# Biostratigraphy, geochemistry and sedimentology of Middle to Late Jurassic strata in the Strážovce section (Strážovské vrchy Mts), Krížna Nappe of the Central Carpathians, Slovakia

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Key words: Oxfordian, Kimmeridgian, C and O isotopes, REE content, radiolarians, basinal collapse, Zliechov Basin, Fatric Unit.

**Abstract.** The Jurassic / Lower Cretaceous sequence of the Strážovce section has been deposited in the central, axial part of the Zliechov Basin. Its most characteristic part – the Ždiar Formation consists of bedded siliceous radiolarian limestones and radiolarites. The radiolarian assemblage typical of the North Tethyan Bioprovince lived during mid Oxfordian – Early Kimmeridgian in a warm upper part of the well stratified water column, partially near to the thermocline. Radiolarian abundance decreases upwards. Productivity decrease is quantified by the share of biogenic SiO<sub>2</sub> as well as by high  $EF_{Si}$  values during sedimentation of both the Ždiar and Jasenina formations.

The geochemical data indicate relatively stable volume of the siliciclastic component of the rocks and a felsic character comparable to the Average Shale. The chemically homogeneous sedimentary signal indicates values of both CPA and  $EF \le 1$  of Ti, Zr, Fe, Na, K, Rb, V and U. The values of EF > 1 signal enrichment of elements with affinity to carbonate minerals (Sr, Mn, P, Y, and Mg). Metal enrichment (Cu, Zn and Ni) indicates metal mobilization from other sources or due to carbonate diagenesis. In comparison to the Average Shale, decreased  $\Sigma REE's$  and negative  $Ce_{ch}$  and  $Eu_{ch}$  anomalies could be regarded as a typical deep sea water signal. The differentiated REE record of higher calcareous beds of the Jasenina Fm. suggests basinal dysoxic conditions. The "bell-shape" of curves (normalized to shale) indicate that REEs were slightly affected by carbonate diagenesis.

The Oxfordian / Kimmeridgian siliceous sedimentation in the Zliechov Basin was influenced probably more by monsoon-controlled input of land derived weathered material than by hydrothermal fluids from the bottom rifts.

# INTRODUCTION

A continuous section of basinal Upper Triassic to Lower Barremian Zliechov sequence of the Krížna Nappe was exposed during road construction between Zliechov and Čičmany villages in 1975 along the 3,5 km long escarpment below the Strážovce Hill in the Strážovské vrchy Mts (Figs. 1–3). It has been described by Borza *et al.* (1980), Michalik (1985), and Grabowski *et al.* (2009).

The stratigraphically oldest (at present rather poorly exposed) part of the section is represented by varicoloured claystones and (higher up) by terrigenous claystone / dolomitic Carpathian Keuper sequence. It is followed by 35 m thick marine carbonates of the Rhaetian Fatra Formation.

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Fig. 1. Localization sketch of the Mt Strážov with designation of the Strážovce road section studied

The Hettangian Kopieniec Formation (up to 70 m thick) consists of shallow marine argillites recording strong fresh water input during start of Jurassic sedimentation.

The Sinemurian – Pliensbachian Janovky Formation is formed of 56 m of well bedded hemipelagic limestones with typical bioturbation (the "spotted" limestones or the "*Fleckenkalk* – *Fazies*" of Alpine authors (*e.g.*, Jacobshagen, 1959) and which contain an abundant ammonite fauna. The Lower Jurassic sequence is terminated by several (8–10) meter thick red marlstones with Toarcian belemnites and an ammonite fauna comparable with the Adnet Formation (Fig. 2). The ammonite shells are mostly dissolved and partially replaced by hematite. The Adnet Fm. is covered by an unnamed limestone formation (called the "ash gray siliceous limestone", or the "Borišov Limestone" by Mišík, 1964, or the "Bositra-crinoidal limestone" by Jach, 2007) with cherts, juvenile bivalves, globochaetes, crinoid ossicles and calcified radiolarians. The thickness of this formation is 6–7 meters only, but it forms the uppermost part of the complex affected by submarine slumping (Borza *et al.*,1980; Michalík, 1985; Fig. 2.).

The Ždiar Formation (Polák *et al.*, 1998) rests on its basement with a sedimentary gap. It consists of well-bedded siliceous radiolarian limestones and radiolarites, separated by only thin shaly intercalations. These beds do not contain any macrofaunal remains, and their position has been designated as Middle Jurassic due to their superposition.

The Ždiar Fm. is conformably covered by the shaly marlstones of the Jasenina Fm. (Borza *et al.*, 1980; figs. 2, 3). The term "Jasenina Fm" was wrongly interpreted in the "Geological map of the Malé Karpaty Mts" by Polák (2011) as a designation for all Upper Jurassic sediments, or erroneously correlated with the Pieniny Limestone Fm. (in Jach *et al.*, 2014). Contrary to the shallower red nodular limestone (Rosso Ammonitico) facies which are widespread in the Upper Jurassic sequences of the Mediterranean Tethys (Mi-



Fig. 2. A sketch of a part of the Strážovce section (simplified from Michalík, 1985) between road signs 1856-1877 m (Lower to Upper Jurassic formations)

chalík, 1994, 2007; Baumgartner *et al.*, 1995; Bernoulli, Jenkyns, 2009), the Jasenina Fm. represents the products of the deeper, axial part of the Zliechov Basin.

Calpionellid remnants in the upper part of the formation (Michalík *et al.*, 1990) indicate the Late Tithonian Crassi-

collaria Zone. The uppermost Tithonian – Lower Cretaceous planktogenic "Biancône" limestone facies represents the Osnica Fm., followed by the Mráznica Fm. (Borza *et al.*, 1980; Vašíček *et al.*, 1983, 1984; Michalík *et al.*, 1990).



Fig. 3. Panoramic photo of the Zliechov–Čičmany road escarpment below the Strážovce Hill, which exposed the Adnet, Ždiar and the Jasenina formations

A – general view; B – radiolarian limestones of the Ždiar Formation, beds No. 124, 125 containing lithoclasts and bioclasts of benthic organisms; C – calcareous radiolarite basal beds (No. 117, 118) of the Ždiar Formation deformed by synsedimentary slumping

The Cretaceous ammonite stratigraphy in the Strážovce section has been studied by Vašíček *et al.* (1983, 1984), and the microbiostratigraphy of the J/K boundary by Michalík *et al.* (1990). The REE content in the Jurassic basinal sequence has been analysed by Méres and Michalík (2006). The geochemistry of the Upper Jurassic and Lower Cretaceous rock sequences in the Strážovce and in the Hlboča sections has been studied by Lintnerová (in Michalík *et al.*, 1995; or in Grabowski *et al.*, 2010). Grabowski *et al.* (2009), in studying the magnetic rock properties, concluded that the sequence of the Strážovce section has been remagnetised during the Late Cretaceous thrust of the Krížna Nappe.

The main goals of this study were:

- a. to precisely define the biostratigraphic subdivision of the Middle Jurassic formations which are poor in ammonites and other index macrofaunal fossils by the study of radiolarian microplankton;
- b. to bring new data explaining the sedimentological evolution of the rather poorly documented Jurassic sequence deposited in the axial part of the marine pull-apart Zliechov Basin;
- c. to characterise the chemical composition of the rocks (on the base of major-, minor-, trace elements and REE data) of the carbonaceous – siliceous sedimentary sequence in specific basinal conditions;
- d. to clarify the influence of terrigenous influx vs the role of intra-basinal sources into the Zliechov Basin during the Middle Jurassic.

## **METHODS**

The rock sequence has been sampled at one meter intervals; compact rock samples suitable for grinding and polishing have been preferred. Microfacies have been analysed by microscopical study of 49 slides (in the Amplival Optical Microscope); the NIS-Elements system of screen analysis has been used for quantitative evaluation of rock constituents.

Major oxides, minor- and trace elements and REE abundance were analysed in 16 whole-rock samples (8 from the Ždiar Fm., 8 from the Jasenina Fm.). Chemical analyses were carried out at the ACME laboratories in Vancouver in Canada. Total abundance of the major and several minor elements (Ni, Cr, Sc) were analysed by ICP emission spectrometry. Loss on ignition (LOI) is the weight difference after ignition at 1000°C. Total carbon and sulphur concentrations were measured using the Eltra 2000 C-S analyzer (not presented here). Other trace elements and REEs were analysed by ICP mass spectroscopy. Totally, 26 microelements (except REEs) were analysed, but only abundances higher than the detection limits of As, Ba, Co, Cs, Cu, Ga, Ni, Pb, Rb, Sc, Sr, Th, U, V, Zr and Y are presented and interpreted in tables. All techniques and processing methods followed the ACME Laboratory guidelines (<u>www.acmelab.com</u>).

The radiolarians have been obtained from seven rocks samples dissolved in HCl (S-102, S-121, S-122, S-127, S-129, S-133 and S-144). Samples from the section studied yielded a moderately preserved radiolarian association which has been studied by SEM.

# LITHOLOGY, MICROFACIES AND SEQUENCE STRATIGRAPHIC ARCHITECTURE OF THE SECTION

The total thickness of the well-bedded (No. 120–142; bedding thickness 4–24 cm) brown-red silicitic limestone sequence of the Ždiar Formation is 45–50 m (Figs. 2–4). The rocks (biomicritic wackestone / packstone) are rich in radiolarian tests (No. 120–127: 11–25%). They are mostly calcified, but sometimes still consist of fibrous chalcedony or quartz. Sponge spiculae and quartz grains of a silt size occur subordinately. Tiny calcite rhombohedrons and irregular aggregates occur in the matrix, pyrite is less frequent.

Six cycles of a eustatic nature have been recognized in the Ždiar Fm. sequence. Their thickness gradually decreases upwards from 8.5–8.0 to 6.5–5.0 meters. The base of each typical cycle is formed by siliceous wackestone / packstone with a relatively common (up to 5%) content of fine quartz silt grains, infrequent radiolarian tests and bioclasts of benthic organisms (Fig. 4).

The basal cycle of the Ždiar Fm. starts with a 20–30 cm thick siliceous packstone layer (No. 118) containing subangular (0.5–20.0 cm) clasts of limestone and/or silicite, plastically deformed by slumping (Fig. 3C). From all samples analysed, the abundance and diversity of radiolarians reaches its maximum (23% of the rock in the microscope; Fig. 4) in beds 120–121, most probably representing the transgressive tract. Radiolarian tests in the upper parts of the cycle (122–123) are less abundant (6–11%), being arranged in thin laminae.

Packstone bed 124 of the second cycle contains more frequent (5.5%) fine quartz grains and sponge spicules. The relatively abundant radiolarian fauna of Bed 126 has not been analysed in detail. Radiolarians in beds 127–128 co-occur with sponge spicules.

The radiolarian diversity in the four following cycles of the Ždiar Fm. sequence is much smaller (Fig. 4). The abundance of radiolarian tests decreases upwards (to 3–9% in average), too. On the other hand, calcareous microplankton remnants (calcareous dinoflagellates, globochaetes and sac-





Share of radiolarian and calcareous microplankton tests rising to the left from the zero axis, the share of benthic organic clasts and quartz grains increasing to the right. The occurrence of radiolarians is denoted in the right side of the figure

cocomas) became more frequent (beds 131, 134, 138). Fragments of larger shells (probably aptychi) have been observed locally (beds 135–140). Numerous cross-sections of thin-shelled bivalves occur here, forming locally 3–4% of the whole rock in the highstand parts of the cycles.

The boundary with the Jasenina Fm. (142–181, Fig. 4) is not sharp. The Jasenina Fm. is built of dark gray (reddish in the lowermost part) argillitic limestones and marls with quartz grains, white mica and chlorite, calcified radiolarians, sponge spicules, thin shelled bivalve shells, crinoid fragments, small aptychi and belemnites. Concentrations of juvenile aptychi occur on the base of the lowermost and of several overlying cycles, and the reddish gray biomicritic wackestone is enriched with radiolarians and calcareous microfossils.

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In higher cycles, benthic shell fragments in dark grey micritic wackestone are corroded, their amount attains 2-4%. Calcareous microplankton remnants consist of saccocomas, globochaetes, calcareous dinoflagellate cysts and crassicollarians. They are always more abundant (6–8%, with maxima of 14% in beds 145 and 152) than radiolaria (4–5%). The thickness of marly intercalations increases upwards. In fact, the upper part of the Jasenina Fm. sequence (170–181) is dominated by marls with marly limestone (mudstone/ wackestone) intercalations.

# GEOCHEMISTRY

## MAJOR ELEMENTS

The sequence of both Ždiar and Jasenina fms is characteristic of low Al<sub>2</sub>O<sub>3</sub>: 2.7–4.5 weight % (%) value relatively to SiO<sub>2</sub>. The SiO<sub>2</sub> content (20–50 hm %) continually decreases upwards and the CaO content (25–40%) increases upwards (Tab. 1). Such a trend is the result of the production of two principal constituents: of (1) organogenic SiO<sub>2</sub> (radiolarians and sponges) and of (2) organogenic CaCO<sub>3</sub> (micro and nanno biota) which temporarily dominated dependant both on nutrients, their accessibility in the surface water and on the preservation conditions in the sediment after burial.

Non-carbonate CaO (or CaO in the silicate phase) was estimated as  $CaO^* = Na_2O$  of the sample (McLennan *et al.*, 1993). Analogically to this the carbonate CaO is  $CaO_{car} = CaO_{tot} - CaO^*$  and together with total carbon content approximate CaCO<sub>3</sub> of the samples (Tab. 1). The CaCO<sub>3</sub> contents estimated ranged from 48 to 61% in the Ždiar Fm. samples to 60 to 74% in the Jasenina Fm. samples and it could imply a continual rise in the calcareous production (Tab. 1).

In comparison with low Al oxide, an increased  $SiO_2$ amount indicates a biogenic origin of silica in the succession. The biogenic silica content (as the potential production factor) was calculated as the "excess of element":  $TM_{ex} = TM_{sample} - Al_{samples} (TM/Al)_{shale}$  where TM is total content of element (Brumsack, 2006). The element content of the Average Shale (Wedepohl, 1971, 1991), or TM/Al ratio respectively, are used in this study (see also Taylor, McLennan, 1985; Brumsack, 2006; Oiu et al., 2015). The biogenic SiO<sub>2</sub> content could comprise 60 to 80% of the total silica in the Ždiar Fm. samples and still be more than 50% in the Jasenina Fm. (Tab. 1). These values are the maximum contents of biogenic silica (radiolarians, sponges) taking into account also the inorganic - free silica phases. The amount of quartz is relatively low as documented by microscopical study (Fig. 4). Inorganic silica precipitated from fluids in an amorphous phase during sedimentation and diagenesis could be also present (especially in the Jasenina Fm. where radiolarian silica production decreased (Tab. 1). In comparison with other samples, the oxide content of the major elements of the siliciclastics decreases in sample 145 – this is the first sample from the Jasenina Fm. Sample 166 from the Tithonian part of the Jasenina Fm. shows also an oxide shift, but less impressive (Tab. 1). Despite this, the total  $SiO_2$  is lower in both mentioned samples. The "free" silica content increases, especially in sample 145, where it forms 83% of total SiO<sub>2</sub>. This could indicate continuous silica enrichment by upwelling. In this (145), or in other beds of the Jasenina Fm., diagenetic processes could also play a role in the silica remobilization.

With the exception of CaO and  $SiO_{2}$ , all major and minor oxides (Tab. 1) suggest positive linkage with Al oxides giving the approximate amount of silicates in the sediment

Table 1

Analyte	SiO <sub>2</sub>	TiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	$P_2O_5$	MnO	Cr <sub>2</sub> O <sub>3</sub>	LOI	CaCO <sub>3</sub>	SiO <sub>2</sub> bio		CIA***	CPA
Sample	[wt. %]																
122	31.73	0.15	3.36	1.21	0.67	34.15	0.34	0.69	0.06	0.23	0.006	27.3	61.53	19.9*	63**	64	86
126	36.65	0.16	3.95	1.99	0.89	29.95	0.22	0.89	0.06	0.16	0.003	24.9	54.1	22.7	62	70	92
129	32.72	0.14	3.34	1.49	0.86	32.9	0.29	0.64	0.05	0.16	0.004	27.3	59.35	21.0	64	66	88
130	39.64	0.13	3.27	1.66	0.73	28.99	0.22	0.72	0.04	0.15	0.003	24.4	52.36	28.1	71	68	90
132	48.45	0.09	2.52	1.16	0.66	25.38	0.24	0.49	0.03	0.14	0.002 >	20.7	45.75	39.6	82	65	86
134	37.48	0.14	3.10	1.67	0.76	30.26	0.27	0.67	0.05	0.16	0.005	25.3	54.58	26.5	71	65	87
140	44.12	0.15	3.65	2.8	0.84	25.56	0.26	0.84	0.05	0.13	0.003	22.2	46.04	31.3	71	66	89
141	39.48	0.13	3.18	1.75	0.88	28.99	0.26	0.60	0.03	0.17	0.003	24.5	52.28	28.3	72	67	88
145	29.69	0.05	1.43	0.78	0.47	36.73	0.03	0.21	0.04	0.22	0.002>	30,0	66.79	24.7	83	54	75
152	27.10	0.10	2.73	1.58	0.84	36.33	0.20	0.53	0.04	0.20	0.002	30.4	65.75	17.4	64	68	89
159	25.58	0.14	3.46	1.40	0.89	36.17	0.32	0.73	0.06	0.15	0.003	31,0	65.24	13.4	52	65	87
162	28.99	0.13	3.60	1.46	0.82	35.35	0.22	0.65	0.07	0.11	0.004	29.1	63.93	18.2	63	68	89
163	27.42	0.16	3.52	1.84	0.94	35.87	0.29	0.70	0.06	0.09	0.004	29,0	64.75	15.0	55	67	88
164	30.80	0.19	4.46	1.85	1.20	32.51	0.28	0.90	0.07	0.10	0.005	27.7	58.65	15.1	49	70	91
166	20.89	0.08	1.94	1.20	0.69	41.22	0.20	0.39	0.05	0.13	0.002 >	33.1	74.65	14.1	67	63	85
167	19.90	0.13	3.10	1.51	0.91	40.10	0.27	0.58	0.04	0.11	0.004	33.3	72.49	9.3	47	66	87

Major and minor components contents of the rocks samples expressed in weight % and derived characteristics

 $CaCO_3 = carbonate CaO \times 1.78$ :  $CaO_{carb}$  is estimated as  $CaO_{tot} - CaO_{detritic}$ .\* - biogenic SiO<sub>2</sub> in wt. %; and \*\* - SiO<sub>2</sub> bio in wt. % of total silica; \*\*\* - CIA : CaO\_{detritic} = Na<sub>2</sub>O (Nesbit, Young, 1984; McLennan *et al.*, 1993); CPA = CIW'' (Culllers, 2000)

and thus they represented detrital input from land into the basin. On the other hand, the somewhat shifted contents of Mg, Mn, and P oxides (especially in sample 145) show correspondence with carbonates and/or with bioapatite.

## TRACE ELEMENTS

The total amount of trace elements is relatively low (Tab. 2) in all samples and proportionally it correlates positively with  $Al_2O_3$ . The trace elements are preferentially combined with siliciclastic minerals in the rocks. The high content of Sr (193–461 ppm) indicates that it is preferentially coupled with the carbonate part of the rock. The higher Sr content (279–461 ppm) in the older part of the section (where CaCO<sub>3</sub> is generally lower), suggests that the mineral composition of CaCO<sub>3</sub> could be different. The Sr amount bounded in CaCO<sub>3</sub> minerals (aragonite or high Mg calcite) could be more or less depressed when re-crystallised to low Mg-calcite (Brand and Veizer, 1980; Morse and MacKenzie, 1990). The formation of low-Mg-calcite could also release Mg, Mn, Fe, P but also the REEs and Y and these are redistributed into (late-) diagenetic micrite or into other Caminerals, respectively. The ratios of Th and Y vs Cr, Sc, Ni, and V could indicate the felsic character of the detrital material, but also the environmental conditions of the basin. On the other hand, the contents of several elements/oxides ( $Cr_2O_3$ , Sc, Th, MnO) are close to the determination limit which calls for caution. Local enrichment by metals Zn, Cu and Pb can be indicated by their total contents in comparison with shale (Tab. 2).

# INDEXES OF THE CHEMICAL ALTERATION AND WEATHERING

These evoke the assumption that Al, as an immobile element, remains and relatively accumulates in a rock residue while CaO, Na<sub>2</sub>O or K<sub>2</sub>O is leached out from the rock (Nesbitt, Young, 1982; Harnois, 1988; Price, Velbell, 2003; Mongelli *et al.*, 2006; Tribovillard *et al.*, 2006). We utilized the chemical index of alteration CIA (CIA\*=[Al<sub>2</sub>O<sub>3</sub> /(Al<sub>2</sub>O<sub>3</sub> + CaO\* + Na<sub>2</sub>O + K<sub>2</sub>O)] introduced by Nesbitt and Young (1982, 1984) as the proxy for the chemical alteration of feldspars to clays (kaolinite). It usually ranges from ~50–60 for fresh rocks to 100 for completely weathered rocks and it is

Table 2

Microelement contents in rock samples analysed, expressed in the ppm. The elements with a content below the detection limit (not listed) are represented by Au, Ag, Be, Bi, Cd, Hf, Mo, Hg, Re, Sb, Sn, Tl

Analyte	As	Ва	Со	Cs	Cu	Ga	Ni	Pb	Rb	Sc	Sr	Th	U	V	Zr	Zn	Y
Sample					-				[ppm]								
122	< 0.5	65	8.5	1.2	35.6	4	22.7	11.8	26.4	4	239	2.7	0.5	21	30.1	23	21.8
126	< 0.5	62	14.3	1.7	37.0	4.9	35.8	10.3	35.9	4	222	2.6	0.6	26	37	34	24.9
129	0.6	53	10.5	1.1	46.3	4.3	31.9	10.1	26.1	4	260	2.6	0.6	24	33.9	34	25.3
130	< 0.5	61	11.6	1.4	21.6	4.2	25.2	10.2	30.4	3	234	2.3	0.5	21	30.6	28	21.3
132	< 0.5	41	17.8	0.8	24.4	3,0	38.5	10,0	20.2	3	194	1.9	0.5	16	23.9	29	19.3
134	0.7	57	9.6	1.3	15.6	4.2	24.6	10.7	28.2	3	264	2.1	0.5	23	32.8	27	26.3
140	< 0.5	59	13.1	1.6	35.0	4.7	32.9	13.2	35.4	4	230	2.7	0.6	26	33.5	33	23.6
141	< 0.5	57	13.1	1.2	20.5	4.4	32	10.5	25.2	4	249	2.1	0.5	24	30.1	33	20.5
145	< 0.5	25	4.6	0.3	13.7	1.7	12.2	15.9	8.5	2	279	1.1	0.5	9	15	15	16.9
152	< 0.5	58	7.5	0.8	27.9	3.6	22.6	11.5	21.2	3	301	1.6	0.5	20	27.2	25	20.5
159	3.3	73	8.4	1.1	25.8	4.6	26.8	9.1	29.0	4	347	2.2	0.7	28	33.2	30	26.5
162	< 0.5	62	4.3	1.3	19.8	4,0	19.7	9,0	31.9	3	368	2.5	0.5	28	29.6	28	22.0
163	1.2	67	3.3	1.4	18.1	4.8	21.4	6.7	29.4	4	308	2.5	0.6	59	34.3	31	19.4
164	4.4	96	8.8	1.8	52.9	5.5	30	11.9	40.2	6	379	3.7	1	58	44.7	33	32.6
166	2.3	42	5,0	0.9	21.8	2.9	13.3	9.1	17.5	3	440	1.7	0.6	33	20	19	21.7
167	1.0	59	3.8	1.3	17.5	3.9	15.9	10.7	25.3	4	462	2.3	0.7	39	27.6	28	25.8
shale *	8.5	580	19	5	29	19	68	20	140	11	170	12	3.7	130	160	95	41

calculated in molar proportions. Because CaO is the major component of calcareous rock, the non carbonate – CaO, respective CaO occurs in silicate phases. It was estimated as CaO\* = NaO of the sample (McLennan *et al.*, 1993). CIA values from 53 to 69 (Tab. 1) are low and they suggest a low level of chemical alteration of the alumino-silicate minerals in the beds. The lowest one (CIA = 53) belongs to sample 145 taken from the base of the Jasenina Fm. The CIA values are lower in comparison with the shale (Average Shale 70– 75) and they generally suggest the potential occurrence of unaltered minerals (feldspars) in both facies of this pelagic limestone (Nesbitt, Young, 1982).

The Chemical Index of Weathering (CIW – CIW' = 100  $\times$  Al<sub>2</sub>O<sub>3</sub> / (Al<sub>2</sub>O<sub>3</sub> + Na<sub>2</sub>O) of Harnois (1988) has been modified by Cullers (2000). To avoid any confusion with the CIW', some authors prefer the designation "Chemical Proxy of Alteration" – CPA (Buggle *et al.*, 2011). Where only Al and Na oxides are taken, the CPA index indicates higher values – from 75 to 92 (Tab. 1). The lowest value (CPA = 75) comes from sample 145. Also the value of bed 166 (85) is relatively decreased.

A comparison of the CIA and CPA suggests that the method of estimation of CaO\* (CaO =  $Na_2O$ ) used is not an optimal solution. Increased potassium content lowered the CIA value, so that this does not document alteration of a primary mineral like K-feldspar adequately, while  $K_2O$  can be fixed by clays, commonly by diagenetic illite (Harnois, 1988; Cullers, 2000). CPA values indicate a level of weath-

ering of the in-coming siliclastic matter to the Shale comparably (75 – sample 145) or higher (85 to 93). Generally, comparably weathered siliclastic matter was derived from the land, being deposited (in a time interval of more than 10 My) in both parts of the pelagic sequence. These data indicate only episodical (local) compositional change (sample 145) of the sediment.

#### THE ENRICHMENT FACTOR

The enrichment factor (EF) concept is also based on the prediction that the Al content (and element/Al ratio, respectively) characterises the amount of elements derived from silicates. When discriminated by the average shale element / Al ratio ( $EF_x = (\text{elements /Al})_{\text{sample}} / (X/Al)_{\text{shale}}$ ), they can identify and quantify detrital, diagenetic or other signals of the rock (Brumsack, 2006; Oiu *et al.*, 2015). Element values are expressed in weight units – % or ppm, and trace elements are commonly expressed as elements/Al × 10<sup>-4</sup>.

EF values of selected major, minor and trace elements are summarized in Table 3 and all EF values higher than 1.0 indicate an enrichment of the element. In comparison with the shale  $EF_{Si}$  in the range 1.9 to 5.9, they can document a high (but differentiated) free silica content in the water which stimulated and/or directed radiolarian (or sponge) productivity. Low EF values of Ti, Zr, Na, K, Rb (but also V and U) in the rock indicate input into basin, more or less

Table 3

Enrichment Factor (EF) values higher than 1 indicated relative accumulation of the element in the samples respective in a "stratigraphic level" and could documented change in production and ecologic conditions *etc.* Not dimensional EFs go from amount of elements in weight unit (wt. % or ppm) and Element/Al ratios of samples and average shale are use to EF expression

	Enrichment Factor (EF)																	
Analyte	Al	Si	Ti	Zr	Fe	K	Na	Rb	Mg	Mn	Sr	Р	Y	Ni	Cu	Zn	V	U
Sample	ple [%]																	
122	177	2.7	0.9	0.9	0.9	1.0	1.1	0.9	1.2	10.4	4.0	1.8	4.7	1.7	3.9	1.2	0.8	0.7
126	209	2.6	0.8	1.0	1.1	1.0	0.6	1.0	1.4	6.1	3.1	1.6	2.6	2.2	3.5	1.5	0.8	0.7
129	176	2.8	0.8	1.1	0.9	0.9	0.9	0.9	1.6	7.3	4.3	1.5	3.0	2.3	5.1	1.8	0.9	0.8
130	173	3.4	0.8	0.9	1.1	1.0	0.7	1.1	1.7	6.9	4.0	1.3	2.6	1.9	2.4	1.5	0.8	0.7
132	133	5.4	0.7	1.0	0.9	0.9	1.0	0.9	1.6	8.4	4.3	1.2	3.1	3.7	3.6	2.1	0.8	0.9
134	164	3.4	0.9	1.1	1.1	1.0	0.9	1.1	1.5	7.8	4.7	1.7	3.4	1.9	1.9	1.5	0.9	0.7
140	193	3.4	0.8	0.9	1.1	1.1	0.8	1.0	1.4	5.4	3.5	1.4	2.6	2.2	3.5	1.6	0.9	0.7
141	168	3.5	0.8	1.0	0.9	1.9	0.9	0.9	1.8	8.1	4.3	1.0	2.6	2.5	2.4	1.8	1.0	0.7
145	075	5.9	0.7	1.1	0.7	0.7	2.2	0.7	2.1	23.3	10.9	2.9	4.8	2.9	3.5	1.8	0.8	1.6
152	144	2.8	0.7	1.0	0.9	0.9	0.8	0.9	1.9	11.1	6.12	1.5	3.0	2.2	3.8	1.6	0.9	0.8
159	183	2.1	0.8	1.0	1.0	1.0	1.0	1.0	1.6	6.6	5.6	1.8	3.1	1.9	2.8	1.5	1.4	0.9
162	161	2.7	0.9	1.0	1.2	1.0	0.8	1.2	1.7	5.4	6.7	2.4	2.9	1.6	2.4	1.6	1.2	0.7
163	186	2.2	0.9	1.0	1.0	0.9	0.9	1.0	1.7	3.9	4.9	1.8	2.2	1.5	1.9	1.5	2.1	0.8
164	236	2.0	0.9	1.1	1.1	0.9	0.7	1.1	1.4	3.4	4.7	1.6	3.0	1.6	4.4	1.3	1.7	1.1
166	102	3.0	0.8	1.1	1.1	0.9	1.1	1.1	2.3	10.2	12.6	2.7	4.5	1.7	4.2	1.7	2.2	1.4
167	159	1.9	0.9	1.0	1.0	0.9	1.0	1.0	1.9	5.5	8.5	1.4	3.5	1.3	2.2	1.6	1.7	1.5

proportional to Al or to aluminosilicates, respectively. In the same way, it proves that the major source of silica could not be represented by detrital matter. The EF<sub>Fe</sub> values close to 1 signalise relatively low mobilization of iron, mainly Fe release from silicates and also the limited occurrence of free Fe oxide (Tab. 3). However, the EF value does not mitigate the role of Fe in the various biogenic or redox processes which obviously run in the water-sediment interstitial zone (Tribovillard et al., 2015). Contrary to Fe, EF values of Mg, P and Mn signalise an enrichment in the sediment. This is clearly indicated in sample 145 due to its lowered content of Al (Tab. 3). High EF values of the elements mentioned (but also of EF of Sr and Fe) can be related to CaCO<sub>3</sub> chemical reactivity or to diagenetic alteration of carbonate-silica matrix and its affinity to low Mg- calcite, respectively. Elements like Mn, Fe, Mg, P, Sr could be adequately incorporated by neo-formed minerals in the local pH or redox circumstances on the basinal bottom. Calcite, but also apatite can attract Y ( $ER_Y > 1$ ) or yttrium- group REEs (HREE). A relative higher EF<sub>P</sub> occurs in the Jasenina Fm. The EF<sub>Zn</sub> (1.2 to 2.1) in the samples indicates a Zn content comparable or higher than in the shale.  $EF_{Cu}$  and  $EF_{Ni}$  values signalise an enrichment of beds (Tab. 3), especially in the samples from the Ždiar Fm. (EF<sub>Cu</sub> from 1.9 to 5.1 and EF<sub>Ni</sub> – from 1.5 to 3.7). Potentially EF can indicate an additional (nondetrital) source of metals which has been active during sedimentation. However, re-mobilization during diagenesis in the redox condition cannot be excluded.

#### THE REE DISTRIBUTION

Total REEs content in the samples (Tab. 4), summed REEs ( $\Sigma$ REE) and light (L) REEs, heavy (H) REEs and their ratios were used to characterise REE distribution (Tab. 5) along the stratigraphic/time interval. The REEs contents normalised to chondrite (ch) were used to express cerium (Ce/Ce\*) and europium anomalies (Eu/Eu\*) according to the equations: Ce / Ce\* = Ce<sub>N</sub> / (La<sub>N</sub> × Pr<sub>N</sub>)<sup>1/2</sup>, or Eu/Eu\* = Eu<sub>N</sub> / (Sm<sub>N</sub> × Gd<sub>N</sub>)<sup>1/2</sup> respectively (Holser, 1978; Taylor, McLennan, 1985; Lintnerová *et al.*, 2013; Oiu *et al.*, 2015).

ΣREE in the range from 59 to 108 ppm is markedly lower than the ΣREE of the shale (Tab. 5). The ΣREE of the Ždiar Fm. samples (76 to 93 ppm) is comparable to the ΣREE of the Jasenina Fm. samples (59–108), despite of the data encompassing a wider range. The LREE/HREE ratio of all samples is comparable to the shale ratio (Wedepohl, 1971, 1991; Oiu *et al.*, 2015). It was also found that ΣREEs is not proportional to the CaO or SiO<sub>2</sub> variations through both the Ždiar and Jasenina fms. The ΣREEs correlate more proportionally with the Al or Zr, Th or Y and P amounts in the sample set. Such a distribution indicates that the amount of REEs in the sediment has been determined by REEs content in incoming silicate debris. However, this distribution can be modified by local factors in a chemically less stable carbonate system.

It can be suggested that the narrow span of all the REEs values signalises a stable state of the deep water basin in

Table 4

								-						
Analyte	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Sample	[ppm]													
122	20.0	18.8	4.5	18.2	3.49	0.77	3.38	054	297	06	164	024	151	021
126	20.4	26.4	5.24	21.9	4.32	0.97	4.10	068	365	071	196	028	163	023
129	22.0	24.1	5.43	23.3	4.31	0.93	4.18	065	381	073	204	031	167	023
130	20.2	22.4	4.71	19.8	3.68	0.86	3.65	058	317	059	163	023	136	019
132	14.7	16.5	3.76	16.9	3.25	0.73	3.24	052	28	051	149	02	116	017
134	19.1	21.6	4.82	21.4	4.30	0.98	4.21	064	362	071	183	024	154	02
140	17.7	23.7	4.67	21.0	4.41	1.40	4.31	066	364	068	178	026	142	021
141	18.1	23.3	4.73	21.0	3.94	0.87	3.81	059	31	061	169	023	148	02
145	15.0	13.6	3.16	13.9	2.40	0.57	2.64	041	227	046	132	019	114	015
152	17.5	16.0	3.92	15.3	2.80	0.72	3.16	05	278	055	143	02	124	017
159	20.3	18.1	5.6	21.8	4.38	0.99	4.40	071	372	078	202	029	165	024
162	16.7	15.5	3.63	14.1	3.1	0.68	2.89	05	269	052	161	021	123	019
163	13.6	17.8	3.57	14.9	2.74	0.67	2.88	048	244	053	15	022	117	02
164	25.6	25.6	6.80	26.8	5.13	1.20	5.38	082	451	092	256	034	224	031
166	15.2	13.5	3.36	14.5	2.74	0.66	3.10	048	244	053	147	02	115	017
167	18.9	18.2	4.23	18.5	3.48	0.80	3.68	057	304	064	179	024	145	021

Amount of REEs in the rocks sample of the Stražovce section

Samples: 122-141 - the Ždiar Formation, 145-167 - the Jasenina Formation

Analyte	Σ REE	LREE	HREE	L/HREE	Ce/Ce*	Eu/Eu*	(La/Yb)N	(La/Sm)N	(Gd/Yb)N	
Sample		[p	opm]		chondrite no	ormalised	shale-normalized			
122	76.85	69.14	7.71	8.97	0.46	0.69	1.23	1.50	1.18	
126	92.47	83.33	9.14	9.12	0.60	0.70	1.16	0.86	1.33	
129	93.69	84.25	9.44	8.92	0.52	0.67	1.22	0.93	1.32	
130	83.05	75.30	7.75	9.72	0.54	0.72	1.37	1.00	1.42	
132	65.93	59.08	6.85	8.62	0.52	0.69	1.17	0.83	1.48	
134	85.19	76.41	8.78	8.70	0.53	0.70	1.15	0.81	1.44	
140	85.84	77.19	8.65	8.92	0.61	0.98	1.15	0.73	1.60	
141	83.65	75.75	7.90	9.59	0.59	0.69	1.13	0.84	1.36	
145	57.21	51.27	5.94	8.63	0.46	0.69	1.22	1.14	1.22	
152	66.27	59.40	6.87	8.65	0.45	0.74	1.31	1.14	1.35	
159	84.98	75.57	9.41	8.30	0.40	0.69	1.14	0.85	1.41	
162	63.55	56.60	6.95	8.14	0.47	0.69	1.26	0.98	1.24	
163	62.70	56.16	6.54	8.59	0.60	0.73	1.80	0.91	1.30	
164	108.21	96.51	11.70	8.25	0.45	0.70	1.60	0.91	1.27	
166	59.50	53.06	6.44	8.24	0.44	0.69	1.22	1.10	1.42	
167	75.73	67.79	7.94	8.54	0.48	0.68	1.21	0.99	1.34	

Homogeneity of the REEs distribution can better documented by LREE and HREE groups contents separation and LREE/HREE and next rations expression

Chondrite (Ch) normalised data are used for cerium (Ce/Ce\*) and europium (Eu/Eu\*) "anomalies" and for binary-element ratios calculations

a relative long time interval (Late Oxfordian to Early Tithonian). Chondrite normalised data were presented to show the negative Ce (0.40 to 0.61) and Eu (0.69 to 0.74) anomalies in the set of samples. Sample 140 with more positive Eu/Eu<sub>ch</sub> – 0.98 (Tab. 5) is an exception. The typical "V"-pattern at the Ce position is clearly visible in all samples normalised to the shale. It can indicate the mobilization of Ce<sup>3+</sup> in redox conditions. This can be controlled by the equilibrated composition of sea water and also by water anoxia (Elderfield, Greaves, 1982; Hannigan, Sholkovitz, 2001; Haley *et al.*, 2004; Jenkyns, 2010). Negative Ce/Ce<sub>ch</sub>\* values are regarded as the typical deep water ones. Chemical homogeneity of the set was tested by La/Yb, La/Sm and Gd/Yb element ratios calculated from normalised data to shale and are summed in the Table 5.

The REEs distribution can be used also as a valuable proxy of environmental and/or ecological condition in the basin (Holser, 1978; Shield, Webb, 2004; Tribovillard *et al.*, 2006; Cao *et al.*, 2012). However, more positive Eu/Eu\* values and the "bell-shape" of the shale – normalised curve (Fig. 5) indicate a middle REE (MREE) enrichment typical of diagenetically stabilised limestone (Haley *et al.*, 2004; Shield, Webb, 2004; Ounis *et al.*, 2009; Lintnerová *et al.*, 2013; Michalík *et al.*, 2013). The La/Sm<sub>ch</sub> ratio (Tab. 5) represents also a diagenetic signal. The diagram (Fig. 5) shows approximately the same pattern of REEs distribution in sample 145.

# THE RADIOLARIAN MICROFAUNA

The radiolarian fauna consisting of 34 species (including one taxon with open nomenclature; Fig. 6) is assembled into 21 genera which exhibit the characteristic features of the Tethyan assemblage with common representatives of Sethocapsidae, Syringocapsidae, Angulobracchiidae, Emiluviidae and Patulibracchiidae (e.g., Baumgartner et al., 1995). The assemblages (Fig. 4) are characterized by a total absence of orbiculiformids, characteristic of higher palaeolatitudes (the Northern Boreal Radiolarian Province; Pessagno, Blome, 1986; Kiessling, 1999), commonly present in the epicontinental seas which bordered the Tethyan basins to the north (Górka, Bak, 2000). However, the assemblages studied represent rather the Northern Tethyan province (according to the paleogeographic model of Pessagno et al., 1984) based on the lack of pantanellids and the scarcity of the "Ristola-type" parvicingulids. The scarcity of representatives of Ristola and Mirifusus, interpreted so far as deepdwellers (Steiger, 1992) is also characteristic.

Increased radiolarian frequency was observed in the lowermost part of the Ždiar Fm. (Fig. 4). The radiolarian assemblage in this part of the section contains two radiolarian groups which had different ecological preferences. The first group comprises specimens belonging to *Homoeoparonaella*, *Tritrabs*, *Tetratrabs*, *Triactoma* and *Emiluvia* which pos-



Fig. 5. REE patterns of the Strážovce section samples

122–141 – the Ždiar Formation; 145–167 – the Jasenina Formation

Diagrams from data normalised to chondrite (1, 2) and normalised to Average shale (Shale: 3,4) indicate mainly geochemical homogeneity of REEs in both sub-sequences

sessed skeletons adapted to host algal symbionts (Matsuoka, 2007; Bąk, 2011). These species represent warm-water, surface-dwelling species living predominately in the surface mixed layer (Bąk *et al.*, in press). The high abundance of this group indicates a well stratified water structure with a thick, warm, mixed superficial layer, and low nutrient export into the deep waters (De Wever *et al.*, 2001). This group is the most diversified and frequent one in samples S-120 to S-122 of the material studied. On the other hand, the same samples contain also radiolarians which belong to the second ecological group, which may represent a subsurface radiolarian assemblage living in colder water near to the thermocline (Bąk *et al.*, in press). In the material studied, this group comprises mostly nassellarians especially *Podobursa*, *Williriedellum* and *Xitus*.

The abundance of radiolarians is reaching its maximum at the end of the lower part of the Ždiar Fm. sequence (Fig. 4). Towards the upper part of the section both radiolarian frequency and diversity diminishes up to the above-lying deposits belonging to the Jasenina Fm. This step-wise change might reflect a decrease of sea surface temperature and changes in the nutrients exchange in the water column (*e.g.*, Abelmann, Gowing, 1996; Wang *et al.*, 2000).

Biostratigraphy. - The age of the radiolarian assemblages is discussed in terms of the Unitary Association Zones (U.A.Z.) defined by Baumgartner et al. (1995). The first sample with an age diagnostic radiolarian assemblage is S-121 (Fig. 4). This radiolarian assemblage is correlated with U.A.Z. 9 and indicates an age not earlier than middle Oxfordian based on the co-occurrence of species such as Sethocapsa (?) sphaerica (Ožvoldová), Parvicingula mashitaensis Mizutani and Pseudodictyomitra primitiva Matsuoka et Yao. Radiolarian species correlating with the U.A.Z. 9 (Middle to Late Oxfordian) are present in samples from interval S-122 up to S-133. The minimum age of the interval is constrained by Emiluvia ordinaria Ožvoldová and Sethocapsa (?) sphaerica (Ožvoldová) which first appeared in this zone. The radiolarian assemblage in sample S-133 (Fig. 4) and above is correlated with U.A.Z. 10 (Early Kimmeridgian) based on the co-occurrence of such radiolar-



Fig. 6. Radiolarians from the Ždiar Fm. in the Strážovce section

A – Paronaella broennimanni, sample 102; B – Homeoparonaella pseudoewingi, sample 102; C – Tritrabs ewingi s.l., sample 102; D – Tritrabs hayi, sample 102; E – Transhsuum maxwelli, sample 102; F – Parvicingula mashitaensis, sample 121; G – Napora deweveri, sample 121; H – Napora lospensis, sample 121; I – Williriedellum crystallinum, sample 122; J – Xitus magnus, sample 122; K – Sethocapsa trachyostraca, sample 129; L – Sethocapsa sphaerica, sample 133; M – Spongocapsula perampla, sample 144.5; N – Higumastra inflata, sample 144.5; O – Emiluvia ordinaria, sample 144.5; P – Angulobracchia biordinalis, sample 121; Q – Obesacapsula cetia, sample 133; R – Mirifusus dianae dianae, sample 121; S – Podobursa helvetica, sample 120; T – Pseudoeucyrtis (?) fusus, sample 122; U – Parvicingula boesti, sample 129; W – Williriedellum carpathicum, sample 122; X – Triactoma jonessi, sample 144.5; scale bars 0.1 cm

ian events as the first appearance of *Obesacapsula cetia* (Foreman) and the last appearance of *Higumastra inflata* Baumgartner in this interval.

## DISCUSSION

# REPLACEMENT OF NERITIC SEDIMENTATION BY A BASINAL ONE

Classical authors (*e.g.*, Winterer, Bosellini, 1981) related Jurassic sedimentary changes in Mediterranean Tethys to the bathymetry increase caused by rapid subsidence of the European continental margin. On the other hand, Muttoni *et al.* (2005) tried to explain the substitution of neritic limestone sedimentation by pelagic radiolarite facies as being due to the CCD shallowing after Mediterranean microplate motion into a more equatorial position during the Jurassic Period.

Lefeld (1974) supposed that missing record of 15 Ma below the Oxfordian – Kimmeridgian siliceous formations (in the Fatric Basin of the Western Carpathians) was removed by dissolution of Bajocian – Callovian strata during the Mid Jurassic collapse. An equivalent gap below the Callovian Ruhpolding Radiolarite Formation has been reported by Gawlick and Schlagintweit (2010) from Lower Tirolic units of the Eastern Alps. Rais *et al.* (2009) explained the reduction of the Middle Jurassic sediment pile along the Northern Mediterranean Tethys shelf rather by strong sea current activity caused by the opening of new seaways at a time of the progressive Pangaea breakup.

Mišík (1964) noted the submarine slump character of the Toarcian – Aalenian "Adnet" complex resting below radiolarites in the Veľká Fatra Mts, Western Carpathians. Collapse breccia and slump deformations below base of the Ždiar Formation in the Strážovce section (Borza *et al.*,1980; Michalík, 1985) date this slumping as pre-Callovian. Huge Pleš Breccia of the Tatric area of the Malé Karpaty Mts has been also interpreted as a collapse breccia associated with sudden post-Toarcian basinal bottom deepening (Michalík, Vlčko, 2011).

The Zliechov Basin has been situated on a sialic crust fragment of the northern Tethyan shelf affected by tension (Michalík, 1993, 1994). While the Triassic changes observed were attributable rather to global climatic variations (Michalík *et al.*, 2007, 2013), the Jurassic evolution has been mostly controlled by a rift subsidence (Michalík, 2007). Sudden deepening during the Middle Jurassic has been recorded by the sequence of hemipelagic limestones through condensed Toarcian Adnet Limestone and Aalenian silicitic limestones to the eupelagic Callovian – Kimmeridgian Ždiar Formation. These Upper Jurassic / Lower Cretaceous sediments were deposited in an extensional ("pull-apart") basin with thinned crust (Fig. 7).

#### SOURCES OF THE DETRITAL MATERIAL

The ratios of Th and Y vs Cr, Sc, Ni and V, which could discriminate the felsic/basic source of material are equivalent to those of the Average Shale. A certain condensation of the Oxfordian strata resulted in the relatively higher content of metals. The contents of several oxides (Cr<sub>2</sub>O<sub>3</sub>, Sc, Th, MnO) are close to the determination limit, which calls for caution. The REEs analysis points to a similar conclusion. The curves and values of the Ce<sub>Ch</sub> and Eu<sub>Ch</sub> anomalies are comparable, indicating a felsic source of the material in the whole sequence studied. Orbitally paced chemical weathering across the Pangea supercontinent which supplied the biosilica production was nonlinearly amplified by mega-monsoons during the early Mesozoic greenhouse world (Ikeda et al., 2017). EF<sub>Ni</sub> and other metals (Cu, Zn) indicate sediment enrichment and an additional (non-detrital) source of metals. This supposition make the interpretation of the character of the detrital source more complicated. Principally, hydrothermal fluids accompanying the rifting of the basin also could enrich the sediment with metals.

## SILICITE- TO LIMESTONE DEPOSITION

Beds saturated with the silica of siliceous radiolarian tests indicate mobilization of both  $SiO_2$  and nutrients by upwelling (Bernoulli, Jenkyns, 2009). On the other hand, the calcitic skeletal particles have been never totally dissolved, which points to the conclusion of a permanent calcite saturation of the seawater with high and stable CaCO<sub>3</sub> content in depths only slightly affected by lysocline (CCD) proximity.

The upwards decreasing biogenic silica content and the substitution of siliceous bioproduction by a calcitic one could have been connected with a change of the nutrition regime. The relative amount of sufficient bases (K<sub>2</sub>O, Na<sub>2</sub>O, CaO) and residual components (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Zr) could serve as proxies of the depositional process. However, the high share of the calcareous component diluted the detrital content so that the calculation models used could be not optimalized. The CIA and CPA data presented here are not quite distinct because the method of aproximation of noncarbonate CaO content does not fit with this relative short data set.

The REEs distribution can be used as a primary proxy of the deep water environment (Haley *et al.*, 2004; Ounis *et al.*, 2009). Ce and Eu anomalies can be used as indicators of redox conditions changing in seawater, in bottom sediment, and potentially also in diagenetic fluids. The REEs distribution model with its negative values of the Ce<sub>ch</sub>\* anomaly (Fig. 5, Tab. 5) and slight depletion in comparison with the Average Shale suggest Ce mobilization (as Ce<sup>3+</sup>) in a dysoxic deep ocean (Elderfield, Greaves, 1982; Hannigan, Sholkovitz, 2001; Haley *et al.*, 2004; Jenkyns, 2010). The REEs distribution is related to a slowly changing redox regime from the Ždiar towards the Jasenina formations.

#### THE ROLE OF DIAGENESIS

Both major components of the sediment (siliceous vs calcareous) changed during diagenesis. Dissolution of siliceous and calcareous tests resulted in a homogenization trend of the rock chemistry. Higher, the Sr content decreasing slightly upwards recorded both the gradual change of the original (aragonitic, high Mg calcite) mineralogy to a low Mg calcite one, and stabilized the limestone in the relatively closed system. Diagenetic calcification can be also indicated by the dependence of the non-detrital Ca on the Sr. Silicite formation was accompanied by diagenetic mobilization of biogenic elements (Si, Mg, P, Mn). Higher ER values of these elements (Tab. 3) can only partially help to distinguish the diagenetic signal from the detrital one or from intrabasinal hydrothermal sources. The EF values signalise relative



Fig. 7. Interpretative model of the Zliechov Basin paleogeographic evolution by pull-apart mechanism under crust tension regime in the Fatric between Rhaetian, Callovian and Valanginian. Adapted from Michalík (2007)

accumulation of metals (Cu, Ni, Zn) in the older part of sequence (Ždiar Fm., Tab. 3). However, the relative values of EF fluctuate in individual beds. EF > 1 values can be associated with condensation, hydrothermal fluid input, upwelling and other synsedimentary processes, but metal enrichment can be caused by postsedimentary stabilization of carbonate mud and silica chert formation.

The "bell-shaped" curve normalized to the Average Shale indicates diagenesis in buried sediment. It resulted in the MREEs mobilization in carbonate complexes, or in the mobilization of biogenic phosphate (from fossils) in various pH and redox conditions. Lowered La/Sm<sub>Ch</sub> values (Tab. 5) in the middle part of the section could signalize diagenetic mobilization (Haley *et al.*, 2004; Ounis *et al.*, 2009). Similarly, the REEs mobilization could be consistent with the Fe mobilization, which could potentially have been disolved in reduced conditions and it could have played this role during REEs diagnetic redistribution of organic matter and clays have to play potentially important role, but these factors were not analysed specifically.

# CONCLUSIONS

- The sedimentary sequence records condensation and even a Bajocian / Bathonian gap in deposition. The bottom in a tectonic regime which was extensional in nature collapsed during the Middle and Late Oxfordian. The sediments in the bottom fill slid towards centre of the basin. Pelagic radiolarian limestones and marly limestones were deposited later on.
- A radiolarian assemblage typical of the North Tethyan Bioprovince lived near to the surface of a well stratified warm water column, partially close to the thermocline. It points to a mid Oxfordian – Early Kimmeridgian age of the sediments. The abundance of radiolarians decreases upwards.
- 3. Geochemical data the CIA CIW and EF indexes (about 1) of Na, K, Fe, Ti, Zr, trace element and REEs values indicate that detrital material came more probably from weathered felsic sources. Thus, Oxfordian /Kimmeridgian siliceous sedimentation in the Zliechov Basin was probably controlled by monsoon invoked input of weathered material from the land. However, it still remains uncertain, if increased silica production and metal enrichment in the Ždiar Fm. supported the existence of other sources (fluids from hydrotherms in the bottom rifts).
- 4. In comparison to the Average Shale, the decreased ΣREE's and negative Ce<sub>ch</sub> and Eu<sub>ch</sub> anomalies could be regarded as a typical deep sea water signal. The differentiated REE record of the higher calcareous Jasenina Fm.

suggests basinal dysoxic conditions. A "bell-shape" of curves (normalized to shale) indicates that REEs were slightly affected by carbonate diagenesis.

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