

Short communication

Slight carbon-isotope perturbation at the J/K boundary (base of the *Calpionella* Zone) – A proxy tool for correlation? A brief summary

Martin Košťák ^{a,*}, Daniela Reháková ^b, Lucie Vaňková ^{a,c}, Martin Mazuch ^a, Jakub Trubač ^d, Rastislav Milovský ^e

^a Institute of Geology and Paleontology, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

^b Department of Geology and Palaeontology, Comenius University in Bratislava, Ilkovičova 6, SK-842 15, Bratislava, Slovak Republic

^c Institute of Geology of the Czech Academy of Sciences, Rozvojová 269, 165 00 Praha 6, Czech Republic

^d Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

^e Earth Science Institute, Slovak Academy of Sciences, Banská Bystrica, Dúmbierska 1, Slovak Republic

ARTICLE INFO

Article history:

Received 10 January 2023

Received in revised form

19 May 2023

Accepted in revised form 5 June 2023

Available online 10 June 2023

Keywords:

Tithonian–Berriasiyan transition
Carbon stable isotopes
Calpionellids

ABSTRACT

Stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) data from bulk rock in the Jurassic–Cretaceous transition are characterised by stability of values in many Tethyan carbonate sections, predominantly those laid down under deeper-water marine conditions. The generally straight trend in the $\delta^{13}\text{C}_{\text{carb}}$ curve at the J/K boundary interval does not show any significant value expressions that are useful for interregional correlation. However, in several bio- and magnetostratigraphically well-calibrated sections that have been studied, especially in the Carpathian–Alpine terrain (and some additional sections elsewhere in Tethys), a very slight carbon isotopic negative excursion directly at the J/K boundary (*sensu* base of the *Calpionella* Zone/*Alpina* Subzone) shows an almost identical trend. We assume it represents a rather weak geochemical marker at the Tithonian/Berriasiyan boundary which, nevertheless, may be identified as a useful tool for stratigraphic correlation.

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1. Introduction

In the past ten years, very intensive and very extensive multidisciplinary studies have been finalised by the Berriasiyan Working Group (BWG), resulting in a proposal for the Global Boundary Stratotype Section and Point (GSSP) for the Berriasiyan Stage (and thus the entire Cretaceous system) (Wimbledon et al., 2020a, 2020b). This step was supported by robust bio-, magneto- and chemostratigraphical data. The decision was founded on a formal vote of the BWG, that endorsed the consensus of the previous twenty years, that the base of the *Calpionella alpina* Subzone was by far the best marker for the stage base – a marker that is more widespread and consistent than any formerly preferred ammonite taxon. However, the expression of the calpionellid eco-morphotype probably does not fit to the conception of the boundary between systems.

Although the bio- and magnetostratigraphy provided relevant correlatable data, the chemostratigraphy (based predominantly on stable isotope $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values) did not play such an important role in the identification of the J/K boundary level.

The carbon and oxygen stable isotope record of the J/K boundary interval has been investigated by many authors in numerous sections (e.g. Weissert and Channell, 1989; Weissert and Erba, 2004; Grabowski et al., 2010a, 2017, 2019; Michalík and Reháková, 2011; Price et al., 2013, 2016; Michalík et al., 2021; and others).

The generally straight trend in the $\delta^{13}\text{C}_{\text{carb}}$ curve in the boundary interval (base of *Alpina* Subzone, Wimbledon et al., 2020a) does not show any significant value expressions useful for interregional correlation (Ogg and Hinnov, 2012; Cramer and Jarvis, 2020). However, a very slight, but recognisable, negative carbon isotopic excursion occurs close to the J/K boundary (*Crassicollaria/Calpionella* Zones boundary; magnetozone M19n2n). It shows an almost identical trend in northern Tethys (Michalík et al., 2009; Košťák et al., 2018; Grabowski et al., 2019; Michalík et al., 2021, and references therein). Slight $\delta^{13}\text{C}_{\text{carb}}$ isochronous perturbations at the base of the *Alpina* Subzone probably reflect smaller changes in the oligotrophic system and may be related to the predominance of

* Corresponding author.

E-mail addresses: martin.kostak@natur.cuni.cz (M. Košťák), daniela.rehakova@uniba.sk (D. Reháková), luke.vankova@natur.cuni.cz, vankoval@gli.cas.cz (L. Vaňková), martin.mazuch@natur.cuni.cz (M. Mazuch), jakub.trubac@natur.cuni.cz (J. Trubac), milovsky@savb.sk (R. Milovský).

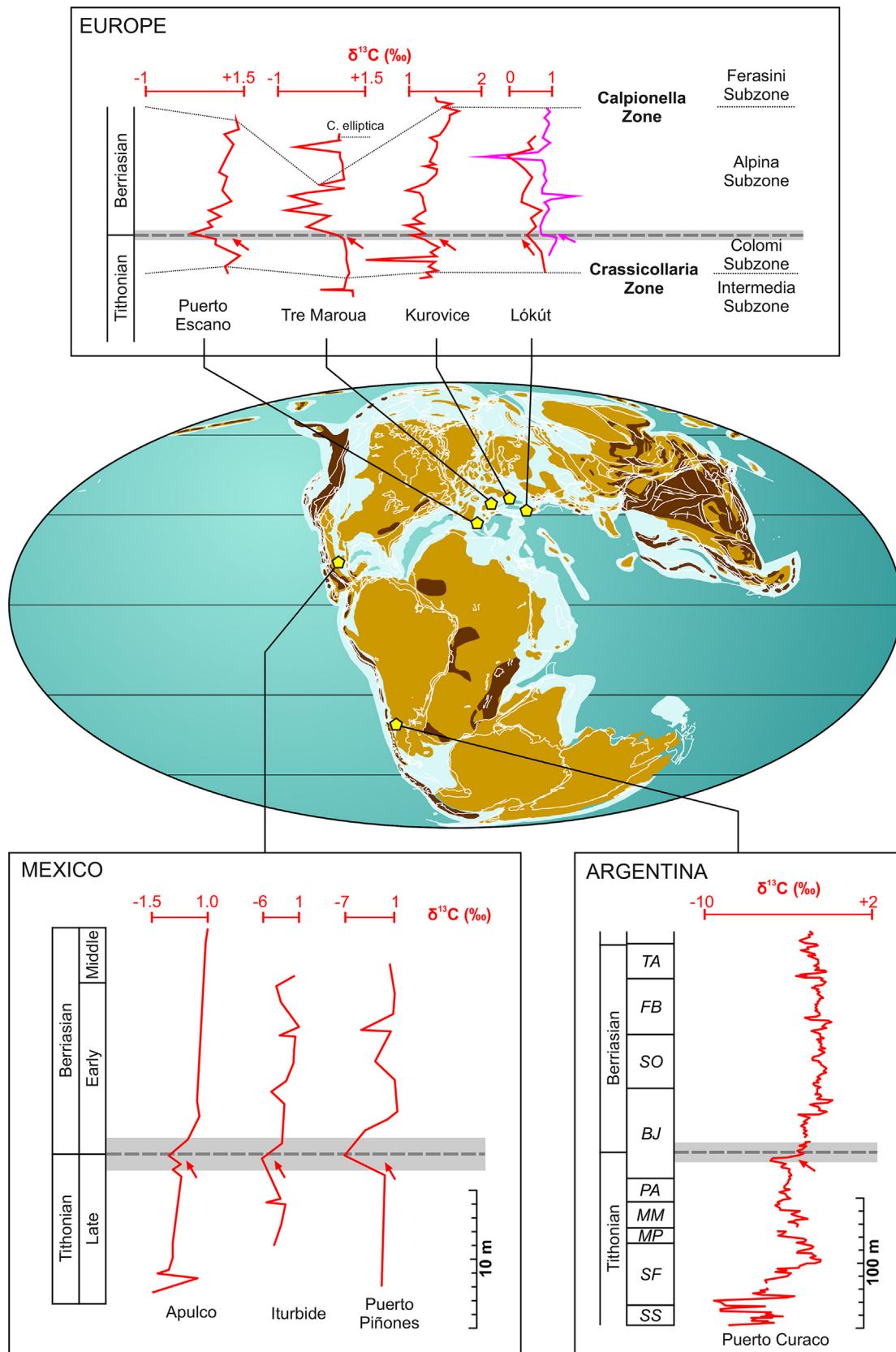


Fig. 1. Palaeogeographic distribution of selected localities (areas) with a negative shift (red arrows) of the $\delta^{13}\text{C}_{\text{carb}}$ (‰) values: Europe – Puerto Escano (Žák et al., 2011); Tré Maroua (Wimbledon et al., 2020b), Kurovice (Košťák et al., 2018; this paper); Lókút (red/left curve – Grabowski et al., 2017; violet/right curve – Price et al., 2016) – all sections represent

smaller globular forms of *Calpionella alpina* among the calpionellid association (Kowal-Kasprzyk and Reháková, 2019), following a bloom of nannofossils, mainly nannoconids (Bornemann et al., 2003; Tremolada et al., 2006).

As noted by Košťák et al. (2018), this slight decrease in the $\delta^{13}\text{C}$ values at the base of the *Alpina* Subzone may have potential for global geochemical correlations (Wimbledon et al., 2020a). This assumption has recently been supported by a large synthesis (Michalík et al., 2021) for Carpathian sedimentary sequences. Published data from Mexico (Adatte et al., 1996; Barragán et al., 2020) show hopeful potential for transatlantic correlation, and new data from the Neuquén Basin (Kietzmann et al., 2021; Blanco et al., 2022) extend this possibility to South America (Proto-Pacific/Panthalassa).

Hereby, we present the possibility of interregional and intercontinental correlation based on combination of calpionellid and chemostratigraphic methods. The Kurovice section (Outer Western Carpathians; Czech Republic) is compared to other Tethyan sections and the possibility of the Trans-Atlantic correlations with Mexican and Argentinian (Proto-Pacific/Panthalassa) sections is briefly discussed.

2. Methods

The bulk carbonate ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) stable isotope compositions from Kurovice section (completely presented herein, all data in ‰ VPDB) were analysed in the stable isotope and organic geochemistry lab of the Earth Science Institute at the Slovak Academy of Sciences, Banská Bystrica (Slovakia). All samples (60–200 mg) used for the stable isotope analysis were carefully taken from a diagenetically unaltered homogenous micritic component of the limestone; bioclasts, calcitic veins, and others were excluded. Samples showing signs of recrystallisation and cement content were also excluded from the analysis. For detailed laboratory equipment and methodology, see Košťák et al. (2018); published data therein concerned the upper part of the section. All samples were taken from the same levels (average distances ~10–15 cm) as those used for the palaeomagnetic and micropalaeontological analyses, which are not included in this paper.

The TOC analyses were also provided for the Tré Maroua section (Laboratories of the Geological Institutes, Faculty of Science, Charles University). The methodologies and section description of Kurovice and Tré Maroua are given in the original publications (Elbra et al., 2018; Wimbledon et al., 2020a).

3. Results

The high resolution sampling in Kurovice provided relevant data for correlation and interpretations in a wider context. The interval between M21r (dinoflagellate cyst *Malmica* Zone) and upper part of M21n zones (dinoflagellate cyst *Semiradiata* Zone) is characterised by large fluctuations in oxygen values (ranging from -4.8 ‰ to -0.5 ‰; this phenomenon may probably be linked diagenesis and/or the flysch-like character of sedimentation in this part of the section) and by a positive trend within carbon values (approximately from 0.0 ‰ to 0.8 ‰). Therefore, a diagenetic overprint in $\delta^{18}\text{O}_{\text{carb}}$ cannot be, however, excluded as suggested by the significant correlation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values ($r \sim 0.66$). The isotopic data from this part are not such relevant (not representing J/K boundary

interval and highly probable diagenetic overprint in $\delta^{18}\text{O}_{\text{carb}}$) and are not used in our interpretations. From Beds 20–21 (lower part of magnetozone M20r) a prominent negative shift is seen in $\delta^{18}\text{O}_{\text{carb}}$ values (from -1.2 ‰ in Bed 19 to -2.2 ‰ in Bed 23 and to almost 3 ‰ in Beds 28–29) and a slight positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values (from 0.6 ‰ VPDB to 1 ‰). From the base of *Tenuis-Fortis* Zone to the base of Remanei Subzone, the trend is characterised by marked positive expressions of oxygen (from -4.82 ‰ VPDB, Bed 38T to -1.77 ‰ VPDB, Bed 44 in $\delta^{18}\text{O}_{\text{carb}}$) and variations in carbon values (from 0.09 ‰ VPDB, bed 37T to 0.98 ‰ VPDB, Bed 45 in $\delta^{13}\text{C}_{\text{carb}}$). This part covers an interval below and at the base of the Kysuca magnetic Subzone.

In the upper part of M20n1n (prior to M19r), a negative shift in $\delta^{13}\text{C}_{\text{carb}}$ (of about 0.5 ‰) is well distinguishable and it may represent a potential for further correlation (see below). The interval between Beds 65–73 coincides with either positive (up to -2.0 ‰) or negative (-3.4 ‰) variations in $\delta^{18}\text{O}_{\text{carb}}$ values and with an almost straight carbon curve. Slight negative shift (magnitude of about 0.5–0.6 ‰) in $\delta^{13}\text{C}_{\text{carb}}$ values typical for the J/K boundary transition is recorded at base of Alpina Subzone. Upwards, the positive trends of oxygen and carbon values continue to the bed 147 (lower M17r Zone, *Elliptica* subzone), where a negative shift in both values are observed. The negative carbon excursion in this level may also represent a potential for correlation (see chapter 4.1. below). All stable isotope data in relation to beds are given in the Supplementary Table 1.

4. Discussion

4.1. Isochroneity of the base of the Alpina Subzone – or causality in relation to bioproductivity?

The $\delta^{13}\text{C}$ values in marine carbonates result from the $^{13}\text{C}/^{12}\text{C}$ ratio of dissolved inorganic carbon. However, the isotopic composition is also linked to the activity of autotrophic organisms (photosynthesis) and bacterial oxidation of organic matter, affecting the $\delta^{13}\text{C}$ content (CO_2) in the surface water (Scholle and Arthur, 1980; Schobben et al., 2017; Al-Mojel et al., 2018; Chen et al., 2022). It has been widely suggested that variation in $\delta^{13}\text{C}_{\text{carb}}$ reflects the initial seawater signal in both cases – regional and global.

The $\delta^{13}\text{C}_{\text{carb}}$ fluctuation has recently been correlated against distribution and quantity of microplankton in the Carpathian system in great detail (Michalík et al., 2021), providing relevant information about the behaviour of the stable isotopic data versus microfossil associations. The bloom/predominance of smaller globular *C. alpina* at the base of the *Alpina* Subzone ("Calpionella event"; Michalík et al., 2021) is followed by a very slight positive trend for $\delta^{18}\text{O}_{\text{carb}}$ recorded at Kurovice, Velykyi Kamianets and Brodno and characterised by a negative shift in $\delta^{13}\text{C}_{\text{carb}}$ values (Figs. 1–3). The latter may indicate a decrease in bioproductivity (and subsequent burial of organic matter) at the base of the *Calpionella* Zone (*Alpina* Subzone). However, upwards (but still within the lower *Calpionella* Zone), an opposite trend – that is, a positive shift in $\delta^{13}\text{C}_{\text{carb}}$ values – is observed, suggesting a return to previous palaeoceanographic conditions (Žák et al., 2011; Košťák et al., 2018; Michalík et al., 2021, and references therein).

Generally, calpionellids preferred rather nutrient-poor environments corresponding to the oligotrophic system (Reháková, 1998; Michalík et al., 2009; linked also to nannofossil

Crassicollaria/Calpionella zones boundary (J/K) transition in carbonates at different environments. Mexico (adopted and improved from Barragán et al., 2020): while the $\delta^{13}\text{C}_{\text{carb}}$ values at Apulco show similarity to those in Europe, values at Iturbide and Puerto Piñones sections are significantly more negative, this phenomenon is linked to a local accumulations of organic matter buried (see the text). Argentina, Neuquén Basin, Puerto Curaco (adopted and improved from Blanco et al., 2022): The $\delta^{13}\text{C}_{\text{carb}}$ variations with a negative peak located closely to the J/K boundary (see the discussion in the text). Palaeogeographical map modified after Golonka (2011). Ammonite zones: TA = *T. alpiliensis*; FB = *F. boissieri*; SO = *S. occitanica*; BJ = *B. jacobi*; PA = *P. andreae*; MM = *M. microcanthum*; MP = *M. ponti/B. peroni*; SF = *S. fallauxi*; SS = *S. semiforme* (Blanco et al., 2022).

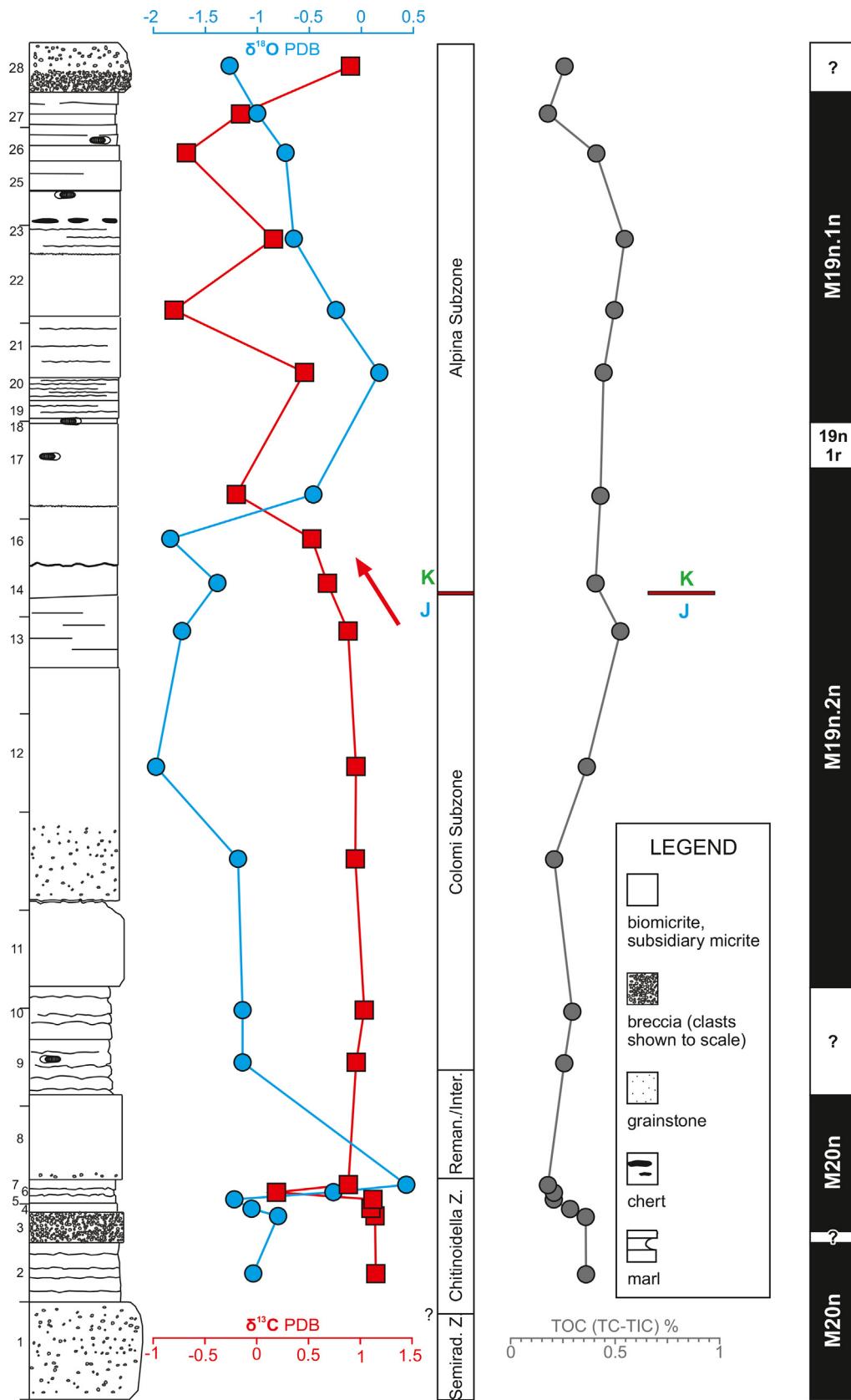


Fig. 2. Stable isotope ($\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, ‰) data from formerly suggested candidate GSSP section Tré Maroua (Wimbledon et al., 2020b; Grabowski et al., 2022a; MK unpublished data). The negative shift of $\delta^{13}\text{C}_{\text{carb}}$ values at the J/K boundary is indicated by red arrow. The TOC content shows almost minimum variation in carbonates at Tré Maroua (this paper) across the J/K boundary (respectively *Crassicollaria/Calpionella* zones boundary) reflecting a very limited potential of organic carbon for stratigraphic correlations in this interval.

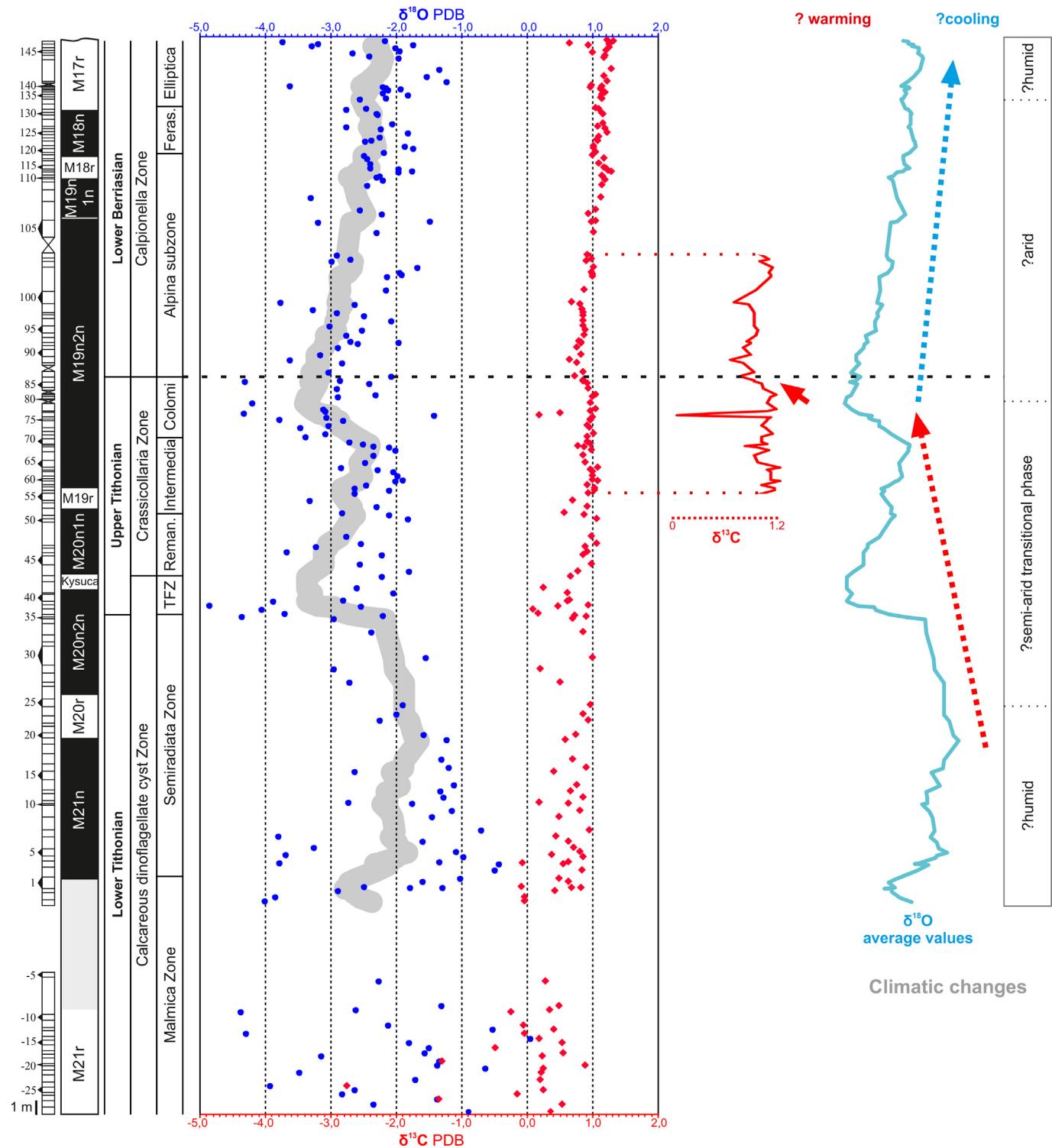


Fig. 3. Stable isotope data ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ from bulk rock, ‰ VPDB) from the entire Kurovice section (this paper; Košťák et al., 2018) in relation to magnetostratigraphy, calpionellid and dinoflagellate cyst biostratigraphy (Elbra et al., 2018). The J/K boundary interval (Crassicollaria/Calpionella zones boundary) falls into the suggested arid/aridification phase sensu Price et al. (2016); Grabowski et al. (2019) and Michalík et al. (2021). A long-term of ?warming trend starting from upper M21n magnetozone (lower Tithonian; with a positive shift of $\delta^{18}\text{O}_{\text{carb}}$ values in the uppermost parts of the M20n2n through the lower part of M19n2n magnetozones). The peak of ?warming slightly precedes the J/K boundary. Upwards, it changes into a long term positive trend of $\delta^{18}\text{O}_{\text{carb}}$ values (?cooling) probably resulting to humidification (sensu Michalík et al., 2021) in the M17r magnetozone. The negative peak of $\delta^{13}\text{C}_{\text{carb}}$ values (red arrow) is highlighted by enlarged scale of values (%), see also Fig. 1. Calpionellid subzones: Reman. – Remanei Subzone; Ferass. – Ferassini; dinoflagellate cyst zonation: TFZ – *Tenuis-Fortis* Zone. The grey and blue smoothed curves are created by data extrapolation.

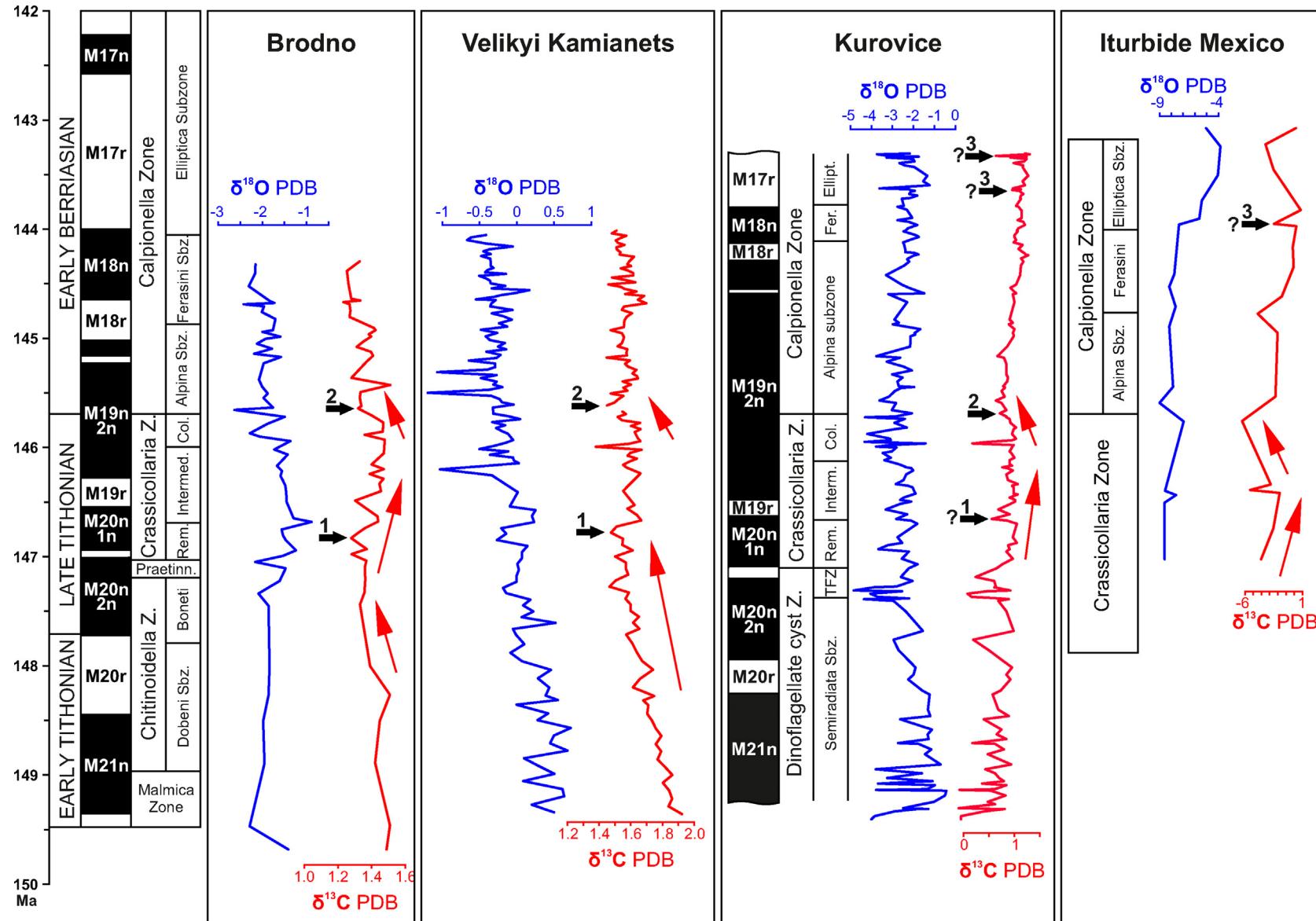


Fig. 4. Comparison of stable isotope data ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ from bulk rock, ‰ VPDB): Brodno (Slovakia) and Velikyi Kamianets (Ukraine) after Michalík et al. (2021, and references therein), Kurovice (this paper) and Iturbide (Mexico; Barragán et al., 2020). Calpionellid subzones: Col – Colomi Subzone; Rem – Remaniella Subzone; dinoflagellate cyst zonation: TFZ – Tenius-Fortis Zone. Numbers 1–3 with arrows: negative shifts of Michalík et al. (2021). Arrows in carbon curves mark positive and negative trends.

distribution, Erba, 1994). Their higher diversity is linked to higher stands of sea level. The opposite trend – the occurrence of mono-specific association of smaller globular *C. alpina* at the J/K boundary – may reflect a sea-level fall (Kowal-Kasprzyk and Reháková, 2019; Ölveczká and Reháková, 2022). This phenomenon is also associated with the radiation and rise in abundance of nannoconids (Tremolada et al., 2006; Michálík et al., 2016). The isochroneity of the base of the *Alpina* Subzone is confirmed by numerous publications (summarised by Wimbleton et al., 2020a). The predominance resulting almost in a monoassociation of smaller *C. alpina*, and a slight negative shift in $\delta^{13}\text{C}_{\text{carb}}$ values may represent a causality in relation to bioproductivity and palaeoceanographic changes – e.g. salinity variations, water masses stratification, nutrient depletion, climatic factors, pCO_2 , etc., Michálík et al. (2009).

Stable isotope data ($\delta^{13}\text{C}_{\text{carb}}$) directly from the J/K transition of numerous sections show a consistent record, respective trend – e.g. negative shift in carbon values (and an opposite, positive shift in $\delta^{18}\text{O}_{\text{carb}}$ values) within the NW Tethys, Central Atlantic (Tethyan – Mexico; Adatte et al., 1996; Barragán et al., 2020) and South-east Pacific (Panthalassa) and are, therefore, correlatable with the global $\delta^{13}\text{C}$ stack (Figs. 1–4).

In Mexican localities (palaeoceanographically linked to the NW Tethys), several sections show a negative shift of carbon values around the J/K boundary – e.g. Iturbide (Fig. 4), Peregrina Canyon, Puerto Piñones and Sierra Jabali (Adatte et al., 1996). In the latter mentioned section, however, the prominent negative peak is documented just above the boundary.

Comparing longer trends in carbon stable isotope record prior to the J/K boundary, we could see some differences between Mexican and European Tethyan sections (Fig. 4) and published data from Argentina. In European Tethyan sections (Carpathians and Transdanubian Mts), a predominantly increasing trend in $\delta^{13}\text{C}_{\text{carb}}$ values is observed (Price et al., 2016; Michálík et al., 2021), while the sections from Western Hemisphere show not so uniform patterns (in Apulco, the carbon values are slightly increasing in the Tithonian; Puerto Piñones shows almost straight but very slightly positive trend; at the Iturbide section, the $\delta^{13}\text{C}_{\text{carb}}$ values increases and then decreases, Fig. 4). In this respect, the Kurovice section (belonging to Carpathian system) partly resembles some Mexican localities (cf. Adatte et al., 1996; Barragán et al., 2020, fig. 5 therein). The lower part of Kurovice section (M21r – lower part of M20n1n) shows clear positive trend (in average, increasing from 0.5 ‰ to 1 ‰). Negative carbon excursions are recorded in the upper part/top of M20n2n (with decrease values of almost 1.0 ‰) and in the M20n1n (lower part of the *Crassicollaria* Zone), decrease of values of about 0.5 ‰ (from ca 1.0 ‰ to 0.5 ‰). The latter mentioned excursion is assumed herein (with question mark) to be an equivalent of the “negative shift 1” sensu Michálík et al. (2021).

From the base of M19r (middle *Crassicollaria* Zone), the very slight positive trend in Kurovice (from the middle/upper part of the *Intermedia* Zone; magnitude of about 0.1 to 0.2 ‰) is almost identical with that seen in Brodno and Velikiy Kamianets (Fig. 4), as well as in numerous other sections (see above). The very slightly positive trend is followed by the “negative shift 2” of Michálík et al. (2021, fig. 9). Upwards (in the lower part of Alpina Subzone, just below the bed 100 in Kurovice), the positive trend starts (from 0.8. to 1.3 ‰ in M17r – *Elliptica* Subzone). Within the lowermost to lower parts of M17r, there are two negative carbon excursions (Fig. 4) which may correspond to the “negative shift 3” recorded in the section Strapková (Michálík et al., 2021; fig. 9; not figured herein). At approximately the same level, a negative shift in values is also reported from Mexico, Iturbide section (Fig. 4) and Puerto Piñones (Barragán et al., 2020, fig 5). The calibrations of these peaks, however, will need further detailed investigations.

Still, no important excursions of the $\delta^{13}\text{C}_{\text{org}}$ from limestones in NW Tethys (including the Mediterranean part) were detected (Grabowski et al., 2022b). The content of organic matter buried in pelagic limestones is accessory reaching values up to 0.5% TOC (TC-TIC; Tré Maroua – Fig. 2). Generally, in northern Tethys, the TOC documents only minor organic matter variations in carbonate sections (for example Brodno – up to about 0.35%; Michálík et al., 2009), and they are not a subject of discussion. However, the marl to marly-limestone intercalations within limestone developments in some sections require further investigation, especially in relation to the “VOICE” event (prior to the J/K boundary recognised herein). This marked $\delta^{13}\text{C}_{\text{org}}$ expression has been recorded only at higher latitudes (Galloway et al., 2020), but recently also in the Southern Hemisphere – the Neuquén Basin (Weger et al., 2022) – and may represent a possible new marker near the J/K boundary, allowing correlation between boreal regions and Tethys (Grabowski et al., 2022b).

4.2. Climatic aspects

It is worth mentioning that oxygen isotopes are not fully accepted as palaeotemperature markers due to a relatively common diagenetic changes. We cannot exclude diagenetical processes in Kurovice section. Carbon isotopes are generally more resistant to diagenetic alteration than oxygen isotopes (Anderson and Arthur, 1983; Paul et al., 1999; Cramer and Jarvis, 2020). We assume that the obtained curves keep primary signal in carbon isotope record, however the oxygen isotopes are more sensitive to alteration during carbonate diagenesis. It is well seen in the lower part of Kurovice section where we assume also stronger diagenetical changes. In closely spaced samples, we observed unrealistically extreme variations (reaching 4.5 ‰ at dinoflagellate cyst *Malmica* Zone, Fig. 3) and we do not use these data for interpretations. However, from the lower dinoflagellate cyst *Semiradiata* Zone upwards, these variations (with two exceptions – base of M21n and uppermost part of M20n2n – dinoflagellate cyst *Tenuis-Fortis* Zone, Fig. 3) are lesser, showing similarities to other Tethyan sections. Therefore, we conclude also a possible role of palaeoclimatic signal (Bodin et al., 2009).

Although the $\delta^{13}\text{C}_{\text{carb}}$ negative shift at the base of Alpina Subzone may be linked to a major microplankton bloom, the $\delta^{18}\text{O}_{\text{carb}}$ excursions may be related to climatic changes at the J/K boundary (Michálík et al., 2021). An increase in bulk rock $\delta^{18}\text{O}_{\text{carb}}$ values may represent a slight cooling trends through the studied sequences (Fig. 3 – between M20n2n and lowermost M19n2n and between the J/K boundary and M17r). This interpretation, however, only partly corresponds with data from Tethys (i.e. Brodno section) and partly to higher latitudes (boreal-Arctic) – such as $\delta^{18}\text{O}_{\text{bel}}$ values (Žák et al., 2011; Zakharov et al., 2014; e.g. -cooling trend between M20n1r and the base of M19n). Therefore, long-term trends in variations of $\delta^{18}\text{O}_{\text{carb}}$ values at the Kurovice section (Fig. 3) will need to be clarified in the future using additional methods.

Michálík et al. (2021) interpreted equal stratigraphical intervals as periods of aridification or as the semi-arid transitional phase in the climate mode sensu Grabowski et al. (2019). The rhythms of arid/humid variations are well recognised especially in the Sub-Boreal basins (Polish Basin) based on-marine (Grabowski et al., 2021; Blażejowski et al., 2022) and also in non-marine strata (Schneider et al., 2018) in the J/K interval. It is notable, that these interpretations are based on carbonate content increase, clay minerals and detrital input decrease input (Grabowski et al., 2019). The general trend within the Tithonian climate in the Carpathians was from a humid period in the lower Tithonian (M21n magnetozone, dinoflagellate cyst *Malmica* Zone), the beginning of aridification in the middle part of the M20r leading to an arid period from

the lower part of the M19n2n (*Crassicollaria* Zone, upper part of *Intermedia* Subzone, linked also to the onset of *Nannoconus*), and a return to humid conditions, possibly located within M17r (Michalík et al., 2021). This climatic interpretation follows the assumptions of Price et al. (2016) and Michalík et al. (2021) and has also been recently adopted for the Kurovice section herein (Fig. 3), where the peak of the warming trend seems to culminate just prior to the J/K boundary, high in the *Crassicollaria* Zone in the *Colomi* Subzone (Fig. 3). However, this assumption needs to be discussed in more detail.

The sedimentation of Kurovice limestones is assumed to lay between aragonitic and calcitic compensation depths (Košťák et al., 2018), therefore, in a deeper setting which was a less subjected to perturbations in salinity and temperature. In this respect, we assume diagenetical affections in some parts of the section, e.g. intervals where we have recorded rather extreme variations (see above).

4.3. Implications for global correlation? Pros and cons

We assume the predominance of the monospecific association of smaller globular forms of *C. alpina*, as well as the accompanying negative shift in $\delta^{13}\text{C}_{\text{carb}}$ values, to be isochronous within the Tethys Ocean in different facies/environments (Fig. 1). For instance, Puerto Escaño represents the environment at the Subbetic Cordillera plateau (Pruner et al., 2010), the Kurovice sequence shows the strong influence of allodapic limestone slumps deposited on lower slopes (Košťák et al., 2018), Tré Maroua is considered to have been deposited in the upper to middle slope environment (Wimbledon et al., 2020b) and Lókút is regarded as a transitional sedimentary space between a deep pelagic basin and a shallower plateau (Grabowski et al., 2010b, 2017). Similar or identical trends of stable isotope curves have been observed in other sites (and in different environments) – Brodno, Hlboča and Strapková (Michalík et al., 2009, 2016; Grabowski et al., 2010a), Borzavár (Szives et al., 2022), Frisoni (Weissert and Channell, 1989) and Velykyi Kamianets (Grabowski et al., 2019), among numerous studied sections.

The newly presented data from South America – the Neuquén Basin (Kietzmann et al., 2021; Blanco et al., 2022; Weger et al., 2022) – represent the promising possibility of further stratigraphical correlation. A significant negative peak in the $\delta^{13}\text{C}_{\text{carb}}$ values is well expressed at the Sierra de la Yaca Muerta (MCD) Neuquén section (periplatform environment) at the Tithonian/Berriasian boundary (Blanco et al., 2022). These authors have used another Neuquén section (Puerto Curaco) for correlations with the Tethyan area and found negative double peaks prior to the J/K boundary (Blanco et al., 2022; Fig. 6). However, the stratigraphical column presented therein is based on Tethyan ammonites, which have somewhat limited potential in this interval (Wimbledon et al., 2020a). On the other hand, the magnetostratigraphic scale clearly documents the position of the upper peak, approximately in the middle part of the M19n magnetozone (lower part of *Berriasella jacobi* Zone). The exact position of the ammonite zonation in this area has recently been summarised by Weger et al. (2022), suggesting the Tithonian/Berriasian boundary in the lower part of the *S. koeneni* Zone, within magnetozone M19n2n (Weger et al., 2022 – fig. 3 therein). When compared to the recently published data of Kietzmann et al. (2021), this boundary falls in the middle part of the M19n, where the *Crassicollaria*/*Calpionella* zones boundary is also established, in the Arroyo Loncoche section (Kietzmann et al., 2021; Fig. 4), that is, close to the J/K boundary, as in the classical sections of Tethys. It is notable that values ($\delta^{13}\text{C}_{\text{carb}}$ in ‰) are significantly different than those in the Tethyan.

However, the negative shift in $\delta^{13}\text{C}_{\text{carb}}$ values is rather small at the J/K boundary interval, and it is recorded sometimes only using

high density sampling. It is notable that the J/K boundary transition in northern Tethys is characterised by extremely low fluctuations in $\delta^{13}\text{C}_{\text{carb}}$ values, and this may also be linked to regional features. Therefore, the recognition of the $\delta^{13}\text{C}_{\text{carb}}$ peak in sections must always be calibrated and confirmed by the application of the stable calpionellid record (and also by calcareous nannofossils and magnetostratigraphic calibration).

5. Conclusions: useful marker for the boundary correlation? Yes, but ...

Tethyan carbonates are generally poor $\delta^{13}\text{C}_{\text{org}}$ reservoirs and $\delta^{13}\text{C}_{\text{carb}}$ values in the J/K boundary interval show extremely small variations.

A negative shift in the $\delta^{13}\text{C}_{\text{carb}}$ values is a slight geochemical marker at the Tithonian/Berriasian boundary, the boundary between the *Crassicollaria* and *Calpionella* zones. Stable isotope data from the J/K transition from selected localities including also former candidate stratotype sections for the boundary show a consistent record, as do other Tethyan (including Mexico) and Argentinian (Proto-Pacific) localities within the global $\delta^{13}\text{C}$ ‘stack’. In this respect, the $\delta^{13}\text{C}_{\text{carb}}$ curve, in combination with calpionellid stratigraphy, represents a useful tool for stratigraphic correlation.

The J/K boundary is also based on the predominance of the ecomorphotype of smaller, globular *C. alpina*. This “Alpina event” is accompanied by a negative shift in $\delta^{13}\text{C}_{\text{carb}}$ values. However, the geochemical signal is relatively weak and we recognise that it does not generally permit its use as proxy for the base of the *Alpina* Subzone. The identification of this $\delta^{13}\text{C}_{\text{carb}}$ excursion is strongly dependent on the presence of a relevant calpionellid record. Calpionellids dominated especially in the predominant deeper-water environments, though they are rarer in shallow-water and reef deposits (Kowal-Kasprzyk and Reháková, 2019; Vaňková et al., 2019). Therefore, the coincidence of the $\delta^{13}\text{C}_{\text{carb}}$ excursion with the onset of predominant small globular *C. alpina* may not be recorded in such settings.

Based on detailed investigation of Kurovice section, we present stratigraphical stability of the “negative shift 2” sensu Michalík et al. (2021). The “negative shifts 1 and 3” are reported from Kurovice with question marks. All three carbon negative shifts are hopeful markers for the further investigations. In this point, we assume Kurovice locality to be suitable reference section for interregional and intercontinental correlations.

Author statement

This summary is predominantly based on published data (partly ours) and completed by new data from two key localities: Tré Maroua (TOC) and Kurovice (stable isotope record from the entire section), both suggested formerly as a candidate GSSP section (Wimbledon et al., 2020a,b).

Acknowledgements

We are sincerely thankful to reviewers J. Grabowski, and two anonymous reviewers for important comments and valuable suggestions which significantly raised quality of the manuscript. Eduardo Koutsoukos is greatly acknowledged for editorial work.

This research is supported by Czech Science Foundation (GAČR) No. 20-10035S and Slovak Research and Development Agency (APVV), project APVV-20-0079 and VEGA 2/0012/20. MK, LV, MM and JT thank also to project COOPERATIO (Faculty of Science, Charles University) and project UNCE/SCI/006 (LV). The study fits in the concept of the research plan of the Institute of Geology of the Czech Academy of Science (No. RVO 67985831).

References

- Adatte, T., Stinnesbeck, W., Remane, J., Hubberten, H., 1996. Paleoceanographic changes at the Jurassic – Cretaceous boundary in the Western Tethys, northeastern Mexico. *Cretaceous Research* 17, 671–689.
- Al-Mojel, A., Dera, G., Razin, P., Le Nindre, Y.-M., 2018. Carbon and oxygen isotope stratigraphy of Jurassic platform carbonates from Saudi Arabia: implications for diagenesis, correlations and global paleoenvironmental changes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 511, 388–402.
- Anderson, T.F., Arthur, M.A., 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and palaeoenvironmental problems (Chapter 1). In: Arthur, M.A., Anderson, T.F., Kaplan, I.R., Veizer, J., Land, L.S. (Eds.), *Stable Isotopes in Sedimentary Geology*. Society of Economic Paleontologists and Mineralogists Short Course, 10. Society of Economic Paleontologists and Mineralogists, Tulsa, pp. 1–151.
- Barragán, R., López-Martínez, R., Chávez-Vergara, B., Núñez-Useche, F., Salgado-Garrido, H., Merino, A., 2020. Geochemical variations across the Jurassic/Cretaceous boundary in central Mexico. Insights for correlation with Tethyan areas. *Journal of South American Earth Sciences* 99, 102521.
- Blanco, L.R., Swart, P.K., Eberli, G.P., Weger, R.J., 2022. Negative $\delta^{13}\text{C}_{\text{carb}}$ values at the Jurassic-Cretaceous boundary – Vaca Muerta Formation, Neuquén Basin, Argentina. *Palaeogeography, Palaeoclimatology, Palaeoecology* 603, 111208.
- Błażejowski, B., Pszczołkowski, A., Grabowski, J., Wierzbowski, H., Deconinck, J.-F., Olempska, E., Teodorski, A., Nawrocki, J., 2022. Integrated stratigraphy and clay mineralogy of the Owiadów-Brzezinki section (Lower-Upper Tithonian transition, Central Poland): implications for correlations between the Boreal and the Tethyan domains and palaeoclimate. *Journal of the Geological Society* 180, <https://doi.org/10.1144/jgs2022-073>.
- Bodin, S., Fiet, N., Godet, A., Matera, V., Westermann, S., Clément, A., Janssen, N.M.M., Stille, P., Föllmi, K.B., 2009. Early Cretaceous (late Berriasian to early Aptian) palaeoceanographic change along the northwestern Tethyan margin (Vocontian Trough, southeastern France): $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Sr-isotope belemnite and whole-rock records. *Cretaceous Research* 30, 1247–1262.
- Bornemann, A., Aschner, U., Mutterlose, J., 2003. The impact of calcareous nannofossils on the pelagic carbonate accumulation across the Jurassic-Cretaceous boundary. *Palaeogeography, Palaeoclimatology, Palaeoecology* 199, 187–228.
- Chen, M., Conroy, J.L., Geyman, E.C., Sanford, R.A., Chee-Sanford, J.C., Connor, L.M., 2022. Stable carbon isotope values of syndepositional carbonate spherules and micrite record spatial and temporal changes in photosynthesis intensity. *Geobiology* 20 (5), 667–689. <https://doi.org/10.1111/gbi.12509>.
- Cramer, B.S., Jarvis, I., 2020. Carbon isotope stratigraphy. In: Gradstein, F., Ogg, J.G., Schmitz, M.D., Ogg, G.M. (Eds.), *The Geologic Time Scale 2020*. Elsevier, Amsterdam, pp. 309–343.
- Elbra, T., Bubík, M., Reháková, D., Schnabl, P., Čížková, K., Pruner, P., Kdýr, Š., Svobodová, A., Švábenická, L., 2018. Magneto- and biostratigraphy across the Jurassic-Cretaceous boundary in the Kurovice section, Western Carpathians, Czech Republic. *Cretaceous Research* 89, 211–223.
- Erba, E., 1994. Nannofoossils and superplumes: the early Aptian "nannoconid crisis". *Paleoceanography* 9, 483–501.
- Golonka, J., 2011. Chapter 6 Phanerozoic palaeoenvironment and palaeolithofacies maps of the Arctic region. *Geological Society, London, Memoirs* 35 (1), 79–129. <https://doi.org/10.1144/M35.6>.
- Galloway, J.M., Vickers, M.L., Price, G.D., Poulton, T., Grasby, S.E., Hadlari, T., Beauchamp, B., Sulphur, K., 2020. Finding the VOICE: organic carbon isotope chemostratigraphy of Late Jurassic–Early Cretaceous Arctic Canada. *Geological Magazine* 157 (10), 1643–1657. <https://doi.org/10.1017/s0016756819001316>.
- Grabowski, J., Michálík, J., Pszczołkowski, A., Lintnerová, O., 2010a. Magneto-, and isotope stratigraphy around the Jurassic/Cretaceous boundary in the Vysoká Unit (Malé Karpaty Mountains, Slovakia): correlations and tectonic implications. *Geologica Carpathica* 61 (4), 309–326.
- Grabowski, J., Haas, J., Marton, E., Pszczołkowski, A., 2010b. Magneto- and biostratigraphy of the Jurassic/Cretaceous boundary in the Lókut section (Transdanubian Range, Hungary). *Studia Geophysica et Geodaetica* 54, 1–26.
- Grabowski, J., Haas, J., Stoykova, K., Wierzbowski, H., Branski, P., 2017. Environmental changes around the Jurassic/Cretaceous transition: new nannofoossil, chemostratigraphic and stable isotope data from the Lokút section (Transdanubian Range, Hungary). *Sedimentary Geology* 360, 54–72.
- Grabowski, J., Bakhmutov, V., Kdýr, Š., Krobicki, M., Pruner, P., Reháková, D., Schnabl, P., Stoykova, K., Wierzbowski, H., 2019. Integrated stratigraphy and palaeoenvironmental interpretation of the Upper Kimmeridgian to Lower Berriasian pelagic sequences of the Velykyi Kamianets section (Pieniny Klippen Belt, Ukraine). *Palaeogeography, Palaeoclimatology, Palaeoecology* 532, 109216.
- Grabowski, J., Chmielewski, A., Płoch, I., Rogov, M., Smoleń, J., Wójcik-Taboi, P., Leszczyński, K., Maj-Szeliga, K., 2021. Palaeoclimate changes and inter-regional correlations in the Jurassic/Cretaceous boundary interval of the Polish Basin: portable XRF and magnetic susceptibility study. *Newsletters on Stratigraphy* 54, 123–158.
- Grabowski, J., Frau, C., Schnabl, P., Svobodová, A., 2022a. Magnetic susceptibility and gamma ray spectrometry in the Tré Maroua section (Tithonian/Berriasian, SE France) – terrigenous input and comparison with Tethyan record. *Volumina Jurassica* XX, 47–58. <https://doi.org/10.7306/VJ.20.2>.
- Grabowski, J., Aguirre-Urreta, M.B., Deconinck, J.F., Erba, E., Frau, C., Li, Gang, Martinez, M., Mutterlose, J., Price, G., Reháková, D., Schmitz, M., Schnabl, P., Szives, O., Wierzbowski, A., 2022b. Recent progress in defining the Tithonian/Berrisaian and Jurassic/Cretaceous boundaries. In: Jagt, J.W.M., Jagt-Jazykova, E., Walaszczyk, I., Źlińska, A. (Eds.), *Abstract Volume, 11th Cretaceous Symposium*, August 22–26, Warsaw, Poland, 2022.
- Kietzmann, D.A., Llanos, M.P.I., Tomassini, F.G., Noguera, I.J., Vallejo, D., Reijenstein, H., 2021. Upper Jurassic-Lower Cretaceous calpionellid zones in the Neuquén Basin (Southern Andes, Argentina): correlation with ammonite zones and biostratigraphic synthesis. *Cretaceous Research* 127, 104950.
- Košťák, M., Vanková, L., Mazuch, M., Bubík, M., Reháková, D., 2018. Cephalopods, small vertebrate fauna and stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) record from the Jurassic-Cretaceous transition (uppermost Crassicollaria through Calpionella Zones) of the Outer Western Carpathians, Kurovice quarry (Czechia). *Cretaceous Research* 92, 43–65.
- Kowal-Kasprzyk, J., Reháková, D., 2019. A morphometric analysis of loricae of the genus *Calpionella* and its significance for the Jurassic/Cretaceous boundary interpretation. *Newsletters on Stratigraphy* 52, 33–54.
- Michálík, J., Reháková, D., 2011. Possible markers of the Jurassic/Cretaceous boundary in the Mediterranean Tethys: a review and state of art. *Geoscience Frontiers* 2 (4), 475–490.
- Michálík, J., Reháková, D., Halászová, E., Lintnerová, O., 2009. The Brodno section – a potential regional stratotype of the Jurassic/Cretaceous boundary (Western Carpathians). *Geologica Carpathica* 60 (3), 213–232.
- Michálík, J., Reháková, D., Grabowski, J., Lintnerová, O., Svobodová, A., Schlögl, J., Sobien, K., Schnabl, P., 2016. Stratigraphy, plankton communities, and magnetic proxies at the Jurassic/Cretaceous boundary in the Pieniny Klippen Belt (Western Carpathians, Slovakia). *Geologica Carpathica* 67 (4), 303–328.
- Michálík, J., Grabowski, J., Lintnerová, O., Reháková, D., Kdýr, Š., Schnabl, P., 2021. Jurassic – Cretaceous boundary record in Carpathian sedimentary sequences. *Cretaceous Research* 118, 104659.
- Ogg, J.G., Hinnov, L.A., 2012. Chapters 26–27 – Jurassic, Cretaceous. In: Gradstein, F., Ogg, J., Schmitz, M., Ogg, G. (Eds.), *The Geologic Time Scale 2012*. Elsevier, Amsterdam, pp. 731–853.
- Ölveczká, D., Reháková, D., 2022. Upper Tithonian Crassicollaria Zone: new data on the calpionellid distribution and subzonal division of the Pieniny Klippen Belt in Western Carpathians. *Acta Geologica Slovaca* 14 (1), 37–56.
- Paul, C.R.C., Lamolda, M.A., Mitchell, S.F., Vaziri, M.R., Gorostidi, A., Marshall, J.D., 1999. The Cenomanian–Turonian boundary at Eastbourne (Sussex, UK): a proposed European reference section. *Palaeogeography, Palaeoclimatology, Palaeoecology* 150 (1), 83–121.
- Price, G.D., Twitchett, R.J., Wheeley, J.R., Buono, G., 2013. Isotopic evidence for long term warmth in the Mesozoic. *Scientific Reports* 3, 1438. <https://doi.org/10.1038/srep01438>.
- Price, G.D., Fózy, I., Pálfy, J., 2016. Carbon cycle history through the Jurassic–Cretaceous boundary: a new global $\delta^{13}\text{C}$ stack. *Palaeogeography, Palaeoclimatology, Palaeoecology* 451, 46–61.
- Pruner, P., Housá, V., Olóriz, F., Košťák, M., Krs, M., Man, O., Schnabl, P., Venhodová, D., Tavera, J.M., Mazuch, M., 2010. High-resolution magnetostratigraphy and biostratigraphic zonation of the Jurassic/Cretaceous boundary strata in the Puerto Escaño section (S Spain). *Cretaceous Research* 31 (2), 192–206.
- Reháková, D., 1998. Calpionellid genus *Remaniella* Catalano 1956 in Lower Cretaceous pelagic deposits of Western Carpathians. *Mineralia Slovaca* 30, 443–452.
- Schneider, A.C., Heimhofer, U., Heunisch, C., Mutterlose, J., 2018. The Jurassic–Cretaceous boundary interval in non-marine strata of northwest Europe – new light on an old problem. *Cretaceous Research* 87, 42–54.
- Scholle, P.A., Arthur, M.A., 1980. Carbon isotope fluctuations in Cretaceous pelagic limestones: potential stratigraphic and petroleum exploration tool. *American Association of Petroleum Geologists Bulletin* 64 (1), 67–87.
- Schobben, M., van de Velde, S., Gliwa, J., Leda, L., Korn, D., Struck, U., Ullmann, C.V., Hairapetian, V., Ghaderi, A., Korte, C., Newton, R.J., Poulton, S.W., Wignall, P.B., 2017. Latest Permian carbonate carbon isotope variability traces heterogeneous organic carbon accumulation and authigenic carbonate formation. *Climate of the Past* 13, 1635–1659.
- Szives, O., Łodowski, D.G., Grabowski, J., Vörös, A., Balázs, S., Price, G., Fózy, I., 2022. The Jurassic/Cretaceous transition in the Bakony Mountains. In: Fózy, I. (Ed.), *Late Jurassic–Early Cretaceous fauna, biostratigraphy and paleotectonic evolution in the Bakony Mountains, Transdanubian Range, Hungary*. Institute of Geosciences, University of Szeged, Geolitera Publishing House, pp. 111–137.
- Tremolada, F., Bornemann, A., Bralower, T.J., Koeberl, C., van de Schootbrugge, B., 2006. Paleoceanographic changes across the Jurassic/Cretaceous boundary: the calcareous phytoplankton response. *Earth and Planetary Scientific Letters* 241, 361–371.
- Vaňková, L., Elbra, T., Pruner, P., Vašíček, Z., Skupien, P., Reháková, D., Schnabl, P., Košťák, M., Švábenická, L., Svobodová, A., Bubík, M., 2019. Integrated stratigraphy and palaeoenvironment of the Berriasian peri-reef limestones at Stramberk (Outer Western Carpathians, Czech Republic). *Palaeogeography, Palaeoclimatology, Palaeoecology* 532, 109256.
- Weger, R.J., Eberli, G.P., Blanco, L.R., Tenaglia, M., Peter, K., Swart, P.K., 2022. Finding a VOICE in the Southern Hemisphere: a new record of global organic carbon? *GSA Bulletin* 2022. <https://doi.org/10.1130/B36405.1>.
- Weissert, H., Channell, J.E.T., 1989. Tethyan carbonate carbon isotope stratigraphy across the Jurassic-Cretaceous boundary: an indicator of decelerated global carbon cycling? *Paleoceanography* 4 (4), 483–494.
- Weissert, H., Erba, E., 2004. Volcanism, CO_2 and palaeoclimate: a late Jurassic-Early Cretaceous carbon and oxygen isotope record. *Journal of the Geological Society, London* 161 (4), 695–702.

- Wimbledon, W.A.P., Reháková, D., Svobodová, A., Elbra, T., Schnabl, P., Pruner, P., Šifnerová, K., Kdýr, Š., Dzyuba, O.S., Schnyder, J., Galbrun, B., Košťák, M., Vaňková, L., Copestake, P., Hunt, C., Riccardi, A., Poulton, T.P., Bulot, L.G., Frau, C., de Lena, L., 2020a. Proposal of Tre Maroua as the GSSP for the Berriasian Stage (Cretaceous System), made on behalf of the Berriasian Working Group of the International Subcommission on Cretaceous Stratigraphy: Part 1. *Volumina Jurassica* 18 (1), 53–106. <https://doi.org/10.7306/VI>.
- Wimbledon, W.A.P., Reháková, D., Svobodová, A., Elbra, T., Schnabl, P., Pruner, P., Šifnerová, K., Kdýr, Š., Frau, C., Schnyder, J., Galbrun, B., Vaňková, L., Dzyuba, O., Copestake, P., Hunt, C., Riccardi, A., Poulton, T., Bulot, L., de Lena, L., 2020b. The proposal of a GSSP for the Berriasian Stage (Cretaceous System): Part 2. *Volumina Jurassica* 18 (2), 119–158.
- Zakharov, V.A., Rogov, M.A., Dzyuba, O.A., Žák, K., Košťák, M., Pruner, P., Skupien, P., Chadima, M., Mazuch, M., Nikitenko, B.L., 2014. Palaeoenvironments and

palaeoceanography changes across the Jurassic/Cretaceous boundary in the Arctic Realm: case study of the Nordvik section (North Siberia, Russia). *Polar Research* 33, 19714. <https://doi.org/10.3402/polar.v33.19714>.

Žák, K., Košťák, M., Man, O., Zakharov, V.A., Rogov, M.A., Pruner, P., Rohovec, J., Dzyuba, O.S., Mazuch, M., 2011. Comparison of carbonate C and O stable isotope records across the Jurassic/Cretaceous boundary in the Tethyan and Boreal Realms. *Palaeogeography, Palaeoclimatology, Palaeoecology* 299, 83–96.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cretres.2023.105617>.