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**New multiproxy record of the Jenkyns Event (a.k.a. Toarcian Oceanic Anoxic Event) from the Mecsek Mountains (Hungary): Differences, duration and drivers**

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## **ABSTRACT**

The oceanic anoxic event in the Early Toarcian, often referred to as T-OAE, led to widespread deposition of organic-rich black shales and geochemical anomalies in elemental distribution and multiple isotope systems in the Early Jurassic ocean. Best characterized by its hallmark carbon isotope anomaly, the event is widely regarded as a prime example of rapid greenhouse warming-related changes in the Mesozoic Earth system. However, despite numerous studies, details of its forcing mechanisms, exact duration, and the role of regional effects remain debated. Here we present new data (high resolution organic carbon isotope, calcareous nannofossil and elemental geochemical analyses) from the black shale-bearing Lower Toarcian section in the Réka Valley, Hungary, with the aim of assessing any regional differences in the sedimentary and geochemical record and their bearing on the underlying oceanographic and climatic processes. Following a short segment with a positive trend at the base of the section, values of our carbon isotope data are turning to a negative trend with a steep, stepwise drop in two negative shifts, reaching their minimum before a positive trend with oscillations characterizing the top part of the section examined. The shape of the curve and nannoplankton biostratigraphy (recognition of zones NJ5b, NJ6 and NJ7) allow reliable correlation of our data with the global carbon isotope perturbation recorded elsewhere in the Early Toarcian. We propose here that it would be fitting to rename the T-OAE as the Jenkyns Event, to honour the seminal contributions of Hugh Jenkyns. Our

cyclostratigraphic analysis suggests that the duration of the negative isotope excursion at Réka Valley is 200 kyr, 350 kyr, or 1 Myr, depending on which astronomical forcing parameter controls the most prominent cyclicity. Spectroscopic analyses suggest that the source of the organic matter, marine algae according to previous studies, did not change considerably during the main negative carbon isotope excursion. The variability observed in major element concentrations and enrichments relative to the average shale in the Réka Valley black shales can be regarded as mixtures of terrigenous aluminosilicates and calcium carbonate as two endmembers. Consequently, the terrigenous compositional endmember of the studied black shales consists of a mixture of an illitic/smectitic and a kaolinitic clay, supports previous suggestions of increased weathering under extremely humid climate in the hinterland during the Jenkyns Event.

**Keywords** oceanic anoxic event, Early Jurassic, Toarcian, carbon isotopes, elemental geochemistry, cyclostratigraphy, nannoplankton biostratigraphy, Fourier transform infrared spectroscopy

## **INTRODUCTION**

The Earth system experienced a major global perturbation in the Early Toarcian (Early Jurassic, ~182 Ma; Jenkyns, 2010). This event is widely recognized by occurrences of organic-rich black shale in the marine sedimentary record. Regionally, it has been exceptionally well studied in stratigraphic successions of the Yorkshire coast in England, where the widespread Jet Rock also represents a level of notable extinction among benthic organisms (Hallam, 1967). Global developments of similar organic-rich

sediments in the Cretaceous were termed Oceanic Anoxic Events by Schlanger & Jenkyns (1976), and it was Hugh Jenkyns who first recognized the analogy and significance of Toarcian deposits and first used a remarkable positive stable carbon isotope excursion (CIE) to characterize its development (Jenkyns, 1985, 1988). Shortly thereafter, signs of a negative CIE interrupting the positive trend were noted by Jenkyns & Clayton (1986, 1997), following an earlier description by Küspert (1982), and described in detail from Yorkshire by Hesselbo et al. (2000). Students and co-workers of Hugh Jenkyns developed high-resolution chemostratigraphies in many Lower Toarcian sections worldwide, including the Paris Basin (Hermoso et al., 2012), the Lusitanian Basin (Hesselbo et al., 2007), western Tethyan margin (Woodfine et al., 2008; Sabatino et al., 2009; Kafousia et al., 2011), and outside Europe in Argentina's Neuquén Basin (Al-Suwaidi et al., 2010; 2016). Together with other studies from the Panthalassa in western Canada (Caruthers et al., 2011) and Japan (Gröcke et al., 2011; Izumi et al., 2012; Kemp & Izumi, 2014), the global nature of the Toarcian CIE has been well-established.

The significance of Tethyan manganese deposits of Early Toarcian age was also recognized by Jenkyns et al. (1991). The Jenkyns school pioneered the use of other isotope systems, including nitrogen (Jenkyns et al., 2001), strontium (Jones et al., 1994), and sulphur (Gill et al., 2011) to further characterize the processes and drivers of the Early Toarcian perturbation.

Much has been learned from the sedimentary and geochemical record of the Toarcian and other, similar, anoxic events and commonly related biotic turnover in the Mesozoic and beyond, summarized in a comprehensive review by Jenkyns (2010), widely utilized for chemostratigraphy and paleoceanographic reconstructions (Jenkyns et al., 2002) and presented as prime examples of rapid greenhouse warming events (Jenkyns, 2003).

The name Toarcian Oceanic Anoxic Event (or T-OAE) has been commonly used recently; alternatively it is also referred to as *Posidonienschiefer* event for its typical development in southern Germany (Jenkyns, 2010). However, there are many similar events in Earth history which are named after pioneers of their study, notably including the Early Cretaceous (Valanginian) Weissert Event (Erba et al., 2004). We propose here that it would be fitting to rename the T-OAE as Jenkyns Event, to honour Hugh Jenkyns' seminal contribution to its understanding, and this name will be used throughout this paper.

Hugh Jenkyns worked on several Toarcian sections in Hungary in the Transdanubian Range (Jenkyns et al., 1991). Another occurrence of organic-rich shale in southern Hungary is shown by Jenkyns (1988), from the Mecsek Mts. The present paper describes new results from the Réka Valley section in the Mecsek Mts., the best outcrop of a 12 m thick black shale unit, first connected with the Jenkyns Event by Dulai et al. (1992). More recent studies at this locality reported on and characterized its high organic carbon content, the black shales containing ~4 to ~8% total organic carbon with kerogen type suggestive of marine algal source (Varga et al., 2007). The carbon isotope composition of the organic matter and both the carbon and oxygen isotope composition of the carbonate fraction were also measured, albeit on a small suite of 10 samples only. Although the carbonate fraction was affected by diagenetic overprint, the organic matter yielded negative  $\delta^{13}\text{C}_{\text{org}}$  values between -28.6‰ and -30.9‰ (Varga et al., 2007), raising the possibility of correlation with the minima of other European sections. A clay mineralogical study confirmed elevated weathering under hot and humid conditions (Raucsik & Varga, 2008), whereas changes in palynomorph assemblages were used to infer the sequence of environmental and biotic change (Baranyi, 2012). Despite these advances, detailed comparison of this section with other coeval sedimentary records of

the Jenkyns Event has been hindered by insufficient biostratigraphy (only preliminary ammonoid (Galácz, 1991) and calcareous nannoplankton studies (Baldanza et al., 1995) exist) and the low resolution of previous carbon isotope data (Varga et al., 2007).

Geographically distinct records of the Jenkyns Event suggest regional differences in its expression (e.g. Schmid-Röhl et al., 2002; Hermoso et al., 2009; Kafousia et al., 2011), therefore new data from underexplored sections could help refine our understanding of the regional effects. Another outstanding issue is the timing and duration of this event. The synchrony of environmental changes has been approached by ammonoid and nannoplankton biostratigraphic correlation (Jenkyns & Clayton, 1997; Mattioli et al., 2008), but some discrepancies remain in the details of biostratigraphic boundaries, onset of black shale sedimentation and phases of the CIE. Orbitally forced cyclicity in the CIE and sedimentary proxies were first recognized by Kemp et al. (2005) and subsequently documented from several sections, but identification of the dominant control remains controversial. This uncertainty affects estimates of the duration of the black shale interval and the negative CIE, where opinions range between ~170–620 kyr (Suan et al., 2008b; Kemp et al., 2011; Huang & Hesselbo, 2014; Boulila et al., 2014). Resolving these issues may be of significance with respect to identifying the drivers of this event, widely regarded to be triggered by volcanism of the Karoo-Ferrar LIP (Pálffy & Smith, 2000) and related greenhouse warming, amplified by methane injection through either gas-hydrate dissociation in marine sediments (Hesselbo et al., 2000) or thermogenic methane from sill emplacement (McElwain et al., 2005; Svensen et al., 2007).

To address these issues, we present here new data from the Lower Toarcian black shale in the Réka Valley, Hungary. From a new, high-resolution suite of samples, a calcareous

nannoplankton biostratigraphic framework is developed, and a  $\delta^{13}\text{C}_{\text{org}}$  curve is presented on the basis of 182 measurements. Because both a well-developed negative CIE and prominent cyclicity are observed in the signal, infrared reflectance spectra and elemental abundance data were obtained on the same samples by FTIR and XRF instruments, respectively. Cyclostratigraphic analysis is used to provide a range of astrochronologic estimates for the duration of the black shale interval, the negative CIE, and the largely correlative NJ6 nannoplankton zone. The shape of the  $\delta^{13}\text{C}$  curve, the magnitude of the CIE and the amplitude of its cycles are compared with other sections for new insights. Elemental geochemical data are utilized to characterize the weathering regime and climate in the continental hinterland. The results are then used to assess the regional differences in the sedimentary and geochemical record of the Jenkyns Event, and their bearing on the underlying oceanographic and climatic processes.

## **GEOLOGICAL SETTING AND STRATIGRAPHY**

The Mecsek Mountains are located in the southwestern part of the Pannonian Basin in Hungary (Fig. 1). This east-west trending mountain range is the only area within Hungary with surface exposures of the Mecsek structural unit, which comprises a thick package of Permian and Mesozoic strata, and itself forms part of the Tisza Mega-unit (Csontos & Vörös, 2004; Haas & Péro, 2004). The Tisza Mega-unit was part of the European margin after the Variscan orogenic cycle in the Late Palaeozoic and Early Mesozoic. Its separation from the European continental margin started with the Middle Jurassic rifting and later Mesozoic tectonic movements in the Tethys. The Mecsek Unit reached its present day position through complex tectonic processes related to the Alpine orogeny in the Paleogene and Neogene (Csontos et al., 2002). The Late Triassic



and Early Jurassic evolution of the Mecsek Basin was controlled by a half-graben system related to continental rifting between the Tisza block and the European margin. Gradual deepening during the Late Sinemurian and Pliensbachian led to the deposition of the intensively bioturbated Hosszúhetény Calcareous Marl Formation in an open marine basin (Raucsik & Merényi, 2000). This lithofacies is named informally as spotted marl and it represents the equivalent of the widely known “Fleckenmergel” or “Allgäu” facies of the European margin of the Neotethys (Horváth & Galácz, 2006; Főzy, 2012). The Upper Pliensbachian and lowermost Toarcian part of the formation is monotonous spotted marl with intercalated turbiditic sandstone beds, crinoidal limestone and organic-rich limestone, reflecting an environment where sea level, climate change, and tectonically controlled subsidence influenced the depositional regime (Raucsik & Varga, 2008). In the Lower Toarcian, organic-rich silty claystone, marlstone and a distinctive, ~12 m thick black shale succession occurs, recently distinguished as a separate lithostratigraphic unit, the Rékavölgy Formation (Főzy, 2012). The organic-rich, in some parts laminated, shale suggests anoxic conditions in the Mecsek Basin in the Early Toarcian and is recognized as the local stratigraphic expression of the Jenkyns Event (Dulai et al., 1992; Varga et al., 2007). In the overlying strata the spotted marl facies returns and continues up to the Bajocian, lithostratigraphically assigned to the Komló Calcareous Marl Formation.

The studied section at Réka Valley provides the best outcrop of the recessive, and elsewhere only very poorly exposed, Lower Toarcian black shale unit. The section is located in a narrow tributary valley of the northern side of the NE-SW trending Réka Valley, south of the village of Óbánya, in the eastern part of the Mecsek Mountains. The basal part of the section comprises bioturbated and clay-rich spotted marl facies with intercalated sandstone beds, overlain by a ~12 m thick succession of organic rich black

shale, including intervals of brown to grey bituminous laminated shale, with intercalated beds and lenses of calcareous and sandy turbidite. Fish remains, pyrite framboids, fragments of plant remains and bivalves are common in the black shale (Dulai et al., 1992; Raucsik & Varga, 2008). In the overlying strata at the top of the measured section the spotted marl facies returns.

The age and ammonite biostratigraphy of the section has not been precisely defined due to the scarcity of index species. Ammonites of the genus *Hildaites* from the black shale and *Harpoceras* cf. *exaratum* from the highest part of the black shale interval suggest the presence of the Lower Toarcian Falciferum ammonite standard zone (Galácz, 1991; Dulai et al., 1992). The assignment was supported by limited calcareous nannofossil data reported in Baldanza et al. (1995) and Varga et al. (2009).

## **MATERIAL AND METHODS**

In our field work in August 2014, the intermittent natural outcrops at the steep side of the tributary ravine of Réka Valley were cleaned to access the unweathered rock for sampling. Four parallel trenches with adequate overlap were excavated to connect and expand the natural outcrops, allowing measurement and description of a detailed sedimentary section. The total thickness of the sampled interval of the section is 19.5 m on which high resolution sampling has been carried out applying 0.05 m spacing, wherever outcrop conditions permitted. In total, 460 bulk sediment samples, 100–200 g each, were obtained from the partially overlapping measured stratigraphic sections RVA, RVB, RVC and RVD. Easily recognizable lithologic marker horizons allow the accurate correlation of these sections with earlier studies made at Réka Valley. Splits of the collected samples were investigated for calcareous nannofossil content, organic

carbon stable isotope measurements, elemental geochemistry and infrared spectroscopic analyses.

### **Calcareous nannofossils**

The calcareous nannoplankton assemblage was studied in 68 smear slides from the section, at a regular sampling resolution of 0.3 m, except for five levels where sandstone interbeds were avoided. Slide preparation followed the standard technique described by Bown (1998) which is known to retain the original composition of the nannoplankton assemblages of the sediments. The slides were studied in oil immersion at 1000<sup>×</sup> magnification under cross-polarized light using an Olympus BX51 microscope. Forty fields of view per slide were scanned and all of the observed specimens were counted to assess the abundance distribution of nannoflora.

### **Organic carbon isotope analysis**

Bulk organic matter carbon isotope analysis was performed on 182 samples from the studied stratigraphic interval. Parts of the section were analysed either with a 0.1 m or with an increased 0.05 m sample spacing, as outcrop conditions did not allow completely uniform sampling steps throughout (see Supplementary Data). First, ~1 g of the sample material was powdered by using an agate mortar and pestle. The powdered materials were then placed in centrifuge tubes and then treated two times with 10% HCl (agitated and left for 1 hour after each treatment) to remove all the carbonate phases. The remaining solution was pipetted off and replaced with deionized H<sub>2</sub>O. After leaving the sediment to settle for two hours, this neutralisation process was repeated ten times. Carbon isotope analysis of the remaining organic matter was conducted at Plymouth

University, using an Isoprime isotope ratio mass spectrometer connected to an Isoprime Microcube elemental analyser. Carbon isotope ratios are expressed using the internationally accepted  $\delta$  notation in per mil (‰) relative to the Vienna Pee Dee belemnite (VPDB) standard. Instrument calibration was achieved using three international standards, USGS 40 (l-glutamic acid,  $\delta^{13}\text{C} = -26.389\text{‰}$ ), USGS 24 (graphite,  $\delta^{13}\text{C} = -16.049\text{‰}$ ) and IAEA CH-7 (polyethylene,  $\delta^{13}\text{C} = -32.151\text{‰}$ ). The standard deviation on replicates in run analyses of the USGS 40 standard was  $\pm 0.12\text{‰}$ .

### **Elemental geochemical analyses**

The use of a handheld XRF device was chosen to efficiently gather elemental abundance data for cyclostratigraphic and elemental geochemical analyses. The measurements were made on 2–3 g of powdered bulk rock material from a suite of 184 samples that represents a 10 cm stratigraphic resolution. Powdered samples were poured onto a piece of paper and were piled up to achieve an appropriate height (1-2 cm) of the sample column. The sensor was pressed directly against the powder during measurements. The instrument's nozzle was thoroughly cleaned after each measurement. The instrument used for this study was a Thermo Scientific Niton XL3t 900 GOLDD+ (Geometrically Optimized Large Area Drift Detector) portable XRF analyser with 50 kV X-ray tube with silver target (Ag anode). Helium purging was also applied for appropriate measuring of light elements (Mg, Al, Si, S, Cl, P). The apparatus has several company-preset calibrations for given matrices, of which the Mining and TestAllGeo calibrations were used for our samples. The average uncertainty of the XRF measurements is 15-20%, depending on the particular element (see Supplementary Data). For the measurements three different certified standards were used (DC72301,

GBW07111 and a Hungarian one (from SZIKTTI)). A total of 22 elements (Ti, Mo, Zr, Sr, Rb, Th, Pb, As, Zn, Cu, Fe, Mn, Cr, Ca, K, S, Ba, Nb, Al, P, Si, Mg) were measured. Duration of each measurement was 120 seconds or more, using four energy filters ('Main, Low, High, Light') for 30 seconds each, except for the 'Light' filter which was applied for slightly longer to obtain more accurate values of light elements (Mg, Al, Si, P, S, Cl). The standardless fundamental parameters method with Compton-normalization was used by the XRF apparatus for quantitative analysis and results were also checked by viewing the corresponding spectra with the NDT (Niton Data Transfer, version 8.0.0) software. Mathematical and statistical data processing was done using Excel and Statistica 12 software packages. The different elemental signals derived from XRF measurements are independent of each other, therefore show the variations in the content of the various elements in the bulk rock sample. Analytical quality data including detection limits and precision are tabulated in the Supplementary Data.

### **Fourier transform infrared spectroscopy (FTIR)**

Infrared spectroscopy uses IR radiation to measure what fraction of the incident radiation is absorbed at a particular wavelength, which can be used to establish semi-quantitative measures of mineral and organic matter composition (Farmer, 1974; Griffiths, 1983; Thompson et al., 2009). FTIR uses Fourier transform to convert the raw wavelength data collected by a detector into spectra (Griffith, 1983). Attenuated total reflectance (ATR) is a rapid technique which is a useful initial step to characterize minerals and organic matter with minimal sample preparation (Stuart, 2004). ATR is based on the phenomenon of total internal reflection (Bruno, 1999) and measures the changes which occur in an internally reflected infrared beam which come in contact with

the sample through a diamond crystal. When the sample is placed in contact with the ATR crystal the resulting evanescent wave is attenuated in the regions of the IR spectrum where the sample absorbs energy (Stuart, 2004). Measurements were carried out on splits from the same suite of 184 samples at 0.1 m spacing as used for the stable isotope and XRF analyses. The samples were first ground into powder using an agate mortar and pestle. For each sample 16 scans were recorded in the 4000–400  $\text{cm}^{-1}$  spectral range with a resolution of 4  $\text{cm}^{-1}$ . The measurements were carried out using a Bruker Vertex 70 spectrometer controlled by OPUS 7.2 software, at the Institute for Geological and Geochemical Research of the Hungarian Academy of Sciences.

### **Time series analysis for cyclostratigraphy and astrochronology**

Cyclostratigraphic analyses were made on bulk rock  $\delta^{13}\text{C}_{\text{org}}$ ,  $\text{CaCO}_3$ , and  $\text{CH}_2_{\text{FTIR}}$  signals. The turbidite beds were excluded from the stratigraphy as these strata are instantaneous event deposits that do not record the cyclic variations in the studied proxies. Thus the analyses were performed using a corrected section thickness of 18.5 m.

Data processing was performed using Matlab (2015b) along with R (3.2.4) and the Astrochron R package (Meyers, 2014). Prior to the spectral analysis, the raw data series were linearly interpolated every 0.1 m, long-term trends were removed, and the data series was padded with zeros to 256 data points to accelerate calculations (Cooley & Tukey, 1965). The  $\delta^{13}\text{C}$  dataset was detrended using a second order polynomial regression, as this method provided the best result for removing the long-term trend of the negative excursion without affecting the low-frequency cyclicities. The  $\text{CaCO}_3$  and the  $\text{CH}_2_{\text{FTIR}}$  signals were detrended using linear regressions. For spectral analyses the

multitaper method was used by applying three  $2\pi$ -tapers ( $2\pi$ -MTM; Thomson, 1982). Confidence levels were calculated using robust red-noise modelling, modified according to Tukey's end-point rule (Tukey, 1977; Mann & Lees 1996; Meyers, 2014). To isolate certain frequencies from the rest of the series, Taner band-pass filters were applied (Taner, 2003). The length of the Milankovitch periodicities in the Toarcian were calculated from the La2004 astronomical solution (short eccentricity: 100 kyr, obliquity: 35 kyr, precession: 25 kyr; Laskar et al., 2004).

## RESULTS

### **Nannofossil assemblages and biostratigraphy**

The preservation of coccoliths in the studied material is good and has not been affected by significant diagenetic overprint, as no calcite resorption or overgrowth was observed. The diversity is intermediate, a total of 12 taxa have been identified. A reduced size of coccoliths is noted along the section, especially noticeable in the dominant genus *Lotharingius* (Fig. S1 A-B), with specimens commonly as small as 4-5  $\mu\text{m}$ .

Most of the biostratigraphically important Late Pliensbachian–Early Toarcian calcareous nannoplankton species are well represented in the section, allowing the recognition of calcareous nannoplankton bioevents which are used here as the primary means of age assignment, in the absence of a good ammonite record.

Three nannoplankton zones, NJ5b, NJ6 and NJ7 have been recognized using the biostratigraphic scheme of Bown (1998). The zonal assignments are based on the following primary and secondary nannofossil marker events.

*Lotharingius hauffi* (Fig. S1A-B), *Lotharingius sigillatus* (Fig. S1E), *Biscutum finchii* (Fig. S1C), and *Crepidolithus impontus* (Fig. S1D) were found in the lowermost sample. Based on their co-occurrence, the base of the studied section is assigned to the NJ5b *Crepidolithus impontus* Subzone. The Pliensbachian-Toarcian boundary is thought to fall within this subzone but it is not recognized in the studied material. The first occurrence (FO) of *Carinolithus superbis* (Fig. S1F) is recorded at 7.1 m and used to define the base of NJ6 *Carinolithus superbis* Zone. Its upper boundary and the base of the overlying NJ7 *Discorhabdus striatus* Zone is recognized by the FO of *Discorhabdus striatus* (Fig. S1G) and the last occurrence (LO) of *Biscutum finchii* at 14.85 m.

Beside the zonal marker species, *Bussonius prinsii* (Fig. S1H), *Watznaueria* sp. (Fig. S1J), *Orthogonoides hamiltoniae* (Fig. S1L), *Zeugrhabdotus erectus* (Fig. S1I), and *Schizosphaerella* sp. (Fig. S1K) occur in the Lower Toarcian calcareous nannoplankton assemblage. *Lotharingius* and *Crepidolithus* are numerically dominant over other taxa in the assemblage. *Mitrolithus jansae* has not been recorded, its absence is notable as it is a characteristic species of Tethyan nannoplankton assemblages at several other localities.

The abundance of the nannofossil assemblage is insufficient for a fully quantitative palaeoecological analysis, as viewing 40 fields of view per slide yielded less than 100 specimens in a large number of samples. However, counting all the observed specimens allowed generation of an abundance distribution curve, suitable for a first-order approximation for nannoplankton productivity changes (Fig. 2). In the calcareous marl in the lower part of the section, the nannofossil abundance is variable. Higher up, in the carbonate-poor and organic-rich shale the abundance is generally low except for two significant peaks (at 10.8 and 13.3 m) which correlate with maxima in the CaCO<sub>3</sub> content. In the upper marl interval, from 15.6 m, the nannofossil abundance starts to



increase and reaches a third major peak at 17.9 m, again coincident with a CaCO<sub>3</sub> maximum. The abundance increase is coincident with the positive trend in the  $\delta^{13}\text{C}_{\text{org}}$  data.

The zonal nannoplankton biostratigraphy presented here is the best tool for chronostratigraphic subdivision in the section, through correlation with standard ammonoid zones established in other European sections. The NJ5 *Lotharingius hauffi* Zone is correlative to the ammonoid standard Margaritatus, Spinatum and Tenuicostatum zones, i.e. it ranges from the Upper Pliensbachian to the lowermost Toarcian. The NJ5b subzone, recognized in the studied section, is restricted to the Spinatum and Tenuicostatum zones and straddles the stage boundary. Zone NJ6 is correlated with the Falciferum Zone in the Lower Toarcian and includes the most organic-rich sediments both in this section and at other localities. The NJ7 *Discorhabdus striatus* Zone is correlated with an interval encompassing the topmost Falciferum to Levesquei zones, from the Lower to Upper Toarcian, of which here only the lowermost part is present.

### **Carbon isotope record**

In general, the  $\delta^{13}\text{C}_{\text{org}}$  data obtained from bulk organic matter show negative values (on average -30.84‰) and characteristic patterns throughout the sampled section (Fig. 2). The  $\delta^{13}\text{C}_{\text{org}}$  values range from -32.9‰ to -27.6‰, with an average of -30.9‰. Changing trends in the  $\delta^{13}\text{C}_{\text{org}}$  curve allow us to distinguish three intervals, with potential for chemostratigraphy and interpretation of changes in the carbon cycle. The boundaries of these intervals, together with some other local minima, maxima, and inflection points in the curve are noted as useful features for correlation with other sections. Interval 1 is

restricted to the lowermost 2.1 m and is characterized by an overall positive trend up to  $-27.6\text{‰}$  at 1.8 m, followed by a sharp drop of  $-4.2\text{‰}$  over the next 0.3 m, reaching  $-31.8\text{‰}$ . The inflection point at 1.8 m marks the onset of the CIE. Interval 2 lies between 2.1–14.8 m, and it starts with a transient rebound followed by a second step of a somewhat less steep drop of  $-3.2\text{‰}$ , to a value of  $32.4\text{‰}$  at 3.7 m. This interval includes the lithologic change at the termination of spotted marl facies and the onset of black shale sedimentation at 2.65 m. Carbon isotope values remain very negative, reach their minimum at 7.0 m, and show cyclic oscillations of an amplitude of  $\sim 2\text{‰}$  throughout Interval 2. An overall positive trend with continuing oscillations characterizes Interval 3 in the top part of the section. It starts at an inflection point at 14.8 m, marking the recovery phase after the CIE, with a rebound to less negative values of up to  $-27.8\text{‰}$ . This interval includes the uppermost 1.5 m of the black shale and the overlying spotted marl. The studied part of the section terminates without any flattening of the  $\delta^{13}\text{C}_{\text{org}}$  curve.

### **Elemental geochemistry and carbonate content**

Statistical evaluation of the concentration data (see the Supplementary Data) revealed distinguishable groups of the elements analysed by the XRF method. The first group includes Si, Al, Ti, K, Zr, Rb and, at lower positive coefficients, Th, Mg, and Pb. These elements are commonly carried by detrital aluminosilicate phases in siliciclastic sedimentary rocks. Ca and Sr form the second group, associated with  $\text{CaCO}_3$  phases. Fe, Mn and Cr comprise the third group at a lower level of significance. Cu, Zn and Mo show moderate positive correlation coefficients and are separated from all other measured elements. The remainder of the elements (S, P, Ba) do not show significant correlation.

In order to evaluate the elemental geochemistry of the studied samples in the framework of dilution of detrital components by CaCO<sub>3</sub>, organic matter and authigenic minerals, the elemental concentrations are normalized by Al and enrichment factors relative to average shale (Wedepohl, 1991) are calculated. The enrichment factor for any element, hereafter EF(e), is calculated as follows:

$$EF(e) = (C(e)_{\text{sample}}/C(Al)_{\text{sample}})/(C(e)_{\text{shale}}/C(Al)_{\text{shale}})$$

where C is the concentration.

The Al-normalised EFs of the major elements considerably fluctuate in the samples. Si, Ti, Mg and K are depleted relative to the average shale, whereas Ca shows a moderate overall enrichment with mean EF of 2.78. Fe, Mn and P have positive mean EF values of <2, thus they do not display significant authigenic enrichment (see Supplementary Data).

Large ion radius lithophile elements such as Rb, Sr, Ba and Pb show different distributions regarding their mean EFs. A general depletion in Rb characterizes the entire studied section. Although EF values for Sr, Ba and Pb are generally <2, there are six, two and one samples of these elements, respectively, which yield moderate authigenic enrichments with EF>2. Concentrations and the EFs of the transitional elements (As, Cr, Cu, Mo, Zn) vary widely, remaining under detection limit in numerous samples. However, Mo shows significant enrichment, Cu and Zn show a mean depletion within this group of redox sensitive elements. Mean EF values of As and Cr remain <2 (see Supplementary Data).

The carbonate content was determined by using the molecular weight of calcium carbonate (Ca wt% x 2.5). The distribution of CaCO<sub>3</sub> along the section is not showing any

remarkable trend either. Although a significant drop to a minimum value of 1.6 wt% can be observed around ~2.2 m and an abrupt peak where the values are increasing to 20 wt% at ~11 m. Nevertheless, a gentle general increase in the carbonate content is apparent upward in the section.

### **Fourier transform infrared spectroscopy (FTIR)**

The characteristic wave numbers of the identified bands of the organic matter appear at 2850  $\text{cm}^{-1}$  and 2925  $\text{cm}^{-1}$  which represents C-H and C-H<sub>2</sub> bonds (Stuart, 2004; Movasaghi et al., 2008). The carbonate molecules have two characteristic peaks in stretching vibration mode (where interaction with infrared radiation induces a change in the bond length among the atoms, and such changes in the dipole of the molecule cause the observed absorption). These are considered the most prominent absorption features, at 1420  $\text{cm}^{-1}$  and 876  $\text{cm}^{-1}$  (Chester & Elderfield, 1967; Muller et al., 2014). The baseline was automatically corrected in the Opus 7.2 software by rubber band correction with 64 baseline points and two iterations of joining the points of lowest absorbance on a peak (Stuart, 2004). An integration method was set up using peak intensity to a local baseline to measure the organic matter and carbonate variation during the whole section. The organic matter was not observable in the lower part of the section. The stratigraphically lowest sample with calculated peak intensity value occurs at 2.8 m and the highest one is at 17.4 m. The results are presented in the Supplementary Data and in Fig. S2. Apparently, cyclic changes in the spectra occur throughout the section in both the CH and CH<sub>2</sub> peaks. The highest intensity values range between 0.0038 and 0.0049 with peaks at 3.7, 5.9, 7.0, 9.2, 11.2 and 15.1 m. The magnitude of oscillation between the highest and lowest values reaches 0.004 over

stratigraphic intervals of 0.4–0.8 m. The three carbonate bands appear throughout the entire record but we processed only the 1420 cm<sup>-1</sup> band which represents the CO<sub>2</sub><sup>-3</sup> stretching, whereas the other two bands overlapped through the whole section with the Si-O and Al-Al-OH and Al-Mg-OH bands, which are characteristic for common silicate minerals (Madejová & Komadel, 2001).

### **Cyclostratigraphy and astrochronology**

The 2 $\pi$ -MTM power spectrum of the  $\delta^{13}\text{C}_{\text{org}}$  signal shows a peak over 99% confidence level (CL) at 1.60 m, and peaks reaching 95% CL at 0.37 and 0.25 m (Fig. 3). The 2 $\pi$ -MTM power spectrum of the CaCO<sub>3</sub> signal shows peaks over 99% CL at 2.13, 0.29 and 0.24 m, a peak reaching 95% CL at 0.39 m, and a peak reaching 90% CL at 1.11 m. The 1.60-m peak in the  $\delta^{13}\text{C}_{\text{org}}$  signal and the 2.13-m peak in the CaCO<sub>3</sub> signal have higher spectral power compared to the other cyclicities. The multitaper analyses of the CH<sub>2</sub><sub>FTIR</sub> signal shows peaks over 95% CL at 2.33, 1.60, 0.98, 0.78, 0.44, 0.29, 0.27 and 0.23 m. The more equalized power of the peaks on this latter power spectrum is due to the incomplete data series.

To isolate the prominent cyclicity from the rest of the series band pass-filters were applied. The frequency domains of the filter were set to include the most prominent 1.1 m – 2.3 m cyclicity, present in all three proxy signals, but to exclude the low-power and high-frequency cyclicities. The peaks adjacent to the prominent cyclicity in the low-frequency domain are thought to represent the modulation of the prominent cyclicity caused by the variations in the sedimentation rate and are therefore included in the filters. Of particular interest is Interval 2 that corresponds to the CIE and in which ten key cycles occur in the  $\delta^{13}\text{C}_{\text{org}}$  and the CaCO<sub>3</sub> signals in the same phase. Two additional

cycles are detected in the preceding Interval 1 and three to four cycles can be counted in Interval 3. In the CH<sub>2</sub>FTIR signal 7–10 cycles can be distinguished between 3 m and the end of Interval 2 (Fig. 3).

## DISCUSSION

### Nannoplankton biostratigraphy of the Jenkyns Event

Due to the scarcity of macrofossils and a lack of a detailed ammonoid biostratigraphic study, nannofossils offer good independent support for correlation of the CIE at Réka Valley and other sections. Previously, Baldanza et al. (1995) studied five samples, including two from the lower half of the black shale and three from the underlying beds from this locality. Without providing clear evidence, a correlation of the black shale with the ammonite standard *Falciferum* Zone was suggested. Two other samples from the black shale were previously studied by E. Mattioli, whose identifications were reported in Varga et al. (2009). Although none of the zonal indices were found, *Carinolithus poulabronei* from the lower and *Wautzneria fossacincta* and *W. colacicchii* from the upper sample led her to establish the presence of the *C. superbus* and *D. striatus* zones (Mattioli in Varga et al. 2009).

In this study, the base of both the NJ6 and NJ7 zones are more tightly constrained, on the basis of the FO of *C. superbus* and *D. striatus*, respectively. There are only a handful of other sections where the sequence of calcareous nannoplankton bioevents and the onset and termination of both the black shale sedimentation and the CIE can be assessed. At Réka Valley, the base of Zone NJ6 falls within the black shale, thus it follows the onset of the CIE and deposition of organic-rich sediments. This is in contrast with other sections,

as the FO of *C. superbis* precedes the start of the Jenkyns Event in Dotternhausen, Yorkshire, Pozzale (Mattioli et al., 2004), Peniche (Mattioli et al., 2008) and the Paris Basin (Mattioli et al., 2008; Boulila et al., 2014). Because the nannoplankton abundance in this part of the Réka Valley section is rather low, and there are few other indices of this zone apart from its primary marker species, the unexpectedly high local FO of *C. superbis* may be due to collection failure. On the other hand, the boundary between zones NJ6 and NJ7 is firmly established by the closely spaced LO of *B. finchii* and the FO of *D. striatus*. This level occurs immediately below the top of the black shale, in the last part of the CIE characterized by rising  $\delta^{13}\text{C}$  values. This stratigraphic position is equivalent to that observed in Dotternhausen (Mattioli et al., 2008). In Peniche (Mattioli et al., 2008) this zonal boundary was not recorded at the level predicted by the chemostratigraphic correlation, whereas in the Paris Basin (Mattioli et al., 2008; Boulila et al., 2014) it occurs significantly higher than the termination of the CIE. Apparently the rarity of marker bioevents around the Jenkyns Event, exacerbated by a drop in abundance of coccoliths broadly coincident with the onset of CIE as also noted in other sections (Hermoso et al., 2012), may compromise the precision of nannofossil biostratigraphy in this interval.

Several authors discussed the palaeoecological significance of Toarcian calcareous nannoplankton taxa (Baldanza et al., 1995; Mattioli et al., 2004, 2008; Ferreira et al., 2015). The assemblage of the studied section is dominated by *Lotharingius*, thriving under mesotrophic to eutrophic conditions and stratified water masses. Another common genus, *Watznaueria*, is thought to tolerate elevated surface water temperatures. The small size of *Lotharingius* may be a response to the calcification crisis related to the Jenkyns Event (Tremolada et al., 2005), also reflected in the overall low abundance of nannoplankton. The transient peaks of abundance during the CIE could

represent of periods of blooms under temporarily ameliorating environmental conditions.

### **Chemostratigraphical correlation of the Réka Valley section**

The  $\delta^{13}\text{C}$  record of the Jenkyns Event is eminently suitable for stratigraphic correlation for its characteristic pattern replicated through numerous high-resolution studies worldwide (Jenkyns, 2003; Al-Suwaidi et al. 2010; Caruthers et al. 2011; Kemp & Izumi, 2014; Al-Suwaidi et al. 2016). The majority of the data originates from European sections, of which correlation is presented here with Peniche in the Lusitanian Basin (Hesselbo et al., 2007), Yorkshire (Hesselbo et al, 2000; Kemp et al., 2005, 2011), the Sancerre core (Hermoso et al., 2009, 2012) and Lorraine (Ruebsam et al., 2014) in the Paris Basin, the Denkingen core (Suan et al., 2015) near the longer known Dotternhausen section (Röhl et al., 2001) in SW Germany, and the Tethyan sections of Valdorbia in the Appenines (Sabatino et al., 2009) and Sega d'Ala in the Trento Platform of the Southern Alps (Woodfine et al., 2008). The suggested chemostratigraphical correlations are illustrated in Fig. 4. The simple subdivision of Hesselbo et al. (2007) is followed here, because it was developed in the GSSP section for the Toarcian stage at Peniche, it is based on consistently high quality and high resolution data, and it gained wide acceptance (Suan et al., 2008b; Kemp et al., 2011; Huang & Hesselbo, 2014). The three intervals identified in the Réka Valley  $\delta^{13}\text{C}$  curve are therefore correlative to those separated by distinctive levels labelled 1 to 4 in Hesselbo et al. (2007).

Level 1, the Pliensbachian-Toarcian CIE is not captured in the Réka Valley section which starts higher up. The onset of the CIE associated with the Jenkyns Event is marked by a sharp and large drop in  $\delta^{13}\text{C}$  values in all sections. The 4.2‰ shift in Réka Valley is



among the largest recorded for the initial step in  $\delta^{13}\text{C}_{\text{org}}$  data. Level 2 marks the local minimum reached in this step, and the beginning of Interval 2, i. e. the main negative CIE. At the base of Interval 2, a transient rebound and a second step of a major negative shift is also well correlatable among all sections. In the Réka Valley section, this second step is also well expressed and its magnitude ( $-3.2\text{‰}$ ) is one of the largest recorded anywhere. The same holds true for the next several cycles, as Interval 2 is characterized in nearly all sections by cyclic fluctuations which are decreasing in magnitude upsection. Despite the similarities in this pattern, subtle differences exist in the overall shape of the curve in Interval 2. Réka Valley displays a bowl-shaped curve, with sustained negative values over a considerable stratigraphic distance, resembling those from Peniche, Yorkshire, SW Germany, and Valdorbia. Sancerre and Lorraine from the Paris Basin are characterized by V-shaped curves with a more pronounced, narrow minimum. Records from the shallow marine sections of the Trento Platform differ in their “Aladdin lantern” shape, where a minimum is reached in the lowermost part of Interval 2, followed by a gentle rise in values.

Level 3 is also present in every section. This level is defined by the inflection point heralding the recovery from the CIE, from where a gradually increasing trend in  $\delta^{13}\text{C}$  values is observed in Interval 3. However, the definition of this level remains ambiguous in certain sections.

Level 4 is marked by termination of the gradual shift to more positive values and a flattening of the  $\delta^{13}\text{C}$  curve at Peniche and all the other expanded sections. This level is not captured in the data from Réka Valley, where it is predicted to occur higher upsection, in a part not sampled in the present study.

## **The carbon isotope record of the Jenkyns Event**

The remarkable carbon isotope anomaly during the Jenkyns Event is commonly characterized by a broad positive excursion with a sudden interruption by an abrupt, globally observed negative excursion (CIE). The proposed sources of the isotopically light carbon include volcanic degassing of CO<sub>2</sub> during the magmatism of the Karoo-Ferrar large igneous province, thermogenic methane generated through related sill emplacement (McElwain et al., 2005; Svensen et al., 2007), or the dissociation of methane-hydrate from deep-sea sediments driven by concomitant greenhouse warming (Hesselbo et al., 2000; Kemp et al., 2005). The carbon isotope anomaly is preserved in different records, including bulk carbonate, belemnite skeletal carbonate, bulk organic matter and fossil wood (e.g. Hesselbo et al., 2000, 2007; Schouten et al., 2000; Suan et al., 2008a, 2010; Sabatino et al., 2009; Ullmann et al., 2014), suggesting that both the ocean and atmosphere system were affected. However, the magnitude of the CIE differs among the records, with typically larger shifts in bulk  $\delta^{13}\text{C}_{\text{org}}$  (e.g. -7‰ in Sancerre; Hermoso et al., 2012) than in bulk  $\delta^{13}\text{C}_{\text{carb}}$  (e.g. from 3‰ in Peniche; Hesselbo et al., 2007, to -6‰ in Sancerre, Hermoso et al., 2012). Changes in the contribution of various sources of organic matter, isotopically lighter marine algal OM versus heavier terrestrial plant OM, was suggested to explain the difference (van de Schootbrugge, 2013) and supported by measured changes in the Hydrogen Index (Suan et al., 2015).

In this context, it is instructive to analyse the Réka Valley  $\delta^{13}\text{C}_{\text{org}}$  curve which shows similar features, trends and values to other sections from the European epicontinental seaway. The magnitude of the observed CIE (5.3‰, defined as the difference between the value at the start of the CIE and the most negative value) is not exceptional as it falls within the range of observations from other locations. On the other hand, the magnitude

of the first and second step in the negative shift at the beginning of the CIE exceeds that of Yorkshire, which otherwise features one of the largest overall  $\delta^{13}\text{C}_{\text{carb}}$  anomalies of -8‰ (Kemp et al., 2011). The magnitude of the first two negative steps in the CIE observed at Réka Valley is challenging to explain. The Mecsek Basin was located close to the European margin of the Neotethys in the Early Jurassic (Horváth & Galácz, 2006). This palaeogeographic setting may have facilitated local development of upwelling and related  $\text{CO}_2$ -recycling, which could further affect the isotopic composition of  $\text{C}_{\text{org}}$  (Schouten et al., 2000), beside the global addition of isotopically light carbon from methane-hydrate dissociation and volcanic sources. Regional differences in the  $\delta^{13}\text{C}_{\text{org}}$  records of the Jenkyns Event are more commonly ascribed to changes in the organic matter source and variation in the ratio between terrestrial and marine organic matter (French et al., 2014; Suan et al., 2015). The lack of further, more detailed organic geochemical studies preclude a definitive explanation but existing data favour the speculation of paleoceanographic drivers. Cyclic fluctuations in  $\delta^{13}\text{C}_{\text{org}}$  during the CIE are also well developed in Réka Valley. Our FTIR measurements are useful to quantify and characterize the organic content and its variation throughout the section. One region commonly used for the assessment of organic matter in sedimentary rocks is the methylene group at  $2800\text{ cm}^{-1}$  –  $3000\text{ cm}^{-1}$  and the vibrational stretching of  $\text{CH}_2$  at  $2850\text{ cm}^{-1}$  and  $\text{CH}$  stretching at  $2923\text{ cm}^{-1}$  (Movasaghi et al., 2008; Pistorius et al., 2009). These two bands occur throughout the section, but their detection was compromised in the lowermost 3 m and at the top of the section in the spotted marl facies, due to the overlap with the  $\text{OH}$  stretching bands of the clay minerals and other silicates. The two methylene bands show a good correlation ( $r=0.77$ ) and similar variation throughout the section, arguing against significant changes in organic matter sourcing. The organic matter probably originates from marine algae, as suggested by Rock Eval pyrolysis in a

previous study (Varga et al., 2007), but proper identification by FTIR is not possible due to the lack of these bands in the FTIR spectra. However, similar and largely synchronous cyclicality in the CH and CH<sub>2</sub> signals (see below) argues against strong variations in the source of organic matter.

Major environmental change affected the plankton communities before and after the Jenkyns Event, but a largely invariable marine algal source for the OM during the CIE is further supported by recent results of Baranyi (2012). Her study of palynomorphs in the Réka Valley section documents a significant change in the dinoflagellate assemblage to an impoverished *Nannoceratopsis*-dominated community, broadly coeval with the initial two steps of the CIE preceding the onset of black shale deposition. This stage was followed by the temporary disappearance of all dinoflagellates, and high abundance of sphaeromorphs, regarded to belong to the opportunistic group of prasinophyte algae, together with a lack of terrestrially derived phytoclasts. This stage is equivalent to the interval of black shale deposition, and is followed by the gradual return of more diverse palynomorph assemblages.

Cyclic fluctuations in the  $\delta^{13}\text{C}_{\text{org}}$  curve in Réka Valley is not restricted to Interval 2, it occurs in Interval 1 and 3 as well. Analogous, similarly persistent orbitally forced fluctuations in  $\delta^{13}\text{C}_{\text{org}}$  are reported from the Hettangian and Lower Sinemurian mudrocks in SW England (Ruhl et al., 2010).

Differences in the shape of the CIE, described in the context of chemostratigraphic correlation above, may have a bearing on the regional differences in development of the Jenkyns Event. The bowl-shaped curve of Réka Valley is similar to other sections in the European epicontinental seaway, explained by their palaeogeographic position (Fig. 1). However, the protracted CIE without a start of rebound is more clearly expressed here

than in other sections. This feature is useful for model-data comparisons, as modelling studies attempt to simulate the cause and effect of the carbon cycle perturbation (Beerling & Brentnall, 2007).

### **Duration of the Jenkyns Event**

The duration of the Jenkyns Event is still debated despite the plethora of published studies on Toarcian localities. Short eccentricity, obliquity as well as precession were all proposed by various authors as the dominant factor driving the cyclic changes. The new data from Réka Valley are used here to provide astrochronological estimates for the duration of the CIE, understood in the narrow sense to be represented by Interval 2 in Fig. 4, and our new results are discussed in the context of previously published studies.

One of the first cyclostratigraphic studies on the Jenkyns Event was based on  $\text{CaCO}_3$  and  $\delta^{13}\text{C}_{\text{org}}$  signals measured in the Yorkshire section (Kemp et al., 2005). The authors identified precession as the dominant astronomical forcing parameter, considering radiometrically dated correlative sections and the likely dominant astronomical forcing parameter at the palaeolatitude of deposition. Suan et al. (2008b) proposed a ~550 kyr duration for the main negative excursion, corresponding to Interval 2 in Réka Valley, based on  $\text{CaCO}_3$  measurements from Peniche and grayscale signal from Dotternhausen, and assigned the dominant forcing to short eccentricity. Sabatino et al. (2009) analysed  $\text{CaCO}_3$  and  $\delta^{13}\text{C}_{\text{org}}$  signals from Valdorbja and the Monte Mangart section in the Julian Alps (Italy/Slovenia) and assigned a ~500 kyr duration for the negative CIE suggesting short eccentricity forcing. Kemp et al. (2011) revised the cyclostratigraphy of the Yorkshire section by making new, high-resolution  $\delta^{13}\text{C}_{\text{org}}$ ,  $\text{CaCO}_3$ , and sulphur concentration measurements, and proposed two possible durations for the negative

excursion assuming precession or obliquity as the key driver of the cyclic changes: the minimum duration of the excursion based on 21 kyr precession cycles is calculated as 168–189 kyr, whereas the maximum duration for the same interval, based on 36 kyr obliquity forcing, is 288–324 kyr. Boulila et al. (2014) studied the ~165 m long section of the Sancerre core from the Paris Basin. They made high-resolution magnetic susceptibility measurements, in which signal they identified long and short eccentricity, obliquity, precession and sub-Milankovitch cyclicities. For the CIE they estimated a duration of ~300 kyr, while suggesting obliquity as the dominant forcing factor. Huang & Hesselbo (2014) provided new cyclostratigraphic constraints for the Peniche, Yorkshire, Dotternhausen, and the Valdorbia sections. Based on the bulk rock  $\delta^{13}\text{C}_{\text{carb}}$  signal from Peniche, which is considered to be the most complete section, they suggest a 620 kyr duration for the negative excursion. They argue that the prominent cyclicity revealed by the previous studies is, in fact, the short eccentricity signal. They also suggest that the main forcing parameter behind the climate change shifted from precession-eccentricity before the CIE to obliquity during the CIE, and then back to precession-eccentricity. Ruebsam et al. (2014) presented magnetic susceptibility measurements from Lorraine in the Paris Basin, from which a ~600 kyr duration for the CIE was proposed. Apart from the cyclostratigraphic estimates, independent age constraints based on belemnite  $^{87}\text{Sr}/^{86}\text{Sr}$  stratigraphy in Yorkshire provide an approximate duration of ~560 kyr for the CIE of the Jenkyns Event (i.e. equivalent of Interval 2) (McArthur et al., 2000).

In the Réka Valley section a key ~2 m cyclicity is present in the  $\delta^{13}\text{C}_{\text{org}}$  and the  $\text{CaCO}_3$  signals, while the  $\text{CH}_2_{\text{FTIR}}$  signal records a cyclicity of comparable frequency. Unambiguous identification of the specific orbital components is not possible based on the available data, therefore we propose three possible durations for the CIE based on

short eccentricity, obliquity, or precession forcing. Ten prominent cycles are counted in the part of the analysed signals that match the correlative interval of the CIE related to the Jenkyns Event. The best estimate for the duration of the negative excursion at Réka Valley, based on precession, obliquity and short eccentricity, is therefore 200 kyr, 350 kyr, and 1 Myr, respectively.

The cyclicity observed in the carbon isotope records of several European sections are interpreted to reflect orbitally controlled short pulses of methane-hydrate dissociation events (Sabatino et al. 2009; Kemp et al. 2011; Huang & Hesselbo, 2014). Similarities between the Réka Valley and other European section's carbon isotope record suggest that the same phenomenon exerted a major control on the carbon isotope record in the Réka Valley. In addition, both the  $\delta^{13}\text{C}_{\text{org}}$  and the  $\text{CaCO}_3$  signals are also thought to reflect fluctuations in the productivity of marine organisms, as their main cyclicity is in the same phase.

### **Palaeoenvironmental interpretation from elemental geochemistry**

The conspicuous grouping of elements by their abundance in the samples, the variability in major element concentrations, and enrichment factors relative to the average shale suggest that the black shale is best regarded as a mixture of two endmembers, terrigenous aluminosilicates and marine carbonates (Fig. 5A-B). Despite the rather monotonous lithology, a wide range of compositional fluctuations are depicted in the Al-Si-Ca and Al-K-Ca ternary systems. This observation suggests that the significant changes in chemical composition are controlled primarily by a dilution effect. In addition, the scatter and position of the data points show that the terrigenous component of the studied samples can be characterised as Al-enriched shale.

Consequently, the terrigenous compositional endmember of the studied black shales consists of a mixture of an illitic/smectitic and a kaolinitic clay with an enhanced role of the kaolinite, a clay mineral which contains stoichiometrically only  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  in its layer silicate structure, contrary to illite and smectite which contain other cations as well (Weaver, 1989; Moore & Reynolds, 1997). Previous clay mineral studies documented that the Réka Valley black shale has high kaolinite content suggesting elevated weathering rates in the hinterland during deposition (Raucsik & Merényi, 2000; Raucsik & Varga, 2008). The Early Toarcian global warming and a resultant acceleration of the hydrological cycle delivered nutrients and freshwater to shelf seas worldwide by enhanced weathering and runoff (Bailey et al., 2003; Jenkyns, 2003; Cohen et al., 2004). A high proportion of kaolinite occurs in Lower Toarcian strata in the Peritethyan areas of the European epicontinental seaway (Dera et al., 2009), in the Lombardian Basin of the Southern Alps (Deconinck & Bernoulli, 1991), in the hemipelagic Lusitanian Basin (Duarte, 1998) and the Polish Basin (Brański, 2010), suggesting increased humidity and intense weathering in the continental hinterland during the Jenkyns Event. The observed shift in the trend of data points can be caused by a kaolinite-rich terrigenous load relative to the average shale, therefore our present geochemical data support the scenario of increased continental hydrolysis during the Jenkyns Event in the hinterland of the Mecsek Basin.

According to Plank & Langmuir (1998), geochemical variations in elemental composition, including the abundance of some alkaline metals (K, Rb, Cs), are linked to changes in the lithological composition, as their ratios in sediments are controlled by continental input and can be characterized using the  $\text{K}_2\text{O}/\text{Rb}$  ratio. In marine sediments, the alkaline elements are mainly hosted in terrigenous minerals and their distributions are predominantly controlled by dilution of biogenic material. Low  $\text{K}_2\text{O}/\text{Rb}$  ratios are



characteristic features of highly weathered and recycled sources because Rb (together with Cs) tends to be less mobile during the hydrolysis than K (Nesbitt et al. 1980; Tanaka & Watanabe, 2015). High  $K_2O/Rb$  ratios are typical of sediments rich in rock fragments derived from acidic volcanics or volcanoclastics and of sediments that have suffered K metasomatism (Plank & Langmuir, 1998). The studied samples are sharply divided into two populations, one of which shows high Rb content relative to the overall trend with  $K_2O/Rb$  ratio typical of siliciclastics derived from the upper continental crustal rocks (Fig. 6). Samples falling in this field likely represent intervals of extremely enhanced continental weathering. The stratigraphic distribution of these samples shows that more than half of them cluster in the lower part of the section between 2.4 m and 5.5 m, in the lower part (i. e. first two cycles) in Interval 2, suggesting that weathering was most intense at the beginning of the CIE. A similar timing of peak weathering is suggested by a Ca isotope anomaly in the Peniche section (Brazier et al., 2015).

## CONCLUSIONS

Deposition of a 12 m thick black shale unit in the Lower Toarcian section of Réka Valley has been previously associated with anoxic conditions during the Jenkyns Event, but results from a high-resolution sampling are reported here for the first time. The new data from the Mecsek basin, located east of other well-studied sites in the Early Jurassic European epicontinental seaway, adds to our understanding of overall similarities and subtle regional differences of the sedimentary and geochemical record of the Jenkyns Event. Nannoplankton biostratigraphy allow recognition of Lower Jurassic zones NJ5b, NJ6 and NJ7 and permit correlation with several classical sections. The obtained  $\delta^{13}C_{org}$  curve is subdivided into three intervals, which are readily correlatable with those

established at Peniche (Hesselbo et al., 2007) and recognized in all other high-resolution datasets. The bowl-shaped main negative CIE has a magnitude of -5.3‰ locally, and the first two steps are essential in its development, with drops of -4.2‰ and -3.2‰, respectively. The onset of black shale deposition follows the second carbon isotope step, after which  $\delta^{13}\text{C}$  values remain very negative but are cyclically fluctuating. The recovery interval of the CIE with rising but still fluctuating values precedes the termination of black shale deposition. FTIR analyses suggest that only the amount but not the main source of the organic matter changed cyclically during the CIE. The  $\delta^{13}\text{C}$  and FTIR data, together with elemental abundances (primarily Ca and Ti) measured by the XRF method, are the basis for cyclostratigraphy. Interval 2 of the main negative CIE is shown to comprise 10 cycles. Assuming these to represent a Milankovitch cyclicity, new astrochronologic estimates can be made for the duration of the CIE as 200 kyr, 350 kyr or 1.0 Myr, based on precession, obliquity, or short eccentricity forcing, respectively. These values are within the range of previously proposed durations. Enhanced weathering in the hinterland is supported by the elemental analyses, indicative of kaolinite dominance in the terrigenous clay fraction. The most intense period of weathering is recorded in the lower part of the section, below and at the onset of black shale sedimentation. The expanded stratigraphic record of the Jenkyns Event in black shale facies in the Réka Valley holds promise for subsequent more diverse studies.

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## FIGURE CAPTIONS

**Fig. 1.** (A) Location of the Réka Valley section (orange star) in southern Hungary. (B) Global palaeogeographic setting of the western Tethys (boxed area enlarged in (C)) during the Early Jurassic (after Woodfine et al., 2008). (C) Early Jurassic palaeogeographic configuration of the western Tethys (after Bassoulet et al. 1993 and Mattioli et al. 2008), showing the location of the Réka Valley section in the Mecsek basin (orange star) and other localities with  $\delta^{13}\text{C}$  record of the Jenkyns Event discussed in the text: 1– Peniche (Lusitanian Basin), 2 – Yorkshire, 3 – Denkingen, Dotternhausen (SW German Basin), 4 – Sancerre, Lorraine (Paris Basin), 5 – Valdorbia (Umbria-Marche

Basin), 6 – Trento Platform. (D) Outcrop view of the naturally exposed part of the Lower Toarcian black shale in the Réka Valley. (E) Close-up view of slabs of the laminated black shale in the Réka Valley section.

**Fig. 2.** Stratigraphic distribution of  $\delta^{13}\text{C}_{\text{org}}$  data, nannofossil abundance counts,  $\text{CaCO}_3$  content,  $\text{K}_2\text{O}/\text{Rb}$  ratios, and  $\text{CH}_2_{\text{FTIR}}$  measurements along the Réka Valley section. On the lithology log black colour denotes the black shale, i.e. the Rékavölgy Formation, and brown denotes the spotted marl, i.e. the underlying Hosszúhetény Formation and the overlying Komló Formation. Turbiditic sandstone interbeds are coloured green. First occurrence (FO) and last occurrence (LO) of nannofossils are from this study.

**Fig. 3.**  $2\pi$ -MTM power spectra of the detrended  $\delta^{13}\text{C}_{\text{org}}$ ,  $\text{CaCO}_3$ , and  $\text{CH}_2_{\text{FTIR}}$  signals. The blue shaded areas show the range of the filters corresponding to the prominent  $\sim 2$  m cyclicity. The frequency domains of the filters are set as 0–1.13 cycles/m, 0–1.25 cycles/m, and 0–1.1 m in the case of the  $\delta^{13}\text{C}$  signal, the  $\text{CaCO}_3$  signal, and the  $\text{CH}_2_{\text{FTIR}}$  signal, respectively. The thick blue lines superimposed on the detrended signals are the filter output signals. The thick dashed lines show the lower and upper boundary of Interval 2 (see Fig. 4).

**Fig. 4.** Chemostratigraphic correlation of several well-known Lower Toarcian sections with the Réka Valley section. The  $\delta^{13}\text{C}$  curves are from Hesselbo et al. (2007, Peniche), Kemp et al. (2011, Yorkshire), Suan et al. (2015, Denkingen), Hermoso et al. (2012,



Sancerre), Ruebsam et al. (2014, Lorraine), Sabatino et al. (2009, Valdorbia), Woodfine et al. (2008, Trento).

**Fig. 5.** (A) Al-Si-Ca ternary diagram (Rachold & Brumsack, 2001) of black shale samples from the Réka Valley section. (B) Al-K-Ca ternary diagram (Hutcheon et al., 1998) of black shale samples from the Réka Valley section.

**Fig. 6.** K<sub>2</sub>O/Rb diagram (Plank & Langmuir, 1998; Di Leo et al., 2002) of black shale samples from the Réka Valley section.