

# Climate change at the Triassic/Jurassic boundary in the northwestern Tethyan realm, inferred from sections in the Tatra Mountains (Slovakia)

JOZEF MICHALÍK<sup>1</sup>, ADRIAN BIROŇ<sup>1</sup>, OTÍLIA LINTNEROVÁ<sup>2</sup>, ANNETTE E. GÖTZ<sup>3</sup> AND KATRIN RUCKWIED<sup>4</sup>

<sup>1</sup>*Slovak Academy of Science, Geological Institute, Dúbravská 9, Box 106, 84105 Bratislava, Slovakia.  
E-mail: geolmich@savba.sk; biron@savbb.sk*

<sup>2</sup>*Comenius University, Faculty of Sciences, Mlynská dolina, 84215 Bratislava, Slovakia.  
E-mail: lintnerova@fns.uniba.sk*

<sup>3</sup>*Darmstadt University of Technology, Institute of Applied Geosciences, Schnittspahnstrasse 9, 64287 Darmstadt, Germany. E-mail: goetz@geo.tu-darmstadt.de*

<sup>4</sup>*Shell International Exploration and Production B.V., Kessler Park 1, 2288 GS Rijswijk, The Netherlands.  
E-mail: Katrin.Ruckwied@shell.com*

## ABSTRACT:

Michalík, J., Biroň, A., Lintnerová, O., Götz, A.E. and Ruckwied, K. 2010. Climate change at the Triassic/Jurassic boundary in the northwestern Tethyan realm, inferred from sections in the Tatra Mountains (Slovakia). *Acta Geologica Polonica*, **60** (4), 535–548. Warszawa.

Sedimentological, palynological, clay mineralogical and carbon isotope studies were carried out on the Triassic/Jurassic (T/J) boundary interval in the NW Tethyan Realm. The analyses are based on two sections in the Slovakian Tatra Mountains (Western Carpathians): the Široký Žľab section in the Meďodoly Valley and the Furkaska section above the Juráňova Valley. Clay mineralogical analysis suggests an increasing intensity of chemical weathering in the hinterland due to increasing humidity. The palynological data do not allow the inference of a major T/J boundary mass extinction event. The observed striking increase in spores points instead to sudden climatic change, interpreted as a result of distant volcanic activity associated with the onset of rifting of Pangea. The  $\delta^{13}\text{C}_{\text{org}}$  excursion across the T/J boundary follows the globally documented perturbation of the carbon cycle during this period. It may be used for a more precise regional and global correlation.

**Key words:** Triassic/Jurassic boundary; Palynology; Carbon isotopes; Clay mineralogy; Palaeoclimate.

## INTRODUCTION

The Late Triassic–Early Jurassic boundary is marked by a change from a dry climate regime into more humid conditions. This overturn is clearly recognizable by an abrupt change in the palaeobiological, sedimentary and isotopic record. The climate change is also often suggested as the main cause of the T/J boundary extinction

event, one of the most prominent features of the Phanerozoic fossil record, although its possible causes are still highly controversial and hotly debated (Kiessling *et al.* 2007; Gómez *et al.* 2007; Tanner and Lucas 2007).

During Rhaetian–Early Jurassic times the central Western Carpathian part of the northern Tethyan shelf was locally influenced by terrestrial input from the hin-

terland. In emerged areas, terrigenous deposits of the Carpathian Keuper are covered by Rhaetian sediments represented by lacustrine to palustrine black silty shale (Tomanová Formation) with abundant plant fragments (Michalík *et al.* 1988), intercalations of quartz sandstones locally with dinosaur footprints (Michalík *et al.* 1976; Niedźwiecki 2004) and sphaerolitic iron ores. The clay minerals are dominated by kaolinite (Kraus 1989; Środoń *et al.* 2006). Two microfloral associations have been described by Planderová (in Michalík *et al.* 1976): lacustrine shales yielding sporomorphs such as *Taenispores* sp. and *Protohaploxylinus* sp. and a pollen-dominated (*Classopollis*) association preserved in fluvial sandstones. The macroflora is dominated by Triassic ferns (Hlušík in Michalík *et al.* 1988). The Rhaetian palynomorph assemblage of the Fatra Formation is characterized by numerous specimens of *Ricciisporites tuberculatus*. The marine fraction is dominated by the dinoflagellate cyst *Rhaetogonyaulax rhaetica*. This microflora is very similar to the *Ricciisporites tuberculatus* Zone of the Polish scheme published by Orłowska-Zwolińska (1983) and the *Ricciisporites-Polypodiisporites* Zone of the southeast North Sea Basin published by Lund (1977), both indicating middle to late Rhaetian age. The lowermost Hettangian palynomorph assemblage of the Kopieniec Formation is characterized by a significant increase in trilete laevigate spores, mainly *Deltoidospora* spp. and *Concavisporites* spp. The dinoflagellate cyst *Dapcodinium priscum* replaces *Rhaetogonyaulax rhaetica* in the marine fraction. The

overlying Lower Jurassic sequence consists of shallow marine sandy limestones.

The area farther to the south was inundated by a shallow sea (Michalík 2007). Rhaetian neritic carbonates of the Fatra Formation were overlain by shales of the Hettangian Kopieniec Formation. The Fatra Formation, well exposed in the Tatra Mountains (Gaździcki *et al.* 1979, Michalík *et al.* 2003, 2007; Text-fig.1), consists of bioclastic limestones and marls deposited in a proximal marine setting. Its benthic fauna comprises index foraminifers (*Triasina hantkeni*), bivalves (*Rhaetavicula contorta*), corals (*Retiophyllia paraclathrata*) and brachiopods (*Austrirhynchia cornigera*). A diversity decrease at the base of the uppermost member of the Fatra Formation indicates freshwater input. Eutrophication caused by continental run-off resulted in retreat of oligotrophic carbonate platform ecosystems (Soták in Michalík *et al.* 2003).

The Rhaetian Fatra Formation is overlain by dark brown clays of the so-called "Boundary Clay" Member, and by sandstones of the "Cardinia Sandstone" Member of the Lower Jurassic Kopieniec Formation. Based on microfacies analyses and a negative  $\delta^{13}\text{C}_{\text{carb}}$  excursion, the boundary interval is placed near to the lithological boundary (Michalík *et al.* 2007).

In the context of the IGCP 458 (Triassic-Jurassic Boundary Events) project, Michalík *et al.* (2007) investigated environmental changes within the T/J boundary interval in the Western Carpathians. The present study focuses on sedimentological and palynological



Text-fig. 1. Map showing the location of studied sections (Furkaska, Široký Žľab) in the Tatra Mountains

features, as well as on carbon isotope signatures of organic matter and on clay mineral distribution with respect to a global climatic change during Late Triassic–Early Jurassic times.

## MATERIALS AND METHODS

The study is based on sample sets of two key sections in the Tatra Mountains (Text-fig. 1). The Široký Žľab section is situated in the Meďodoly Valley below Mt Ždiarska Vidla and represents the marginal part of the basin affected by fluvial influx. The Furkaska section is located above the Juráňova Valley in the Western Tatra Mountains, documenting deposits of the proximal basin (Michalík *et al.* 2003, 2007). Finally, the Kardolína section is exposed on the western slope of Mt Pálenica near Tatranská Kotlina. The T/J boundary interval was sampled ‘bed-by-bed’ and studied in thin sections.

### Palynological analyses

Palynofacies analysis of the Furkaska section was carried out on a total of 12 samples, taken from shaly layers and carbonate beds. All samples were prepared using standard palynological processing techniques, including HCl (33%) and HF (73%) treatment for dissolution of carbonates and silicates, and saturated ZnCl<sub>2</sub> solution (D ≈ 2.2 g/ml) for density separation. Residues were sieved at 15 μm mesh size and slides mounted in Eukitt, a commercial resin-based mounting medium. The relative percentages of sedimentary organic constituents are based on counting at least 400 particles per slide.

### Isotope analyses

For δ<sup>13</sup>C<sub>org</sub> analyses 38 samples were selected from the “transitional member” of the Fatra Formation in the Furkaska section and 10 samples from the Jurassic Kopianiec Formation in the Široký Žľab section. Total organic (TOC) and inorganic (TIC) carbon contents were measured with a C-MAT 550 mass spectrometer. TIC values were recalculated to CaCO<sub>3</sub> content to assess the carbonate content in the rocks and to select samples for the C isotope analyses of organic matter. Total organic carbon isotope analyses were carried out after carbonate dissolution. Samples were boiled in dilute (10%) hydrochloric acid, rinsed repeatedly with de-ionized water to remove chlorides and dried at 60 °C. The δ<sup>13</sup>C measurements were performed by flash combustion in a Fisons 1108 elemental analyzer coupled with a Mat 251 isotope ratio mass spectrometer in a continuous flow regime. The sample size was adjusted to contain a

sufficient amount of organic carbon to obtain external reproducibility of 0.15 ‰ for δ<sup>13</sup>C<sub>org</sub> for all types of samples with NBS 22 as the reference material. Isotopic data are reported in the usual delta (δ) notation relative to the Vienna International Isotopic Standard (VPDB).

Carbon (and oxygen) isotope analyses were carried out on the bulk carbonate fraction of samples from the T/J boundary interval of the Furkaska section and on samples from the uppermost carbonate beds from the Široký Žľab section using a Finigan MAT-2 mass spectrometer. The values are reported in terms of Vienna-PDB (V-PDB) in the standard δ notation in ‰, with a precision of 0.01‰. Both types of isotope analyses were carried out in the Czech Geological Survey Laboratory in Prague.

Both the carbon and oxygen isotope ratio results from carbonates of the Fatra Formation were previously discussed by Michalík *et al.* (2007). Due to the very low carbonate content in the lowermost Jurassic beds, the δ<sup>13</sup>C<sub>carb</sub> isotope data obtained did not document the typical carbon isotope excursion reported in the T/J boundary interval elsewhere. The δ<sup>13</sup>C<sub>carb</sub> data were graphically correlated with newly obtained values of δ<sup>13</sup>C<sub>org</sub> from the T/J boundary interval of both sections. The δ<sup>18</sup>O<sub>carb</sub> data by Michalík *et al.* (2007) served as a criterion of sample suitability for δ<sup>13</sup>C<sub>carb</sub> analysis only. Although they can be used to discuss the diagenetic overprint, they could not be directly related to the diagenetic temperature data of clays reported in this paper.

### Clay mineralogical analyses

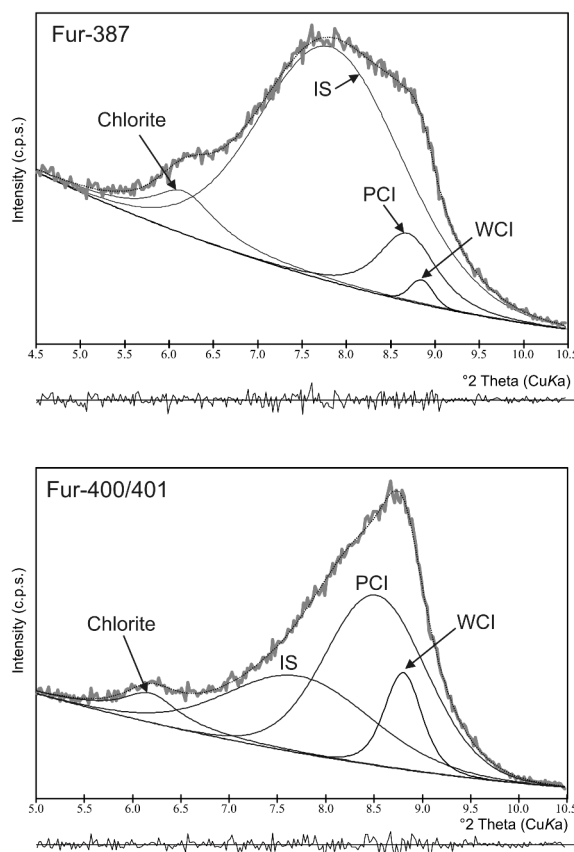
A total of 45 Upper Triassic–Lower Jurassic sediment samples (claystones, mudstones, marls and marly limestones) of the Furkaska and the Široký Žľab sections was investigated by X-ray diffraction (XRD). The sampled intervals cover the uppermost part of the Carpathian Keuper, the entire Fatra Formation and the lowermost part of the Kopianiec Formation.

The samples used for clay mineralogy determination were washed, crushed and subsequently ground with pestle and mortar, sieved under 0.16 mm, soaked in distilled water, ultrasonically disaggregated, and then treated chemically following the standard procedure of Jackson (1975). The <2 and <0.2 μm fractions were separated by gravity settling in Atterberg cylinders and by centrifugation, respectively. The suspensions were then coagulated with saturated NaCl. The Ca<sup>2+</sup> was introduced as the only exchange cation using CaCl<sub>2</sub> solution (three times for 24 hours). Finally, the suspension was cleaned of the excess electrolyte by repeated centrifugation followed by dialysis. The material was dried and oriented preparations were produced.

The “infinite thickness” of preparations (10 mg/cm<sup>2</sup>) required for semi-quantitative determination of clay minerals was controlled by precise weighing (Moore and Reynolds 1997).

XRD analyses were performed on a Philips PW1710 diffractometer using CuK $\alpha$  radiation (40 kV, 20 mA) and a diffracted beam graphite monochromator. The beam was collimated with a 1° divergence slit and a 0.2 mm receiving slit. Recordings were carried out both in air-dried state and after vaporisation with ethyleneglycol at 60°C overnight. Samples were scanned from 2–50° 2 $\theta$  with step size 0.02° 2 $\theta$  and 1.25 seconds counting time. Additionally, randomly oriented preparations of <2  $\mu$ m fractions of selected samples were prepared using side-loading method and measured from 55–70° 2 $\theta$  (5 s per 0.02° 2 $\theta$  step) in order to determine the *d* (060) value of phyllosilicates.

Identification of clay minerals was conducted mainly according to the position of the (001) series of basal reflections on the three XRD diagrams (Brown and Brindley 1980; Moore and Reynolds 1997). The identification of the mixed-layer illite-smectite and



Text-fig. 2. Relative estimation of the illite and illite-smectite content in 10-Å diffraction band (WCI – well-crystallized illite, PCI – poorly crystallized illite, according to Lanson 1997); A – Furkaska section, bed 387, B – Furkaska section, beds 400/401

measurements of the percentage of expandable component layers (%S) were performed by peak-position methods (Środoń 1980, 1984; Dudek and Środoń 1996) on XRD patterns obtained from oriented, glycolated preparations of <0.2  $\mu$ m fractions.

The percentage of clay minerals in the <2  $\mu$ m grain-size fraction was estimated semi-quantitatively by measuring the integrated peak areas of their (main) basal reflections on air-dried oriented mounts. Computer-based evaluation of XRD patterns was carried out using Krumm's (1994) WINFIT program, which determines the peak areas by the peak fitting through a symmetrical Pearson VII profile function. In order to estimate relative illite and illite-smectite contents, mathematical decomposition of reflection near 10 Å was employed. The concept of Lanson (1997) was adopted, which defines the complex 10-Å diffraction band as being composed of three major components: mixed-layer illite-smectite, poorly crystallized illite, and well-crystallized illite. Examples of such decomposition are shown in Text-fig. 2. In this study, the sum of integrated areas of poorly and well-crystallized illite bands is used to express the illite content.

The chlorite (002) + kaolinite (001) doublet at 7.3 Å was used to determine their relative contents. To resolve peak areas from both minerals, coincident peaks were subdivided using the intensity ratio of chlorite (004) at 3.54 Å and kaolinite (002) at 3.58 Å (Biscaye 1964). Relative clay mineral contents were calculated by using empirically estimated weighted factors according the formula: kaolinite/2.5 + chlorite/2 + mixed-layer illite-smectite + illite = 100% (Weir *et al.* 1975).

Since no attempt was made to evaluate the accuracy of the method, these measurements should be considered as semi-quantitative. However, it was not our goal to identify exact quantities of minerals but to show vertical clay mineral trends.

## RESULTS

### Palynofacies and palynology of the Furkaska section

Sedimentary organic matter from the Furkaska section is dominated by terrestrial particles (Text-fig. 3). The marine fraction is very small and composed mainly of the dinoflagellate cyst species *Dapcodinium priscum* and *Rhaetogonyaulax rhaetica*. Degraded organic matter (DOM) makes up to 50 % of the palynofacies assemblage.

The distribution pattern of organic particles points to very shallow marine conditions. The relatively high amount of DOM indicates a high-energy depo-

sitional system. In the lower part of the Furkaska section, which belongs to the Rhaetian Fatra Formation, the ratio of pollen grains and spores is well balanced. A striking spore shift in bed 408 changes this proportion to a spore-dominated sporomorph assemblage during the Early Hettangian time interval (Text-fig. 3). However, the dominance of phytoclasts and sporomorphs within the palynomorph assemblage points to an oxidizing environment with a close proximity to fluvio-deltaic sources (cf. Tyson 1995, p. 448).

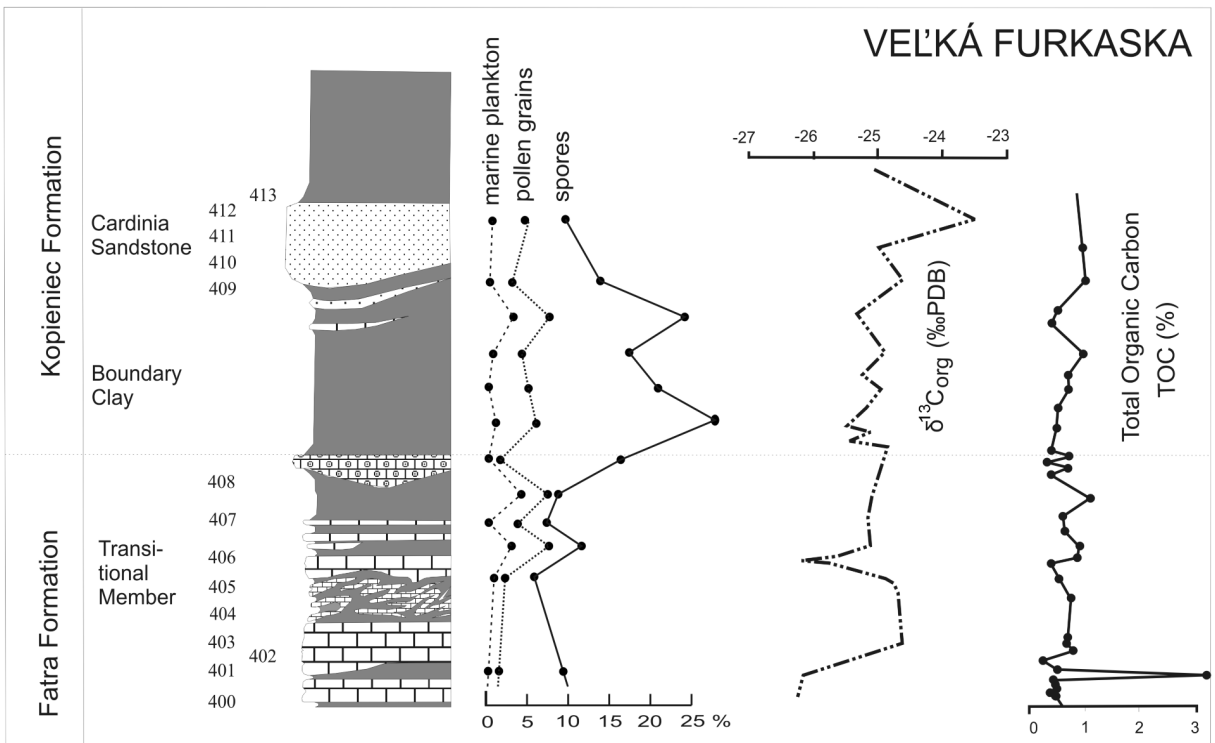
The sporomorph assemblage is very similar to the assemblages of the Polish Basin (Orłowska-Zwolińska 1983) and to the assemblages of the Austrian Kössen Beds (e.g., Kuerschner *et al.* 2007), displaying a close palaeogeographic relationship of these areas during Rhaetian and Hettangian times. Palynomorphs of the Furkaska section in the Slovakian Tatra Mountains are well preserved and show distinct changes within the boundary interval. The sudden increase in the abundance of trilete spores, mainly *Deltoidospora* spp. and *Concavisporites* spp., the last appearance of *Corollina* spp., and the first appearance of *Pinuspollenites minimus* are diagnostic features for the recognition of two distinct palynomorph assemblages.

A Principal Components Analysis (PCA) was performed on 11 samples and 59 sporomorph species as

variables (Text-fig. 4). The principal plane for the first two principal components is shown in Text-fig. 4. The distances between the projected points on this plane are a measure of similarity (cf. Marinoni 2006). The smaller the distance, the higher is the similarity. The PCA results show that all Jurassic samples that were taken above sample horizon 408 are well clustered whereas samples below sample horizon 408 can be clearly distinguished from the sample upsection. All samples in the “Jurassic cluster” are characterized by a very high abundance and diversity of trilete spores. Sample 400/401 is the lowest and oldest sample in the Furkaska section. It can clearly be identified as an outlier indicating a different pattern regarding the variables analysed. Previous studies detected a striking change in the microfloral assemblage from the middle to the upper Rhaetian (Kuerschner *et al.* 2007). The PCA results presented here can therefore be regarded as multivariate evidence for this microfloral change between the middle and upper Rhaetian. A very similar clustering pattern was identified in the Cluster Analysis which was carried out with the same data set as used with the PCA (Ruckwied and Götz 2009).

#### Organic matter and $\delta^{13}\text{C}_{\text{Org}}$ analyses

Low values of TOC (0.1 to 0.4%) observed in the carbonate sequence of the sections studied indicate

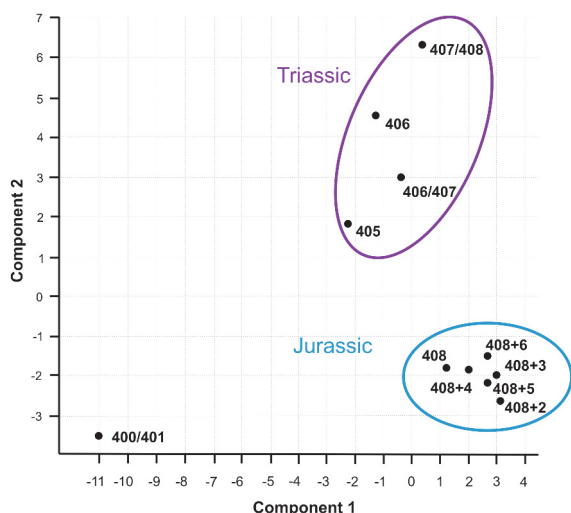


Text-fig. 3. Relative abundance of palynomorphs (marine plankton, pollen grains, spores) of total sedimentary organic matter (palynomorphs, phytoclasts, degraded organic matter), total organic carbon (TOC) content and  $\delta^{13}\text{C}_{\text{Org}}$  values; Furkaska section

normally aerated water conditions (Text-figs 5 and 6). An increased content of TOC (1.24 % and 2.83 %) was detected in two samples from the uppermost part of the Fatra Formation (398/399, 400) in the Furkaska section only. Generally, the enrichment in organic matter indicates an over-production and/or an increased input of organic matter from the hinterland followed by its effective burial during sedimentation. One such  $C_{org}$ -enriched bed occurs above the limestone bed with the last megalodonts (398/399) and the second one is intercalated in so called "spherulae beds" (Michalík *et al.* 2007). Both layers are overlain by limestones poor in fossils. Nevertheless, the organic carbon enrichment can hardly be directly related to a biotic extinction event.

Occasional TOC increase to 0.6–0.7 % (Text-fig. 5) in the T/J boundary interval and in the lowermost part of the Hettangian Kopienec Formation (0.7–0.9 %) is expected to correspond with a higher input of terrestrial organic matter carried together with detritic sediment from the weathered hinterland. Specific iron-enriched (oolite) sediments and kaolinite clay occurrence in the T/J boundary interval suggests an increased weathering due to climatic change in the emerged area. This interpretation is in accordance with sedimentological and palynological data.

The  $\delta^{13}C_{org}$  values of marly sediments of the Furkaska section range between –24.78 and –29.36 ‰ (Text-fig. 5). Isotope values from this part of the Fatra Formation are close to –27 ‰. A positive excursion of the  $\delta^{13}C_{org}$  (–25 ‰) appears above bed 401 in the uppermost part of the so called "transitional beds" (Michalík *et al.* 2007) with a high TOC content. This part of the sequence contains a synsedimentary slump



Text-fig. 4. Principal Components Analysis of palynological samples from the Furkaska section

and small channels filled with redeposited oolitic and detrital material. The first negative  $\delta^{13}C_{org}$  excursion occurs just above the slump (bed 406), still below the top of the carbonate deposits of the Fatra Formation, accompanied by a striking negative  $\delta^{13}C_{carb}$  excursion (Michalík *et al.* 2007). The two basal members of the Hettangian Kopienec Formation (the Boundary Clay, as well as the Cardinia Sandstone) are characterized by a slightly positive trend of the  $\delta^{13}C_{org}$  curve. The second, major negative  $\delta^{13}C_{org}$  excursion (up to –29.36 ‰, i.e. –4 ‰ in comparison with the average) occurs upsection, in the calcareous "lower limestone member" (Gaździcki *et al.* 1979, Michalík *et al.* 2007; beds 415–416). In conclusion, the  $\delta^{13}C_{org}$  values (around –28 ‰) fit with a typical Hettangian excursion (Ward *et al.* 2007).

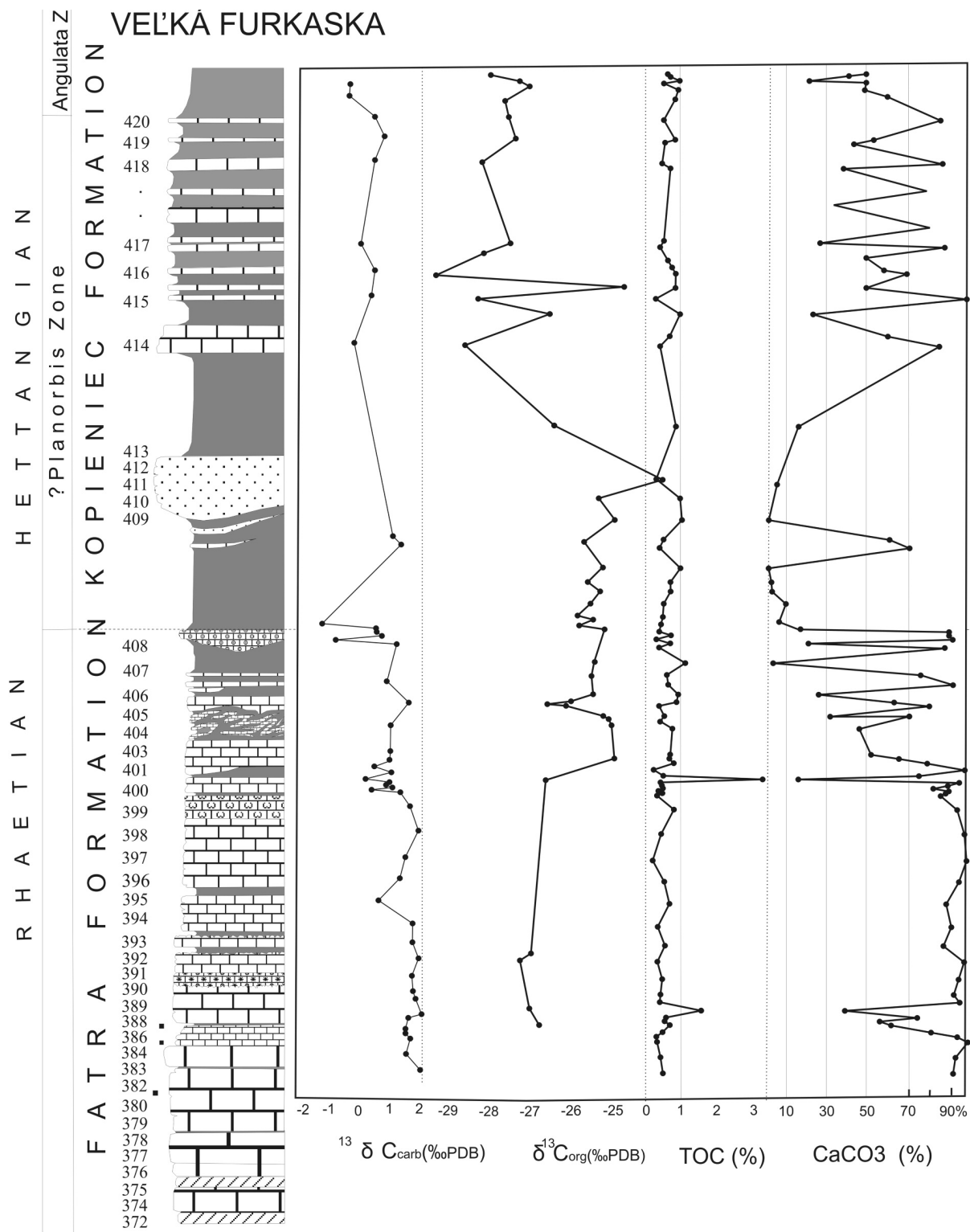
$\delta^{13}C_{org}$  values of the Kopienec samples from the Široký Žľab (Mt. Vidla) section range between –25.81 and –27.47 ‰ (Fig. 6). Although the  $\delta^{13}C_{org}$  data from this section are not supported by any new palynological or micropalaeontological sampling yet, the  $\delta^{13}C_{org}$  data resemble the second negative isotope excursion observed in the Furkaska section and, together with the clay mineralogical data, point to an early Hettangian humid event.

### Clay mineralogy

In the Furkaska section, mixed-layer illite-smectite and illite dominate the entire stratigraphic interval, constituting 79% to 98% of the clay mineral fractions (Text-fig. 7). However, their relative ratios vary significantly. In general, the content of illite-smectite increases from the Carpathian Keuper (34% on average) towards the Kopienec Formation (47% to 85%). An increase in illite-smectite coincides with a decreased illite content from 65% to 4%. This continuous trend is disturbed near the Fatra/Kopienec Formation boundary (between beds 400 and 407) where illite suddenly reaches a local maximum of 63%. Mixed-layer illite-smectite shows R1 or R>1 (R = Reichweite; Reynolds 1980) type of ordering. The percentage of expandable (=smectitic) layers gradually increases upsection with a rapid increase from ~6% to ~20 %S observed at the Carpathian Keuper/Fatra Formation boundary. Kaolinite appears in the uppermost part of the Fatra Formation (~2%), increases gradually to reach a peak abundance of 11% below bed 409 in the Kopienec Formation and decreases to ~5% (Text-fig. 7) upsection. Chlorite is present throughout the section, varying between 4% and 21%. Traces of mixed-layer chlorite-smectite occur sporadically; however, this phase was not included in semi-quantitative calculations.

Besides the quantitative mineralogical changes, the compositional variability of clay minerals was also recorded. The XRD characteristics of illitic material

separated from Carpathian Keuper mudstones reveal significant octahedral substitution of Fe, as indicated by a low 002/001 intensity ratio, as well as by the *d*



Text-fig. 5. Distribution of organic carbon and  $\delta^{13}\text{C}_{\text{org}}$  in the T/J boundary interval of the Furkaska section

(060) spacing near 1.503 Å. Text-fig. 7 also shows the variability of the octahedral composition of chloritic minerals across the profile expressed as a variation of the intensity ratio R (Fransolet and Schreyer 1984). Fe-Mg chlorite ( $R < 0.46$ ) dominates the entire section with two exceptions encountered in the upper part of the Fatra Formation (between beds 387 and 389 and between beds 405 and 406), where it is replaced (or mixed) with Mg-Al variety ( $R = 0.64\text{--}0.94$ ). Its sudoite-like composition was also confirmed by the position of the 060 reflection varying between 1.509 and 1.511 Å.

In the Široký Žľab (Mt. Vidla) section, illite-smectite (83%) prevails over illite (8%) in the uppermost part of the Carpathian Keuper mudstones only (Text-fig. 8). In contrast, Rhaetian and Hettangian claystones are marked by a slight dominance of illite over illite-smectite. Percentages of both minerals in this interval show steady-state distributions oscillating around average values of 50% and 35% respectively. The Carpathian Keuper mudstones contain R1 ordered IS with the % S in a 21–17% range. These values are slightly higher than those observed in overlying strata where expandabilities vary from 18% to 9% S (R1 or  $R > 1$  ordering). Chlorite is a minor (4% to 14 %) but omnipresent component in the material studied. No clear vertical trend of chlorite distribution was observed. Kaolinite is sparse in the Carpathian Keuper and in the Fatra Formation (<3%). The lower part of the Kopianec Formation is marked by a gradual increase in kaolinite, which reaches a maximum of 9% in bed 46. However, kaolinite disappears in the uppermost sample of the section (bed 47).

## DISCUSSION

Clay minerals and their relative abundance may record information on climate, however, the influence of eustasy, burial diagenesis and reworking should be also taken into account. Particularly, the relative abundance of kaolinite (the most important climate-sensitive clay mineral indicator in this study) as a detrital mineral may be affected by proximity of the depositional area to the source area and by the intensity of postsedimentary alteration (Chamley 1989; Thiry 2000; Ruffell *et al.* 2002).

The degree of diagenesis of the Mesozoic samples is relatively high as indicated by advanced illitization observed in shales of both sections. The low content of smectite interlayers (<5–25% S) and the R1 to  $R > 1$  ordering of IS indicate diagenetic conditions

corresponding to a burial temperature of at least 160–170°C (e.g. Pollastro 1993; Środoń 1999). Estimated temperatures are in good accordance with data given by Środoń *et al.* (2006) for Mesozoic sedimentary units of the Polish part of the Tatra region. Also the presence of unusual sudoite-like Mg-Al chlorite in four samples from the Fatra Formation of the Furkaska section, instead of the commonly encountered tri-trioctahedral chlorite, probably indicates a strong influence of diagenetic fluids with high Mg activity (also accompanied by carbonate dolomitization). However, the above mentioned diagenetic alterations are usually considered to be kaolinite-consuming, rather than kaolinite-producing ones. Therefore, the origin of kaolinite in our samples is interpreted here as detrital. Kaolinite develops typically in tropical soils which are characterized by warm, humid climates, well-drained areas with high precipitation and accelerated leaching of parent rocks (Robert and Chamley 1991; Ruffell *et al.* 2002).

Both sections reveal a strikingly similar distribution of kaolinite. It appears only in the boundary claystones, while underlying strata are free of kaolinite with one exception recognized in the Široký Žľab (Mt. Vidla) section (Kraus 1989). Moreover, the Furkaska section is also characterized by a relatively continuous increase in IS content at the expense of discrete illite. These changes are interpreted here as a response to increasing intensity of chemical weathering in the hinterland due to increasing humidity. The persistent prevalence of IS (most probably originating from a smectitic precursor) in clay-size fractions of both Rhaetian and Hettangian samples, however, may suggest that the source material for these sediments was formed during weathering in seasonally wet and dry climates (Righi and Meunier 1995). Another line of evidence in favour of both climatic and environmental turnover during the Rhaetian comes from a change of chemical composition of illitic material. Authigenic Fe-illite, characteristic of the Carpathian Keuper mudstones, is indicative of playa oxidizing conditions of arid/semi-arid climate (Środoń 1999). The overlying strata of the Kopianec Formation do not show such characteristics.

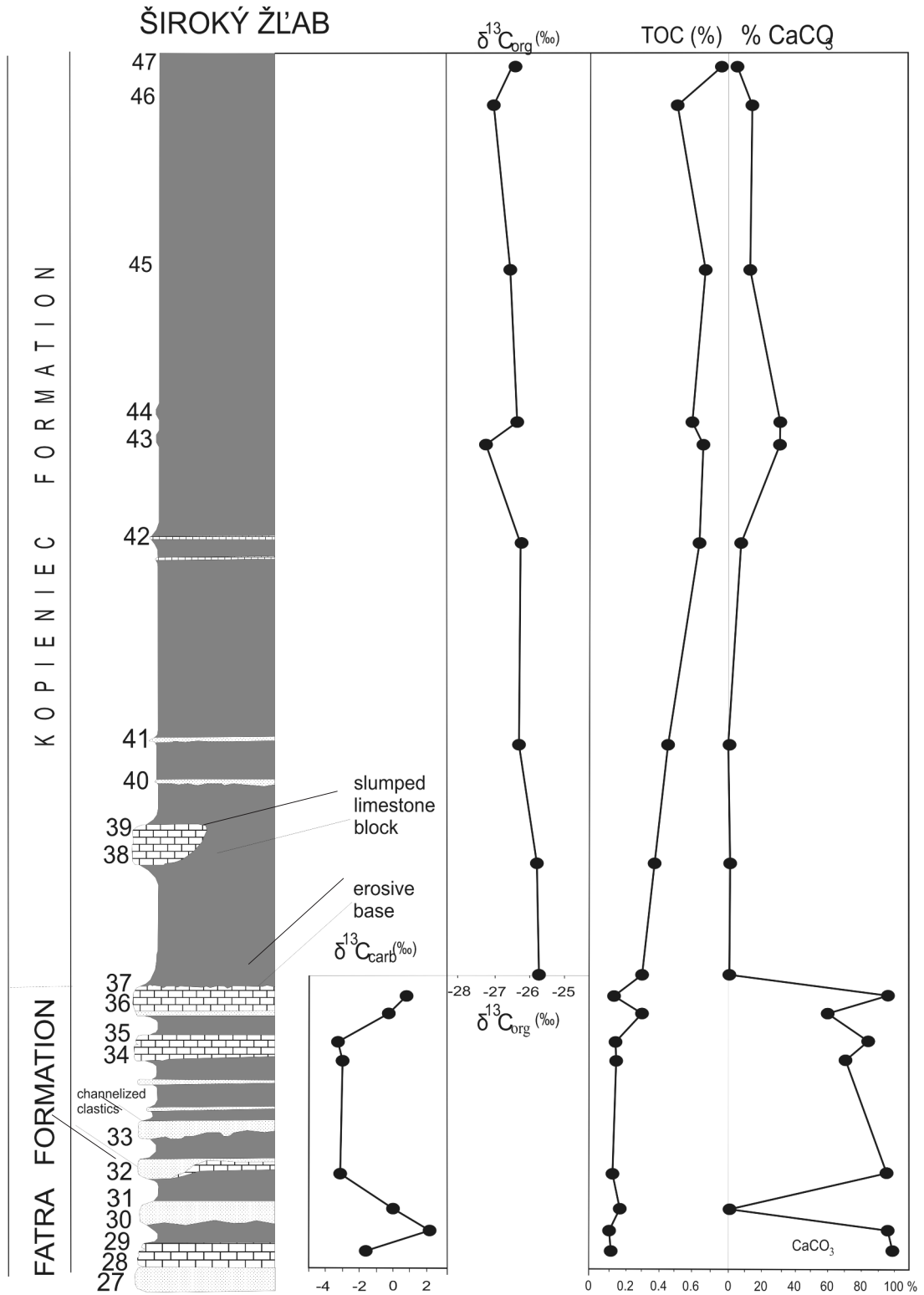
Several authors have tried to use geochemical data as a correlation tool of the T/J boundary (McRoberts *et al.* 1997; Pálffy *et al.* 2001; Hesselbo *et al.* 2002, 2004; Ward *et al.* 2004). Despite many local differences (Williford *et al.* 2007), two negative  $\delta^{13}\text{C}_{\text{org}}$  excursions have been recognized in the T/J boundary interval in different sections world-wide.

The lower negative excursion (about 2–4 ‰ of organic carbon) is isochronous with the LO of Rhaetian



ammonites (Guex *et al.* 2003) and the LO of conodonts (Pálfy *et al.* 2001; Lucas *et al.* 2005). Remarkably, this anomaly occurs close to syndimentary

slumped beds recorded in distant sections of the UK (Simms 2007), Hungary (Pálfy and Dosztály 2000), and Slovakia (Michalík *et al.* 2007).

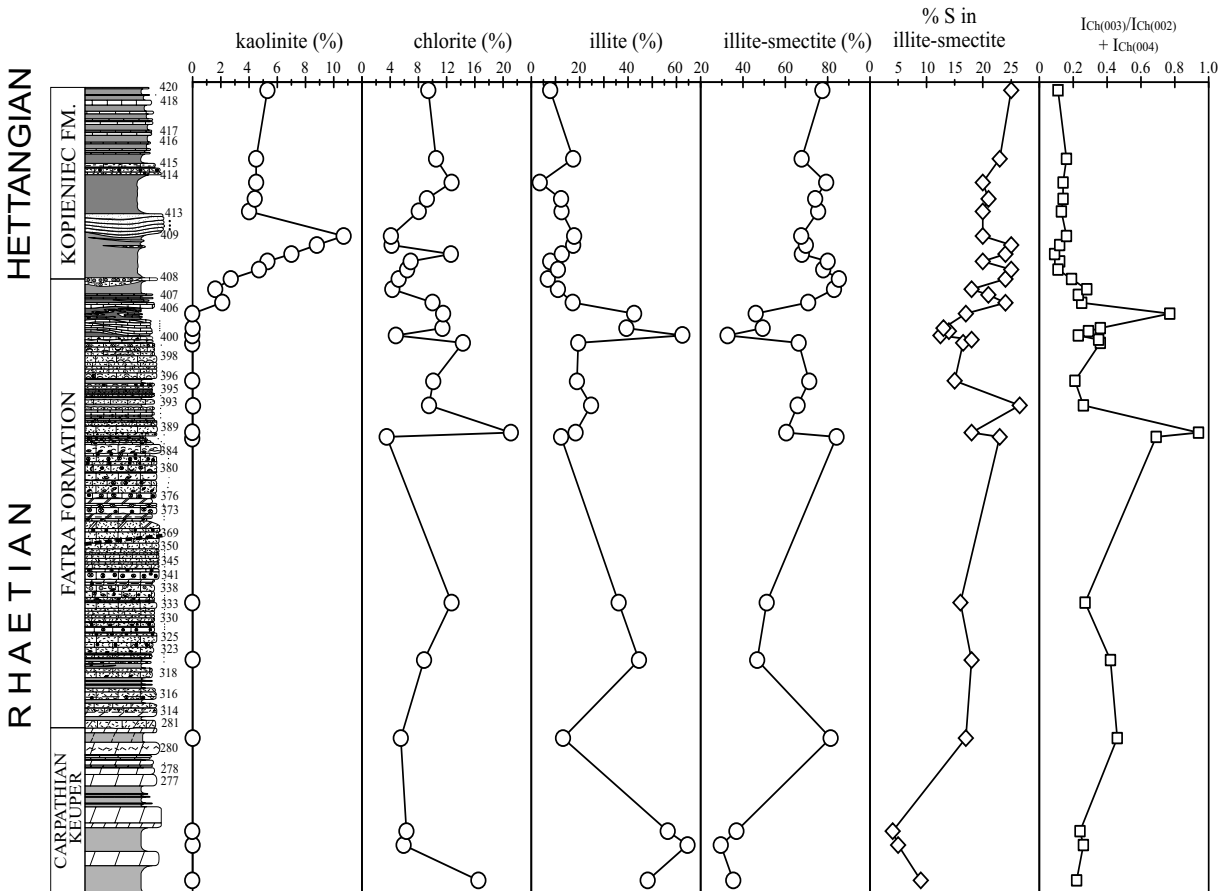


Text-fig. 6. Distribution of organic carbon and  $\delta^{13}C_{org}$  in the T/J boundary interval of the Široký Žľab section

The second negative  $\delta^{13}\text{C}_{\text{org}}$  excursion starts near the FO of the Jurassic ammonite *Psiloceras planorbis* (Hesselbo 2002), *Odoghertyceras* and *Psiloceras marcouxii* (Guex *et al.* 2003), or of *Rhacophyllites* and *Kamerkarites* (Pálfy *et al.* 2001; Ward *et al.* 2001, 2007) and bivalves (McRoberts *et al.* 1997).

Isotope studies of West Carpathians sections confirm a complex character of the isotope curve with two major negative excursions, alternating with positive shifts. We suppose that these excursions reflect an environmental change in the sedimentary basin as well as a change in sea water properties evoked by release of a great volume of  $\text{CO}_2$  (Hautmann 2004; Berner and Beerling 2007). This greenhouse climate evolution continued by clastic sediment influx from the continent into the basin. The change of  $\delta^{13}\text{C}_{\text{org}}$  values corresponds with variations in the content of organic matter. The data indicate a mixed marine and terrestrial origin of organic particles, transported by river and accumulated in a submarine delta fan. The study of recent organic particles has shown that organic matter enriched in humic acid and humins retains its  $\delta^{13}\text{C}_{\text{org}}$  content ( $-27$  to  $-31\%$ , Lamb *et al.* 2007).

The original  $\delta^{13}\text{C}_{\text{carb}}$  has been affected by local postsedimentary (emergence, weathering) changes. Such an alteration is documented in the Široký Žľab section. During lowstands, part of the sequence emerged and eroded, and the limestone was dolomitized and cemented in a vadose-meteoric regime. In consequence, more negative ( $-4\%$ ) values of the  $\delta^{13}\text{C}_{\text{carb}}$  curve, affected by a more intensive diagenetic overprint, were recorded below the sequence boundaries. Sedimentary conditions in more distal parts of the carbonate ramp documented in the Furkaska or Kardolina sections (see Text-fig. 1) were more favourable to the preservation of the primary carbonate isotope ( $\delta^{13}\text{C}_{\text{carb}}$ ) signal. A distinct negative  $\delta^{13}\text{C}$  excursion is clearly recognizable in these sections (Michalík *et al.* 2007). A certain modification of the  $\delta^{13}\text{C}_{\text{carb}}$  content by fresh water input and by carbonate re-crystallization may be expected in lower parts of the sedimentary rhythms, consisting of more porous biosparitic wackestones and packstones, affected by late diagenetic cementation, and even by slight selective dolomitization.



Text-fig. 7. Distribution of clay minerals in the T/J boundary interval of the Furkaska section

## CONCLUSIONS

Both sections reveal a strikingly similar distribution of kaolinite. It appears only in the Boundary Claystone, while the underlying strata are free of kaolinite. Moreover, the Furkaska section is also characterized by relative continuous increase in mixed-layer illite-smectite content (at the expense of discrete illite). These changes are interpreted here as a response to increasing intensity of chemical weathering in the hinterland due to increasing humidity. However, the persistent prevalence of IS (most probably originating from a smectitic precursor) in clay-size fractions of both Rhaetian and Hettangian samples may suggest that the source material of these sediments was formed during weathering in seasonally wet and dry climates.

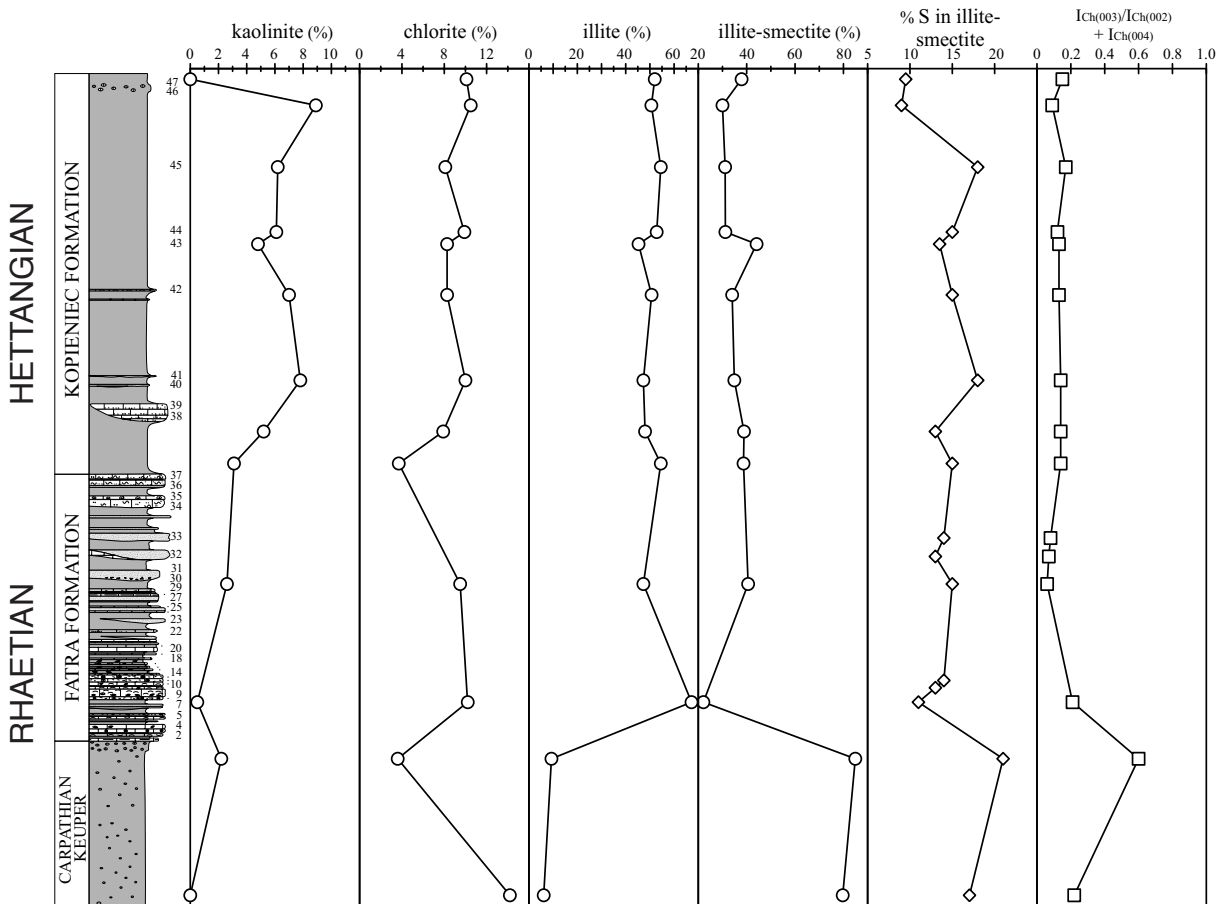
A major T/J boundary mass extinction event cannot be inferred from the palynological data of the NW Tethyan realm. However, the striking increase in spores within the palynomorph assemblage points to a relatively sudden climatic change, i.e., increasing humidity, most probably caused by the volcanic activity of the Central Atlantic Magmatic Province (CAMP) associated

with the onset of rifting of Pangaea during early Mesozoic times.

The  $\delta^{13}\text{C}_{\text{org}}$  excursion within the T/J boundary interval documents a perturbation of the global carbon cycle during this period, recorded also from many other sections world-wide. Two negative  $\delta^{13}\text{C}_{\text{org}}$  excursions correspond to variations in the sedimentary organic matter content, decreasing carbonate content, as well as changes in clay mineralogy, pointing to a major climatic change. Therefore, these signatures contribute to a more precise regional and global correlation.

## Acknowledgments

This study was supported by the Slovakian Science Grant Agency (VEGA) 0196 project, the APVV projects 51-008305, 51-011305 and by the Deutsche Forschungsgemeinschaft (DFG Project GO 761/2-1). The authors also acknowledged the constructive remarks of Dr. Jozsef Pálffy (Hungarian Natural History Museum Budapest) which greatly improved the manuscript.



Text-fig. 8. Distribution of clay minerals in the T/J boundary interval of the Široký Žľab section

## REFERENCES

- Berner, R.A. and Beerling, D.J. 2007. Volcanic degassing necessary to produce a CaCO<sub>3</sub> undersaturated ocean at the Triassic-Jurassic boundary. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 368–373.
- Bertinelli, A., Ciarapica, G., De Zanchi, V., Narcucci, M., Mietto, P., Passeri, L. and Rigo, G. 2005. Stratigraphic evolution of the Triassic-Jurassic Sasso di Castalda succession (Lagonero Basin, southern Apennines, Italy). *Bollettino della Società di Geologia di Italia*, **124**, 161–175.
- Biscaye, P.E. 1964. Distinction between kaolinite and chlorite in recent sediments by X-ray diffraction. *American Mineralogist*, **49**, 1281–1289.
- Brown, G.W. and Brindley, G. 1980. Crystal structures of clay minerals and their X-ray identification. *Mineralogical Society London, Monograph*, **5**, 495 pp.
- Chamley, H. 1989. *Clay Sedimentology*, pp. 1–123. Springer; Berlin – Heidelberg.
- Dudek, T. and Środoń, J. 1996. Identification of illite/smectite by X-ray powder diffraction taking into account the log-normal distribution of crystal thickness. *Geologica Carpathica-Clays*, **5**, 21–32.
- Fransolet, A.M. and Schreyer, W. 1984. Sudoite, di/trioctahedral chlorite: A stable low-temperature phase in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. *Contributions to Mineralogy and Petrology*, **86**, 409–417.
- Gaździcki, A., Michalík, J., Planderová, E. and Sýkora, M. 1979. An Upper Triassic – Lower Jurassic sequence in the Křížna Nappe (West Tatra Mts, West Carpathians, Czechoslovakia). *Západné Karpaty; Geológia*, **5**, 119–148.
- Gómez, J.J., Goy, A. and Barrón, E. 2007. Events around the Triassic-Jurassic boundary in northern and eastern Spain. A review. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 89–110.
- Guex, J., Bartolini, A., Atudorei, V. and Taylor, D. 2003. Two negative δ<sup>13</sup>C<sub>org</sub> excursions near the Triassic-Jurassic boundary in the New York Canyon area (Gabbs Valley Range, Nevada). *Bulletin de Géologie Lausanne*, **360**, 4 pp.
- Hautmann, M. 2004. Effect of end-Triassic CO<sub>2</sub> maximum on carbonate sedimentation and marine mass extinction. *Facies*, **50**, 257–261.
- Hesselbo, S.P., Robinson, S.A., Surlyk, F. and Piasecki, S. 2002. Terrestrial and marine extinction at the Triassic-Jurassic boundary synchronized with major carbon-cycle perturbation: a link to initiation of massive volcanism? *Geology*, **30**, 251–254.
- Hesselbo, S.P., Robinson, S.A. and Surlyk, F. 2004. Sea-level change and facies development across potential Triassic-Jurassic boundary horizons, SW Britain. *Journal of the Geological Society, London*, **161**, 365–379.
- Jackson, M.L. 1975. *Soil Chemical Analysis – Advanced Course*. Madison, Wisconsin.
- Kiessling, W., Aberhan, M., Brenneis, B., and Wagner, P.J. 2007. Extinction trajectories of benthic organisms across the Triassic – Jurassic boundary. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 201–223.
- Kraus, I. 1989. Kaolins and kaolinite clays. *Západné Karpaty; séria Mineralógia, petrografia, geochémia, metalogenéza*, **13**, 7–287. [In Slovak]
- Krumm, S. 1994. WINFIT 1.0: a public domain program for interactive profile-analysis under WINDOWS. XIII Conference on Clay Mineralogy and Petrology, Praha, *Geologica*, **38**, 253–261.
- Kuerschner, W.M., Bonis, N.R. and Krystyn, L. 2007. Carbon-isotope stratigraphy and palynostratigraphy of the Triassic–Jurassic transition in the Tiefengraben section — Northern Calcareous Alps (Austria) *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 257–280.
- Lamb, H.F., Bates, C.R., Coombes, P.V., Marshall, M.H., Umer, M., Davies, S.J. and Dejen, E. 2007. Late Pleistocene desiccation of Lake Tana, source of the Blue Nile. *Quaternary Science Reviews*, **26**, 287–299.
- Lanson, B. 1997. Decomposition of experimental X-ray diffraction patterns (profile fitting): A convenient way to study clay minerals. *Clays and Clay Minerals*, **45**, 132–146.
- Lucas, S.G., Guex, J., Tanner, L.H., Taylor, D., Kuerschner, W.M., Atudorei, V. and Bartolini, A. 2005. Definition of the Triassic – Jurassic Boundary. *Albertiana*, **32**, 12–16.
- Lucas, S.G. and Tanner, L.H. 2007. Tetrapod biostratigraphy and biochronology of the Triassic-Jurassic transition on the southern Colorado Plateau, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 242–256.
- Lund, J.J. 1977. Rhaetic to Lower Liassic palynology of the onshore south-eastern North Sea Basin. *Danmarks geologiske Undersøgelse 2nd Series*, **109**, 1–129.
- Marinoni, O. 2006. Benefits of the combined use of stochastic multi-criteria evaluations with Principal Components Analysis. *Stochastic Environmental Research and Risk Assessment*, **20**, 319–334.
- McRoberts, C.A., Furrer, H. and Jones, D.S. 1997. Palaeoenvironmental interpretation of a Triassic–Jurassic boundary section from Western Austria based on palaeoecological and geochemical data. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **136**, 79–95.
- Michalík, J. 2007. Sedimentary rock record and microfacies indicators of the latest Triassic to mid-Cretaceous tensional development of the Zliechov Basin (Central Western Carpathians). *Geologica Carpathica*, **58**, 443–453.
- Michalík, J., Planderová, E. and Sýkora, M. 1976. To the stratigraphic and paleogeographic position of the Tomanová Formation in the uppermost Triassic of the

- West Carpathians. *Geologickij Zbornik Geologica Carpathica*, **27**, 299–318.
- Michalík, J., Kátlovský, V. and Hlušík, A. 1988. Plant remains in the Tomanová Formation (uppermost Triassic, West Carpathians): their origin, composition and diagenetic alteration. *Geologickij Zbornik Geologica Carpathica*, **39**, 523–537.
- Michalík, J. (Ed.) 2003. IGCP 458: Triassic/Jurassic Boundary Events. Third Field Workshop, Stará Lesná, Slovakia, Tatra Mts, October 11–15 th., VEDA Bratislava, 72 pp.
- Michalík, J., Lintnerová, O., Gaździcki, A. and Soták, J. 2007. Record of environmental changes in the Triassic–Jurassic boundary interval in the Zliechov Basin, Western Carpathians. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 71–88.
- Moore, D.M. and Reynolds, R.C. 1997. X-ray diffraction and the identification and analysis of clay minerals, pp. 1–378. Oxford University Press; Oxford – New York. [Second edition]
- Niedźwiecki, G. 2004. A new find of dinosaur footprints in the Upper Triassic of the Tatra Mountains, southern Poland. *Przegląd Geologiczny*, **53**, 410–413.
- Orłowska-Zwolińska, T. 1983. Palynostratigraphy of the upper part of Triassic epicontinental sediments in Poland. *Prace Instytutu Geologicznego, Wydawnictwa Geologiczne*, **104**, 1–89. [In Polish with English abstract]
- Pálfy, J. and Dosztály, L. 2000. A new marine Triassic – Jurassic boundary section in Hungary. *GeoResearch Forum*, **6**, 173–180.
- Pálfy, J., Demény, A., Haas, J., Hetényi, M., Orchard, M.J. and Vető, I. 2001. Carbon isotope anomaly and other geochemical changes at the Triassic/Jurassic boundary from a marine section in Hungary. *Geology*, **29**, 1047–1050.
- Pollastro, R.M. 1993. Considerations and applications of the illite/smectite geothermometer in hydrocarbon-bearing rocks of Miocene to Mississippian age. *Clays and Clay Minerals*, **41**, 119–133.
- Reggiani, L., Berinelli, A., Ciarapica, G., Marcucci, M., Passeri, L., Ricci, C. and Rigo, M. 2005. Triassic–Jurassic stratigraphy of the Madonna dei Sirino succession (Lagonegro Basin, southern Apennines, Italy). *Bollettino della Società di Geologia di Italia*, **124**, 281–291.
- Reynolds, R.C. 1980. Interstratified clay minerals. In: Brindley, G.W. and Brown, G. (Eds), *Crystal structures of clay minerals and their X-ray identification. Mineralogical Society Monograph*, **5**, 249–303.
- Righi, D. and Meunier, A. 1995. Origin of clays by rock weathering and soil formation. In: Velde, B. (Ed.) *Origin and Mineralogy of Clays*, pp. 43–161. Springer; Berlin – Heidelberg.
- Robert, C. and Chamley, H. 1991. Development of early Eocene warm climates, as inferred from clay mineral variations in oceanic sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **89**, 315–332.
- Ruckwied, K. and Götz, A.E. 2009. Climate change at the Triassic/Jurassic boundary: palynological evidence from the Furkaska section (Tatra Mountains, Slovakia). *Geologica Carpathica*, **60**, 139–149.
- Ruffell, A., McKinley, J.M. and Worden, R.H. 2002. Comparison of clay mineral stratigraphy to other palaeoclimate indicators in the Mesozoic of NW Europe. *Philosophical Transactions of the Royal Society of London*, **A360**, 675–693.
- Simms, M.J. 2007. Uniquely extensive soft-sediment deformation in the Rhaetian of the U.K.: Evidence for earthquake or impact? *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 407–423.
- Środoń, J. 1980. Precise identification of illite/smectite interstratifications by X-ray powder diffraction. *Clays and Clay Minerals*, **28**, 401–411.
- Środoń, J. 1984. X-ray powder diffraction identification of illitic materials. *Clays and Clay Minerals*, **32**, 337–349.
- Środoń, J., 1999: Use of clay minerals in reconstructing geological processes: recent advances and some perspectives. *Clay Minerals* **34**, 27–37.
- Środoń, J., Kotarba, M., Biroň, A., Such, P., Clauer, N. and Wójtowicz, A. 2006. Diagenetic history of the Podhale – Orava Basin and the underlying Tatra sedimentary structural units (Western Carpathians): Evidence from XRD and K-Ar of illite – smectite. *Clay Minerals*, **41**, 751–774.
- Tanner, L.H. and Lucas, S.G. 2007. The Moenave Formation: Sedimentologic and stratigraphic context of the Triassic – Jurassic Boundary in the Four Corners area, southwestern U.S.A. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 111–125.
- Thiry, M. 2000. Palaeoclimatic interpretation of clay minerals in marine deposits: an outlook from the continental origin. *Earth Science Reviews*, **49**, 201–222.
- Tyson, R.V. 1995. Sedimentary Organic Matter. Organic Facies and Palynofacies, pp. 1–615. Chapman & Hall; London.
- Ward, P.D., Haggart, J.W., Carter, E.S., Wilbur, D., Tipper, H.W. and Evans, T. 2001. Sudden productivity collapse associated with the Triassic – Jurassic Boundary mass extinction. *Science*, **292**, 1148–1151.
- Ward, P.D., Garrison, G.H., Haggart, J.W., Kring, D.A. and Beattie, M.J. 2004. Isotopic evidence bearing on Late Triassic extinction events, Queen Charlotte Islands, British Columbia, and implications for the duration and cause of the Triassic/Jurassic mass extinction. *Earth and Planetary Science Letters*, **224**, 589–600.
- Ward, P.D., Garrison, G.H., Williford, K.H., Kring, K.H., Goodwin, D., Beattie, M. and McRoberts, C. 2007. The organic carbon isotopic and paleontological record across the Triassic–Jurassic boundary at the candidate GSSP section at Ferguson Hill, Muller Canyon, Nevada, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 281–289.

- Weaver, C.E. 1989. Clays, Muds, and Shales. *Developments in Sedimentology*, **44**, 1–819. Elsevier; Amsterdam.
- Weir, A.H., Ormerod, E.C. and El-Mansey, M.I. 1975. Clay mineralogy of sediments of the western Nile Delta. *Clay Minerals*, **10**, 369–386.
- Williford, K.H., Ward, P.D., Garrison, G.H. and Buick, R. 2007. An extended organic carbon – isotope record across the Triassic – Jurassic Boundary in the Queen Charlotte Islands, British Columbia, Canada. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **244**, 290–296.

*Manuscript submitted: 10<sup>th</sup> June 2008*

*Revised version accepted: 15<sup>th</sup> October 2010*