio-horizons in the late Campanian–early Maastrichtian interval. CU performed the stable isotope analyses.

Geological setting. The Kladorub section is situated in the western periphery of the Moesian Platform [9]. In terms of tectonics, its location falls in the Kula tectonic unit, which is regarded as a part (extension) of the South Carpathian orogenic system [10]. The succession crops out along the Tsiganski Dol Valley, located ∼ 2.5 km to the southeast of Kladorub Village (Fig. 1; N43°42″30″; E22°39′44″). Here, to the southwest of the exposure, the granodiorites of the Belogradchik pluton (Paleozoic in age) are thrust over the upper Campanian part of the Kladorub Formation. The sedimentary succession is tectonically overturned [5], dipping to the SSW at a low angle (15°–45°) [8]. However, in some intervals, the beds dip steeply to sub-vertically [8]. The section is characterized by continuous sedimentation from the late Campanian to the earliest Ypresian [6], with five intervals of non-exposure in the Upper Cretaceous part (1–10 m; 23–33.5 m; 48.5–54.5 m; 59–61 m; 115.5–122 m; Fig. 2). Lithologically, the succession comprises grey to grey-greenish indistinctly- to medium-bedded silty to fine-sandy marlstones of the Kladorub Formation, occasionally interbedded with thin to medium-thick marly limestones and sandstones [8]. Slump structures occur in the Maastrichtian part of the studied section, ranging in thickness from 1 m to 3 m [8] (Fig. 2). In the present study, only the upper Campanian–Maastrichtian portion of the succession (lowermost 123 m) was investigated.

Material and methods. A total of 164 samples, taken at 0.5-m sampling resolution, have been investigated for their nannofossil and stable isotope content (δ^{13}C and δ^{18}O, Fig. 2). Nannofossils were studied in simple smear-slides, prepared following a standard methodology [11]. They were viewed at 1250× magnification, using an oil-immersion objective lens (×100) on a Zeiss Axioskop 40 microscope equipped with a ProgRes GT3 digital camera. Relative abundances of the species were estimated semi-quantitatively and a qualitative estimate of nannofossil preservation for each sample was also made (see [8] and supplementary data therein for complete dataset). Burnett's [12] UC zonal scheme, as supplemented by Thibault [13], was applied for biostratigraphic subdivision and for pinpointing the main nannofossil datum-levels in the section: first occurrences (FOs), last occurrences (LOs), last consistent occurrences (LCOs). All smear-slides are stored at the Department of Paleontology, Stratigraphy and Sedimentology, Geological Institute of the Bulgarian Academy of Sciences.

Carbon and oxygen stable isotope analyses. Stable isotope analyses were carried out on hand-picked benthic-foraminiferal tests. Benthic foraminifera were isolated from the rock, following the methodology described by Stancheva [14]. The analyses were performed at the University of Exeter, Camborne School of Mines and Environment and Sustainability Institute, Penryn, UK. Measurements were done using a Sercon 20–22 gas source isotope ratio mass spectrometer in continuous flow mode, using in-house reference material CAR (Carrara Marble; δ^{13}C = +2.10‰ V-PDB; δ^{18}O = −2.03‰ V-PDB) and NCA (Namibia Carbonatite, δ^{13}C = −5.63‰ V-PDB; δ^{18}O = −21.90‰ V-PDB). These standards were taken to monitor instrumental bias, drift and precision and ensure accuracy of determined isotope ratios. Reproducibility of the analyses (2 s.d.) for the year when the analyses were carried out was 0.07‰ for δ^{13}C and 0.15‰ for δ^{18}O based on 917 measurements of CAR. All isotopic values are reported in the standard δ-notation in per mil relative to V-PDB.

Results and discussion. ***Calcareous nannofossils.*** The recorded FOs and LOs of key nannofossil markers are illustrated in Fig. 2. The co-occurrence of *Uniplanarius trifidus* (Fig. 3a) and *Eiffellithus eximius* (Fig. 3b) in the lowermost part of the section indicates the presence of subzone UC15d^{TP}. Up-section, key nannofossil events were documented and used to recognize UC15e^{TP}, UC16a^{TP}, UC16b^{TP}, UC17, UC18, UC19 and UC20a–d^{TP}. They include (in stratigraphic

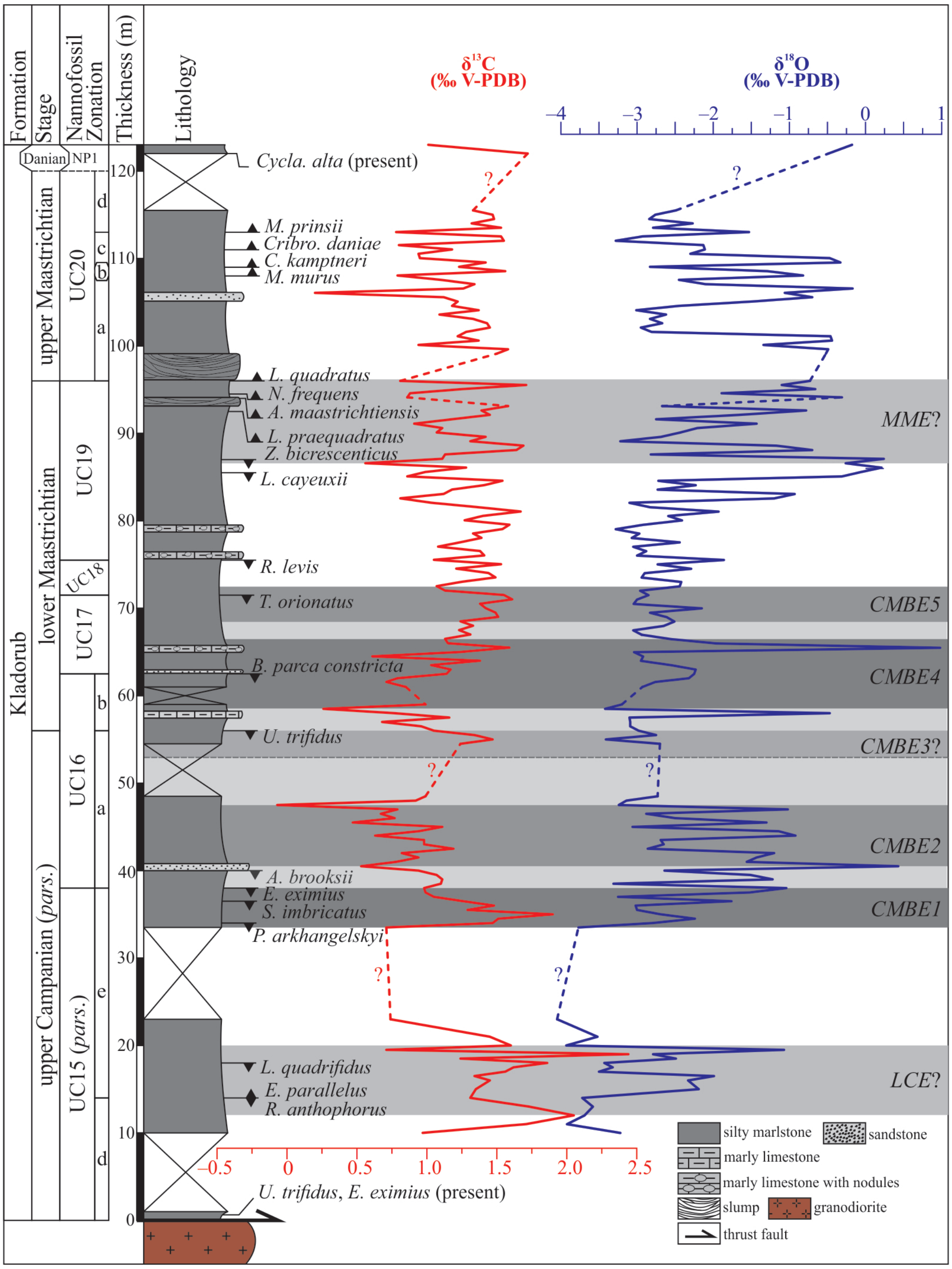

Fig. 2. Integrated nannofossil biostratigraphy (after [8]) and δ^{13}C and δ^{18}O isotope records, derived from benthic foraminifera of the Kladorub section

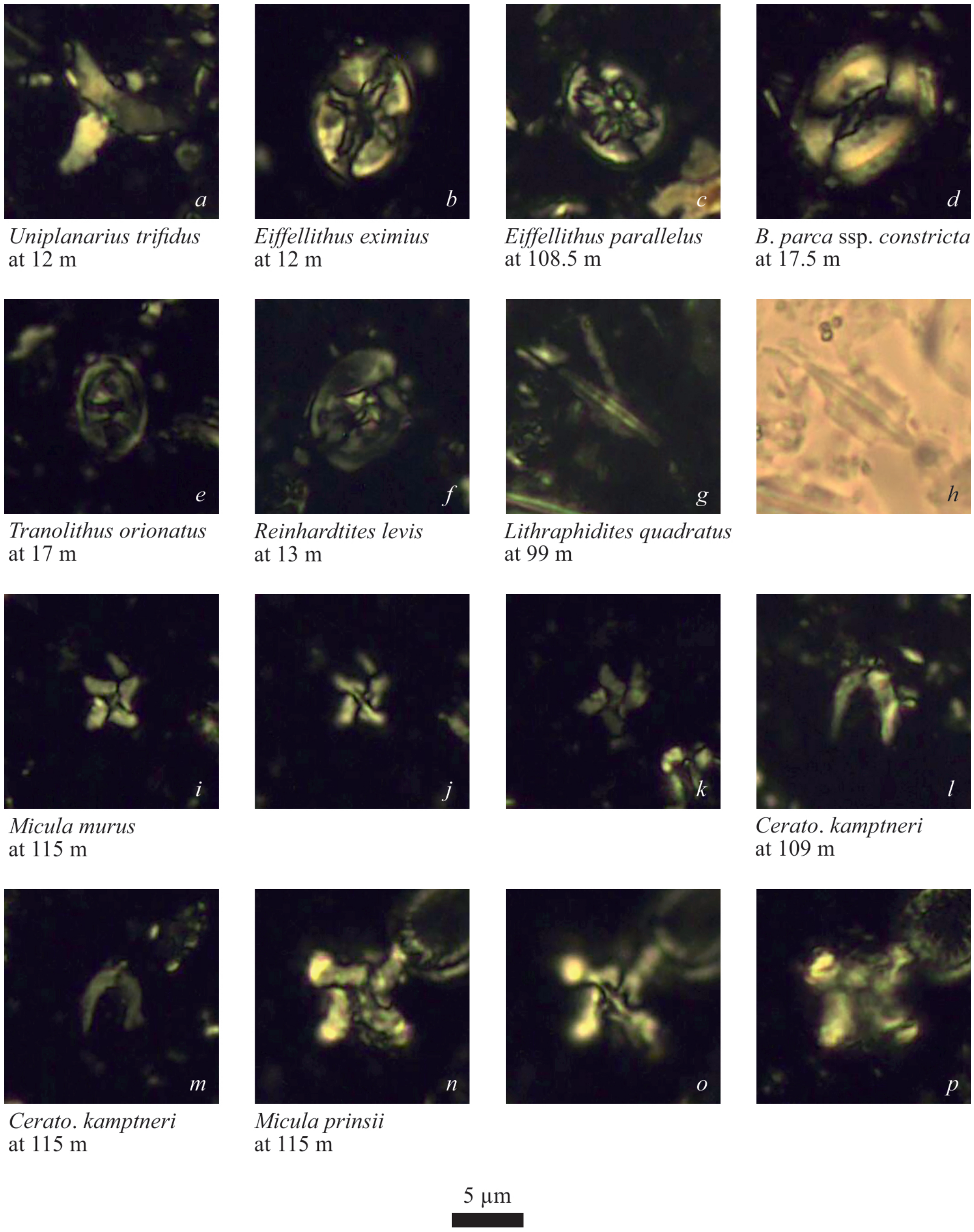

Fig. 3. Stratigraphically significant calcareous nannofossil species from the upper Campanian–Maastrichtian in the Kladorub section. Images were taken in cross-polarized (a–g, i–p) and plane-polarized light (h). Scale bar is the same for all images

order): the FO of *E. parallelus* (Fig. 3c) at 14 m; the LCO of *E. eximius* at 38 m; the LCO of *U. trifidus* at 56 m; the LCO of *Broinsonia parca constricta* (Fig. 3d) at 62 m; the LCO of *Tranolithus orionatus* (Fig. 3e) at 71.50 m; the LCO of *Reinhardtites levis* (Fig. 3f) at 75.50 m; the FO of *Lithraphidites quadratus* (Fig. 3g, h) at 96 m; the FO of *Micula murus* (Fig. 3i–k) at 108 m; the FO of *Ceratolithoides kamptneri* (Fig. 3l, m) at 109 m; and the FO of *Micula prinsii* (Fig. 3n–p) at 113 m (Fig. 2). Biostratigraphically, the CMBE-CIE extends roughly between the LOs of *E. eximius* and *T. orionatus*, i.e., from the uppermost part of UC15e^{TP} to the basal part of UC 18 (Fig. 2). Within the CMBE interval, the LOs of the markers *U. trifidus* and *B. parca constricta* occur, as shown by many recent studies [1,4,15,16]. The LO of *U. trifidus* has been acknowledged as one of the best nannofossil biohorizons for approximating the Campanian-Maastrichtian boundary [13]. We use the abovementioned biostratigraphic events to delineate, subdivide and interpret the successive stages of the CMBE at Kladorub.

Carbon and oxygen isotope geochemistry. The obtained δ^{13}C and δ^{18}O values are plotted against detailed litho-, bio- and chronostratigraphy of the Kladorub section (Fig. 2). Carbon and oxygen isotope co-variation is weak, raising confidence that primary environmental information is retained in the foraminiferal tests at least for the carbon isotope ratios. The acquired carbon and oxygen isotope curves are precisely juxtaposed against the elaborated anchors, i.e. key nannofossil events, in order to decipher and characterize the local expression of the CMBE. At this stage of the study, we can convincingly interpret only the δ^{13}C isotope curve, which happens to be more informative about the CMBE. Furthermore, our carbon isotope data show that the initial cooling event preceding the CMBE, namely the Late Campanian Event (LCE) [17], may also be recorded at the base of the studied section. In the upper Campanian, between 12.00 m and 20.00 m, a distinct negative δ^{13}C excursion is developed, with values shifting from 2.05‰ to 0.74‰ (Fig. 2, Table 1). Possibly, it represents the LCE, because it lies above the FO of *U. trifidus*, exactly as evidenced in many land exposed sections elsewhere (see [1,4] and references therein).

As already mentioned, the CMBE is manifested by a prominent negative carbon isotope excursion (CMBE-CIE), spanning the Campanian-Maastrichtian boundary interval. Superimposed on this negative trend, five minor positive excursions occur, designated by Voigt et al. [1] as CMBE1 to CMBE5.

CMBE1, whose maximum marks the onset of the CMBE-CIE, is situated between 33.50 m and 38.00 m, in the uppermost Campanian (Fig. 2, Table 1). It displays a sharp positive excursion with δ^{13}C values increasing from 0.71‰ to 1.90‰. The next one, CMBE2, is detected between 40.50 m and 47.50 m. It is characterized by a positive excursion with strong double peak and a smaller third one, with values increasing from 0.53‰ to 1.19‰. Peak CMBE2 lies at the interval of major δ^{13}C decrease of the CMBE, and the minimum value reached is −0.07‰ at 47.50 m. The precise location of CMBE3 is obscured by a small

Table 1

Main δ^{13}C events recorded in the upper Campanian–Maastrichtian interval in the Kladorub section

Carbon Isotope Event	Base (m)	Top (m)	Stratigraphic interval	Description
MME? [1]	86.50	96.00	lower Maastrichtian	Positive excursion of 1.15‰ in 3 steps, oscillating from 0.56‰ to 1.71‰
CMBE5 [1]	68.50	72.50	lower Maastrichtian	Positive excursion of 0.46‰, with values increasing from 1.15‰ to 1.61‰
CMBE4 [1]	58.50	66.00	lowermost Maastrichtian	Prominent positive excursion of 1.33‰, with values increasing from 0.26‰ to 1.59‰
CMBE3? [1]	54.50	56.00	uppermost Campanian	Small positive excursion of 0.23‰, with values shifting from 1.24‰ to 1.47‰
CMBE2 [1]	40.50	47.50	uppermost Campanian	Prominent positive excursion of 0.66‰, with values increasing from 0.53‰ to 1.19‰
CMBE1 [1]	33.50	38.00	uppermost Campanian	Prominent positive excursion of 1.19‰ with values increasing from 0.71‰ to 1.90‰
LCE? [17]	12.00	20.00	upper Campanian	Negative excursion of 1.34‰, with values shifting from 2.05‰ to 0.71‰

interval of non-exposure between 48.50 m and 54.50 m, thus its isotope record may be incomplete. Nevertheless, CMBE3 probably occurred between 54.50 m and 56.00 m, represented by a weak positive excursion of 0.23‰, with values shifting from 1.24‰ to 1.47‰ (Fig. 2, Table 1). CMBE4 is a well-expressed, prominent positive excursion of 1.33‰, with values increasing from 0.26‰ to 1.59‰. It is distinguished between 58.50 m and 66.00 m in the lowermost Maastrichtian, directly overlying the Campanian-Maastrichtian boundary. Lastly, CMBE5 shows a positive excursion of 0.46‰, with values increasing from 1.15‰ to 1.61‰ (Fig. 2, Table 1). Voigt et al. [1] speculated that the five small-scale positive excursions of CMBE-CIE appear as cyclic 400–500 kyr-long variations during the long-term δ^{13}C decrease and may record orbitally forced changes in the global carbon cycle. In the upper part of the section, between 86.50 m and 96.00 m, another positive excursion of 1.15‰ occurs. It is in three steps, oscillating from 0.56‰ to 1.71‰. Given its stratigraphic position and long-term trend, it may represent the Middle Maastrichtian warming event (MME; Fig. 2, Table 1).

Remarkably, the measured δ^{13}C values for the entirety of the CMBE-CIE at Kladorub show a more prominent magnitude of 1.97‰ (maximum value in CMBE1 of 1.90‰, minimum value in CMBE2 of −0.07‰) than reported elsewhere. One possible explanation for this difference may be the source material used for the isotope measurements, i.e. benthic foraminifera as opposed to bulk rock samples, although the exact reasons are yet to be explained.

Discussion. It is important to follow some key nannofossil datum-levels at Kladorub and pinpoint their relative stratigraphic position to the recognized carbon isotope events. The LO of *E. eximius* at Kladorub is recorded at the top of CMBE1 (Fig. 2). In the eastern Tethyan Shahneshin section, it occurs within LCE, well before the onset of the CMBE [4]. In other locations, it falls either below or in the lower part of CMBE. This datum has been proved diachronous and unreliable marker at all latitudes, straddling an interval of about 3 Myr (see [1] and references therein). The LO of *U. trifidus,* the next important datum level at Kladorub, is documented at the top of CMBE3 (Fig. 2). Exactly in the same position – at the top of CMBE3, it has been recorded at ODP 1210B [1]. At low latitudes, the LO of *U. trifidus* lies in CMBE4 at the South Atlantic Site 525A, between CMBE3 and CMBE4 at Gubbio and Tercis-les-Bains [1], and between CMBE1 and CMBE4 at Shahneshin [4]. Therefore, this biohorizon appears to be a useful tool for searching the CMBE in low- to mid-latitude successions. The LO of *B. parca constricta* lies within CMBE4 at Kladorub (Fig. 2). The numerous records from other locations suggest that this biohorizon usually lies within the upper half of CMBE. It is recorded within CMBE3 at 1210B, between CMBE4 and CMBE5 at Tercis-les-Bains, in CMBE5 at Gubbio, between CMBE4 and CMBE5 at Kronsmoor, below the top of CMBE5 at Stevns-1, and in CMBE5 at Shahneshin [1,3,4]. The LO of *T. orionatus* lies in CMBE5 at Kladorub (Fig. 2), similarly to Kronsmoor, Gubbio and Shahneshin [1,4]. This datum level also appears to be a relatively reliable marker.

Conclusions. The Campanian-Maastrichtian Boundary Event, marking the first significant global climatic cooling in the Late Cretaceous, has been documented in Bulgaria for the first time. Detailed calcareous nannofossil study of the upper Campanian–Maastrichtian interval of the Kladorub section, SW Bulgaria, proves the completeness of the sedimentary succession, with zones UC15e^{TP} through UC20d^{TP} having been recognized, and provides a firm stratigraphic background for the stable isotope geochemical investigation. Our isotope data, derived from benthic foraminifera, convincingly show that the CMBE-CIE curve displays the well-known superimposed detailed structure of five small positive stages (CMBE1 to CMBE5). The maximum of CMBE1 marks the onset of the CMBE-CIE, while CMBE2 lies in the minimum trough of the CMBE. It is worth noting that the CMBE-CIE in the Bulgarian locality is characterized by a significant magnitude of 1.97‰, reaching its maximum value in CMBE1 (1.90‰), while the minimum value (−0.07‰) is in CMBE2. The Campanian-Maastrichtian boundary, drawn at the LO of the nannofossil species *Uniplanarius trifidus*, lies at the top of CMBE3. Two more neighbouring events bracketing the CMBE, namely the Late Campanian (LCE) and the Middle Maastrichtian events (MME), are possibly also recorded.

Acknowledgements. Dr Valeri Sachanski (Geological Institute, BAS) is warmly thanked for his kind assistance during the fieldwork.

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