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The basic composite section in the Barrandian Lower Devonian succession of the beds using magnetic susceptibility stratigraphy

Opěrný profil barrandienským spodním devonem s použitím magnetosusceptibilitní stratigrafie

Doctoral Thesis

Dizertační práce

Supervised by: Doc. RNDr. Jindřich Hladil, DrSc.
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I declare that this thesis was written by myself and presents my own work developed under the guidance of my supervisor, and all sources have been properly cited. Neither this dissertation, nor any part of it, has been used for acquisition of the same or other academic title.

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Abbreviation index

BCE	Basal Choteč Event
CDT	Canyon Diablo Troilite
CIE a*	red-green axis in CIE 1976 colour space
CIE b*	blue-yellow axis in CIE 1976 colour space
CIE L*	brightness in CIE 1976 colour space
DTW	dynamic time warping
EDX	energy-dispersive X-ray analysis
FM	formation (lithostratigraphic unit)
GLI AS CR, v. v. i.	Institute of Geology of the Academy of Sciences of the Czech Republic
GRS	gamma-ray spectrometry
GSSP	Global Boundary Stratotype Section and Point
ICP-MS	inductively coupled plasma-mass spectrometry
IF	impact factor
INAA	instrumental neutron activation analysis
IRM	isothermal remanent magnetization
LMST	limestone
LREE	light rare earth elements
MS	magnetic susceptibility
MSEC	Magnetosusceptibility Event and Cyclostratigraphy
NPI AS CR, v. v. i.	Nuclear Physics Institute of the Academy of Sciences of the Czech Republic
PAAS	Post-Archaen Australian Shale
R^2	coefficient of determination
REE	rare earth elements
SEM-EMPA	scanning-electron microscopy – electron microprobe analysis
SR	spectral reflectance
TR	trace elements
T-R	transgressive-regressive
V-SMOW	Vienna Standard Mean Ocean Water
XRD	X-ray diffraction

Content

1 Abstracts (English, Czech)

The composite reference section in the Lower Devonian succession was established using the magnetic susceptibility (MS) and gamma-ray spectrometric (GRS) logs from 5 sections representing both deep- and shallow-water environment of carbonate slope systems in the Prague Synform. Both background data and data across the boundaries of geological units or event intervals were acquired with the emphasis on obtaining continuous data series. Such a complex, detailed and multidisciplinary data set (petrophysical, lithological, mineralogical and geochemical parameters) has never been collected here. They were linked to the existing biostratigraphical scales and offer complex information for interregional and global correlations now with the precision of a few centimetres, which is a resolution 10 to 100 fold higher than in any established biostratigraphic scale in the Devonian of the Prague Synform.

Major changes in the MS, GRS logs and mineralogy concentrate to the proximity of the Lochkovian–Pragian boundary (close to the Lochkov–Praha Fm. boundary). At this level, a reversal point in Th/U ratios is observed (dominant Th concentrations in the Praha Fm. vs. dominant U concentrations in the underlying Lochkov Fm. and overlying Zlíchov Fm. There is a general transgressive trend for the Lochkov and Praha Fm. followed by a significant regression close to the Lochkovian–Pragian boundary. Then 3rd-order transgressive pulse, a drop in sedimentation rate and a decrease in carbonate productivity follow. The position of K, Th, MS maxima and barite enrichment in the Praha Fm. is interpreted here as an increase in the flux of non-carbonate impurities (mostly of paramagnetic character). It might reflect a major change in the atmospheric circulation (changes in wind directions or intensities). A regressive trend toward the Zlíchov Fm. commences in the upper parts of the Praha Fm.

Fe-oxides and oxyhydroxides (magnetite, hematite, goethite), pyrrhotite, ilmenite, pyroxene, amphibole, olivine, chlorite, biotite, glauconite, clay minerals (illite, kaolinite, montmorillonite), ankerite, Fe-rich dolomite, pyrite, chalcopyrite, epidote were identified in insoluble residues as the MS carriers. Quartz, muscovite, dolomite, feldspars (orthoclase, microcline, albite), zircon, barite, apatite, rutile were identified as diamagnetic phases. To sum up, minerals with paramagnetic characteristics were revealed as dominant MS carriers. The Lochkov Fm. (to a certain extent also the Zlíchov Fm.) is characterized by an elevated abundance of pyrite–pyrrhotite assemblages and a low abundance of Fe-oxides (goethite prevailing over hematite or magnetite) whereas the Praha Fm. is dominated by Fe-oxides. Geochemical parameters (mostly the REE and trace elements distributions) show very uniform patterns across the entire reference composite section, and are indicative aeolian origin of the limestone impurities.

The correlative MS and GRS patterns (a point of reversal in the Th/U ratio, a drop in MS values followed by oscillations) through the Emsian–Eifelian successions were found regionally but also on very distant places around the world. Tentative global links of the MS pattern across the Basal Choteč Event interval (BCE) were outlined across different palaeogeographical settings between Portugal (Ossa-Morena Zone), Czech Republic (Prague Synform), USA (Nevada, Central Great Basin), Morocco (Anti-Atlas), Uzbekistan (Zeravshan-Gissar Mountain Region). The BCE interval was interpreted as a transgressive pulse connected with upwelling. Mineral assemblages in insoluble residues might be of aeolian origin. MS record is driven rather by grains of paramagnetic characteristics.

Opěrný referenční profil spodnodevonskými vápencovými sledy v pražské synformě pomocí magnetické susceptibility (MS) byl sestaven celkem z pěti jednotlivých profilů reprezentující jak relativně hlubokovodní, tak mělkovodní prostředí karbonátových svahů. Byly získány jak normální pozaďové hodnoty, tak data napříč významnými eventy a hraničními intervaly mezi stratigrafickými jednotkami s důrazem na získání co nejkompletnějšího záznamu. Natolik podrobný a multidisciplinárně pojatý datový set dosud nebyl v pražské synformě shromážděn. Sestává z petrofyzikálních (MS, gamaspektrometrie – GRS), litologických, mineralogických a geochemických parametrů, je provázán s již existujícími biostratigrafickými škálami a nabízí nyní komplexní informaci využitelnou pro regionální, interregionální a globální korelaci s přesností až na několik centimetrů (vyjádřeno časově až s přesností 1 – 10 ka). Toto rozlišení je zhruba 10 až 100krát vyšší než jaké poskytuje jakákoliv biostratigrafická škála devonu v rámci pražské synformy.

Nejvýznamnější změny v MS, GRS záznamu a minerálním složení hornin jsou koncentrovány do těsné blízkosti hranice stupňů lochkov a prag (v blízkosti hranice mezi lochkovským a pražským souvrstvím). Pražské souvrství je charakterizováno stabilním záznamem se zvýšenými hodnotami MS a GRS ve srovnání s podložním lochkovským a nadložním zlíchovským souvrstvím (ems). V úrovni této hranice je významným fenoménem zvrat v průběhu poměru Th/U. V pražském souvrství je celková radioaktivita řízena obsahy Th, zatímco v lochkovském a zlíchovském souvrství dominují obsahy U. Lochkovské a pražském souvrství zachycuje transgresní trend, který je vystřídán významnou regresní událostí v blízkosti hranice lochkov–prag. Následuje transgresní pulz 3. řádu, zpomalení sedimentační rychlosti a snížení karbonátové produkce. Pozice maxim v obsazích K, Th, MS a množství barytu jsou zde interpretovány jako důsledek zvýšeného přínosu nekarbonátového materiálu (materiál s paramagnetickými vlastnostmi). To může odrážet změnu v atmosférické cirkulaci (změny ve větrném proudění – směrů či intenzit). Ve svrchní části pražského souvrství nastupuje opět regresní trend, který pokračuje až do zlíchovského souvrství.

Fe-oxidy a oxyhydroxidy (magnetit, hematit, goethit), pyrhotin, ilmenit, pyroxen, amfibol, olivín, chlorit, biotit, glaukonit, jílové minerály (illit, kaolinit, montmorillonit), ankerit, dolomit s obsahem Fe, pyrit, chalkopyrit, epidot byly identifikovány jako nositelé MS signálu. Mezi diamagnetickými fázemi byly identifikovány křemen, muskovit, dolomit, živce (ortoklas, mikroklin, albit), zirkon, baryt, apatit, rutil. Jako hlavní nositelé MS signálu dominují minerály s paramagnetickými vlastnostmi. Lochkovské (do jisté míry i zlíchovské souvrství) je charakterizováno zvýšeným množstvím pyritu, pyrhotinu a nízkými obsahy Fe-oxidů a oxyhydroxidů, zatímco Fe-oxidy dominují v pražském souvrství. Geochemické parametry (distribuce stopových prvků a REE) ukazují velmi jednotné vzory v průběhu celého referenčního kompozitního profilu a indikují eolický původ vápencových nečistot.

Dobře korelovatelné MS a GRS vzory byly nalezeny v ems–eifelských sledech v úrovni bazálního chotečského eventu (BCE) jak v regionálním (v rámci pražské synformy), tak globálním měřítku (korelace mezi kontinenty, napříč někdejšími oceány) – zvrat v průběhu Th/U a náhlý pokles hodnot MS vystřídaný oscilacemi. Bylo navrženo propojení různých paleogeografických prostředí: Portugalska (zóna Ossa-Morena), České republiky (pražská synforma), USA (Nevada, centrální Velká pánev), Maroka (Anti-Atlas) a Uzbekistánu (oblast Zeravšanského a Gissarského hřbetu, jižní Ťan-Šan). BCE byl interpretován jako transgresní puls spojený s výstupem hlubinných vod (upwellingem). Původ minerálních fází v nerozpustných zbytcích je pravděpodobně eolický. Záznam MS je řízen spíše paramagnetickými fázemi.

2 Introduction

Motivation and objective setting of the thesis

The thesis consists of a selection of 7 main papers (Table 1). The overview provides condensed information on the work plan, individual findings, methods and principal results.

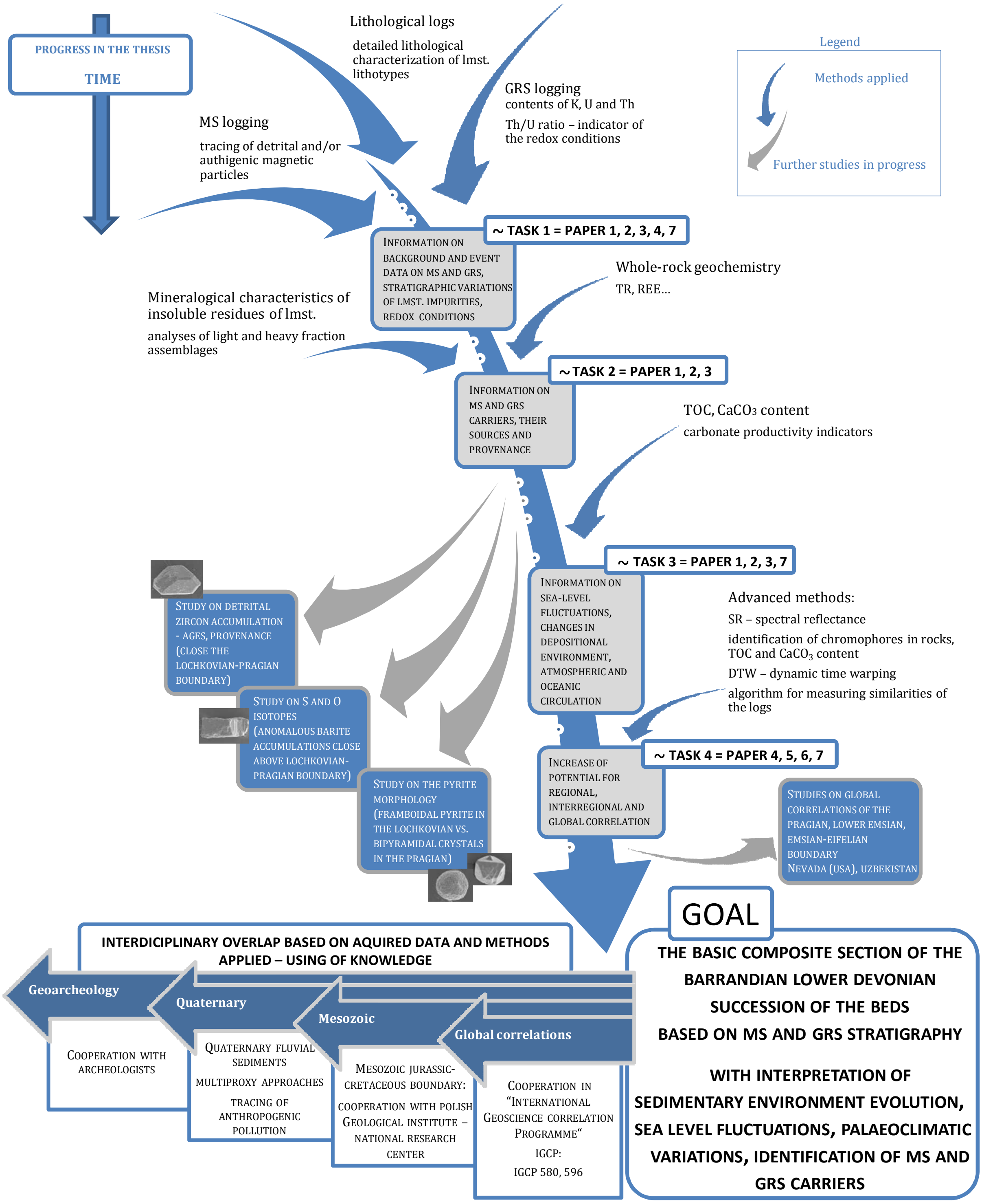
Table 1

1	**Koptíková, L.**, Hladil, J., Slavík, L., Čejchan, P. & Bábek, O., 2010. Fine-grained non-carbonate particulates embedded in neritic to pelagic limestones (Lochkovian to Emsian, Prague Synform, Czech Republic): composition, provenance and links to magnetic susceptibility and gamma-ray logs. *Geologica Belgica*, 13, 4: 407-430.	**IF 0.645**
2	**Koptíková, L.**, Bábek, O., Hladil, J., Kalvoda, J. & Slavík, L., 2010. Stratigraphic significance and resolution of spectral reflectance logs in Lower Devonian carbonates of the Barrandian area, Czech Republic; a correlation with magnetic susceptibility and gamma-ray logs. *Sedimentary Geology*, 225: 83-98.	**IF 1.957**
3	**Koptíková, L.**, 2011. Precise position of the Basal Choteč Event and evolution of sedimentary environments near the Lower-Middle Devonian boundary: The magnetic susceptibility, gamma-ray spectrometric, lithological, and geochemical record of the Prague Synform (Czech Republic). *In*: Brett, C.E., Schindler, E., P. & Königshof, P. (Eds), Sea-level cyclicity, climate change, and bioevents in Middle Devonian marine and terrestrial environments. Palaeogeography, Palaeoclimatology, Palaeoecology, 304, 1-2: 96-112.	**IF 2.646**
4	Ellwood, B.B., García-Alcalde, J.L., El Hassani, A., Hladil, J., Soto, F.M., Truyóls-Massoni, M., Weddige, K. & **Koptikova, L.**, 2006. Stratigraphy of the Middle Devonian boundary: Formal definition of the susceptibility magnetostratotype in Germany with comparisons to sections in the Czech Republic, Morocco and Spain. *Tectonophysics*, 418, 1-2: 31-49.	**IF 1.675**
5	Hladil, J., Vondra, M., Cejchan, P., Vich, R., **Koptikova, L.** & Slavik, L., 2010. The dynamic time-warping approach to comparison of magnetic susceptibility logs and application to Lower Devonian calciturbidites (Prague Synform, Bohemian Massif). *Geologica Belgica*, 13, 4: 385-406.	**IF 0.645**
6	Machado, G., Hladil, J., Slavík, L., **Koptíková, L.**, Moreira, N., Fonseca, M. & Fonseca, P., 2010. An Emsian-Eifelian calciturbidite sequence and the possible correlatable pattern of the Basal Choteč event in Western Ossa-Morena Zone, Portugal (Odivelas Limestone). *Geologica Belgica*, 13, 4: 431-446.	**IF 0.645**
7	Machado, G., Hladil, J., **Koptíková, L.**, Fonseca, P.E., Rocha, F.T. & Galle, A., 2009. The Odivelas Limestone: evidence for a Middle Devonian reef system in western Ossa-Morena Zone (Portugal). *Geologica Carpathica*, 60, 2: 121-137.	**IF 0.963**

Sequential progress of the thesis, individual topics and tasks completed in the progress of time as well as papers published, methods used and case studies emerged as the branches of further research are shown in Chart 1.

This thesis deals with the study of the Lower Devonian marine limestone successions cropping out in the Prague Synform (Melichar, 2004; cf. also Prague Basin – Havlíček, 1981) which lies in the upper central part of the Teplá-Barrandian Unit (i.e., the area first defined by Máška & Zoubek, 1961; or mentioned as the Bohemicum Block by Malkovský, 1979; see also Chaloupský et al., 1995; Melichar, 2003; McCann et al., 2008; or Cháb et al., 2010 for further use) and is a part of the Bohemian Massif and central European Variscan Belt. Data sets on geophysical, petrophysical, geochemical, mineralogical and lithological characteristics of the limestones were obtained using novel high-resolution methods such as MS stratigraphy and GRS in the background of a detailed study of sedimentology and mineralogy of insoluble residues of the limestones. Resulting data sets were intended to complete geophysical and lithological data on the Devonian limestone beds in the Czech Republic acquired by Geršl (2008) in his doctoral thesis in the Eifelian – Frasnian platform limestones in the Moravian Karst Area.

Palaeozoic and mostly Devonian sediments in the Prague Synform have been studied for more than 150 years since Joachim Barrande's times. Most of the studies and papers deal with the biostratigraphy and palaeontology. Therefore, reliable biostratigraphic charts have been established for this area. Methods applied to rocks within this doctoral thesis have never been used to such extent yet. During the first year of data acquisition, we decided to employ an additional low-cost and very effective high-resolution method: outcrop GRS logging through the composite section. The purpose for the use of this method was to extend data on the concentrations and quality of limestone impurities and, consequently, to improve the interpretations of palaeoenvironmental changes. Other proxies and methods such as SR, TOC or $CaCO_3$ content measurements were applied to rocks in selected stratigraphic intervals where additional data were requested by the reviewers of the papers (Paper 2 – TOC and $CaCO_3$ parameters in Koptíková et al., 2010b). The newly acquired data sets proved to be very promising for testing the SR method of chromophores identification in rocks, TOC, $CaCO_3$ contents and its relationship to MS and GRS logs (Paper 2 – SR in Koptíková et al., 2010b), or the DTW and algorithm to MS measurements (Paper 5 – in Hladil et al., 2010b).



PROGRESS IN THE THESIS

TIME

Legend

Methods applied

Further studies in progress

Lithological logs

detailed lithological characterization of lmst. lithotypes

GRS logging

contents of K, U and Th

Th/U ratio – indicator of the redox conditions

MS logging

tracing of detrital and/or authigenic magnetic particles

~ TASK 1 = PAPER 1, 2, 3, 4, 7

INFORMATION ON BACKGROUND AND EVENT DATA ON MS AND GRS, STRATIGRAPHIC VARIATIONS OF LMST. IMPURITIES, REDOX CONDITIONS

Whole-rock geochemistry

TR, REE...

Mineralogical characteristics of insoluble residues of lmst.

analyses of light and heavy fraction assemblages

~ TASK 2 = PAPER 1, 2, 3

INFORMATION ON MS AND GRS CARRIERS, THEIR SOURCES AND PROVENANCE

TOC, $CaCO_3$ content

carbonate productivity indicators

~ TASK 3 = PAPER 1, 2, 3, 7

INFORMATION ON SEA-LEVEL FLUCTUATIONS, CHANGES IN DEPOSITIONAL ENVIRONMENT, ATMOSPHERIC AND OCEANIC CIRCULATION

Advanced methods:

SR – spectral reflectance

identification of chromophores in rocks, TOC and $CaCO_3$ content

DTW – dynamic time warping

algorithm for measuring similarities of the logs

STUDY ON DETRITAL ZIRCON ACCUMULATION - AGES, PROVENANCE (CLOSE THE LOCHKOVIAN-PRAGIAN BOUNDARY)

STUDY ON S AND O ISOTOPES (ANOMALOUS BARITE ACCUMULATIONS CLOSE ABOVE LOCHKOVIAN-PRAGIAN BOUNDARY)

STUDY ON THE PYRITE MORPHOLOGY (FRAMBOIDAL PYRITE IN THE LOCHKOVIAN VS. BIPYRAMIDAL CRYSTALS IN THE PRAGIAN)

~ TASK 4 = PAPER 4, 5, 6, 7

INCREASE OF POTENTIAL FOR REGIONAL, INTERREGIONAL AND GLOBAL CORRELATION

STUDIES ON GLOBAL CORRELATIONS OF THE PRAGIAN, LOWER EMSIAN, EMSIAN-EIFELIAN BOUNDARY NEVADA (USA), UZBEKISTAN

GOAL

THE BASIC COMPOSITE SECTION OF THE BARRANDIAN LOWER DEVONIAN SUCCESSION OF THE BEDS BASED ON MS AND GRS STRATIGRAPHY

WITH INTERPRETATION OF SEDIMENTARY ENVIRONMENT EVOLUTION, SEA LEVEL FLUCTUATIONS, PALAEOCLIMATIC VARIATIONS, IDENTIFICATION OF MS AND GRS CARRIERS

INTERDISCIPLINARY OVERLAP BASED ON AQUIRED DATA AND METHODS APPLIED – USING OF KNOWLEDGE

Geoarcheology

COOPERATION WITH ARCHEOLOGISTS

Quaternary

QUATERNARY FLUVIAL SEDIMENTS

MULTIPROXY APPROACHES

TRACING OF ANTHROPOGENIC POLLUTION

Mesozoic

MESOZOIC JURASSIC-CRETACEOUS BOUNDARY:

COOPERATION WITH POLISH GEOLOGICAL INSTITUTE – NATIONAL RESEARCH CENTER

Global correlations

COOPERATION IN “INTERNATIONAL GEOSCIENCE CORRELATION PROGRAMME“

IGCP:

IGCP 580, 596

Chart 1. Sequential progress of the thesis, individual topics and tasks completed in the progress of time as well as papers revealed, methods used, case studies emerged, branches of further research, implications for the use of the methods in different scientific fields, joint projects and international cooperation.

The original setting of this doctoral thesis was to establish a composed MS profile through entire Devonian sedimentary rocks in the Prague Synform which embraces the stratigraphic interval from the Silurian–Devonian boundary up to the lowermost Givetian when carbonate sedimentation in the Prague Synform ends due to incipient Variscan Orogeny. Due to the huge volume of field work and processing of the results as well as extended method range applied on the rocks, the theme of the thesis was restricted from the original title “The basic composite section in the Barrandian Devonian succession of the beds using magnetic susceptibility stratigraphy“ to the study of Lower Devonian limestone succession of the beds (approved by the Board of PhD. studies I at Charles University in Prague in 2009.

4 GENERAL TASKS HAVE BEEN ASSIGNED IN THIS DOCTORAL THESIS:

1	**COMPOSITE SECTION: ESTABLISHING OF CONTINUOUS MS AND GRS LOGS, CHARACTERIZATION OF THE LOGS AND GENERAL TRENDS ACROSS THE LOWER DEVONIAN STRATA IN THE PRAGUE SYNFORM – BOTH BACKGROUND AND EVENT DATA RECORDS** To obtain a continuous composite section using MS and GRS stratigraphy of the Lower Devonian strata in the Prague Synform with special emphasis on the continuity of the logging not only across important selected stratigraphic points or reference boundary intervals but across whole stratigraphic units and stages to obtain “normal“ background data between these boundaries, intervals or events. Many papers on biostratigraphy, lithology, geochemistry etc. concentrate on the “critical“ intervals and important boundaries between geological units (systems, stages, series, formations…); the aim of this complex study is to propose complete and continuous data – a task never accomplished before. The main criterion for assembling a composite section from convenient individual sections was to cover the possibly most continuous stratigraphic range from the Lower Devonian up to the Lower–Middle Devonian boundary. 5 sections were studied; Figure 1.

2	**INTERPRETATION OF MS AND GRS LOGS IN TERMS OF EUSTATIC, PALAEOCLIMATIC CHANGES, CHANGES IN SEDIMENTARY ENVIRONMENT; QUALITIES, QUANTITIES AND PROVENANCE OF NON-CARBONATE IMPURITIES OF THE LIMESTONES** To obtain a continuous record of palaeoclimatic changes and changes in the depositional environment across the studied interval based on the stratigraphic variations in the amounts, quality and provenance of the non-carbonate material trapped in the limestones as the carriers of MS and GRS logs, and their interpretation in terms of eustatic changes. To provide information on the mineralogy of insoluble residues of the lithotypes and the stratigraphic variations of the TR concentrations, especially the REE distributions, to reveal possible sources of the limestone impurities.
3	**DETAILED LITHOLOGICAL STUDIES ON LIMESTONE LITHOTYPES OF THE COMPOSITE SECTION – EVOLUTION OF SEDIMENTARY ENVIRONMENTS** To interpret sedimentary and diagenetic textures of the studied limestone lithotypes based on a detailed microscopic study, evolution of sedimentary environment and changes across the studied interval.
4	**IMPROVEMENT OF BIOSTRATIGRAPHIC RESOLUTION, POTENTIAL FOR REGIONAL, INTERREGIONAL AND GLOBAL CORRELATION OF THE LOGS** To increase the potential for regional (within a sedimentary basin), interregional and global correlations of this stratigraphic interval using multidisciplinary data sets on MS, GRS, lithological, geochemical and mineralogical properties of the limestone strata in the Prague Synform. To apply high-resolution MS stratigraphy to the composite section and combine it with biostratigraphy which is not available in such resolution in the Lower Devonian beds of the Prague Synform. The resolution of this method is at least 10 to 100 fold higher compared to biostratigraphy, in the scale of centimetres to the first tens of centimetres (Koptíková, 2004).

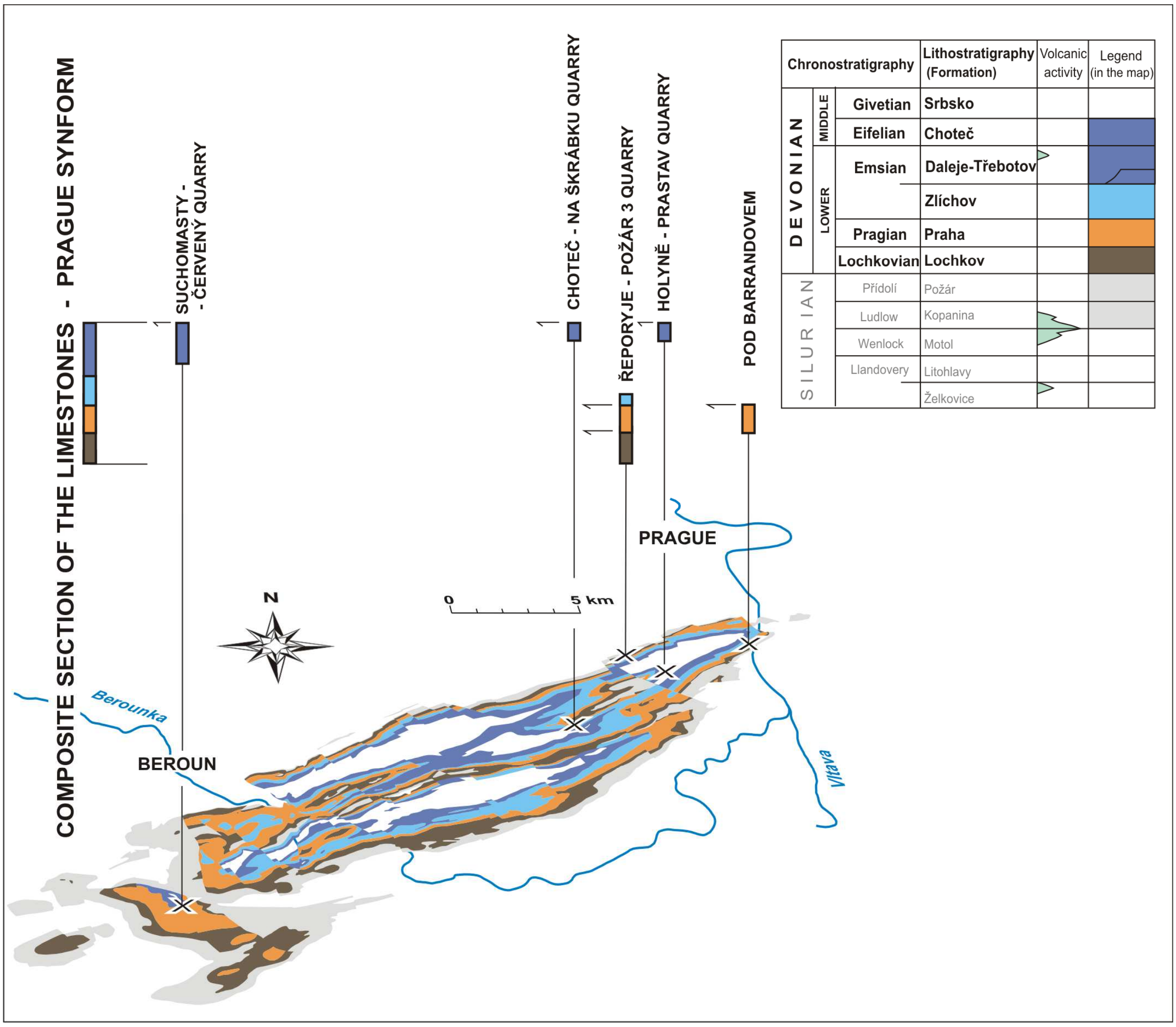


Fig. 1 A simplified map of the Prague Synform with the locations of studied composite sections and their stratigraphic ranges (modified after Koptíková et al., 2010a).

3 Methods

3.1 MS

MS is a dimensionless physical quantity which expresses the magnetization acquired in material exposed to external magnetic field. The use of magnetization depends on the concentration, quality, grain size or morphology of magnetic component in the studied sample. Magnetic properties of atoms result from the character of the electron cloud and the sum of magnetic moments of charged atomic particles (protons and neutrons). Magnetic properties of molecules and phases depend on the properties of atoms and additionally also on crystal lattice field and valence electrons which are responsible for interatomic coupling. A relation between magnetization and magnetic field intensity is expressed as $M = H \times \kappa_m$ where M is magnetization, H is the magnetic field intensity and κ_m is a constant – MS. There are 3 groups of materials in general according to the behaviour in the external magnetic field depending on a total vector sum of magnetic moments: material has diamagnetic characteristics if $\kappa_m < 0$, paramagnetic if $\kappa_m > 0$, and ferromagnetic *s. l.* characteristics (further divided into ferrimagnetic, antiferromagnetic and ferromagnetic *s. s.* materials; see Butler, 1992 or Moscowitz, 1991) if $\kappa_m >> 0$. The low-field MS or sometimes initial susceptibility (Dekkers, 1997; Heller & Evans, 2003) is one of the proxies used in environmental magnetism studies (Thompson et al., 1980; Heller & Evans, 2003), and in studies of natural or anthropogenic materials including solid rocks, soils, dusts, organic tissues, peats or anthropogenic-derived components. MS measurements are suitable to follow the content of magnetic minerals, Fe-bearing minerals particularly.

MS measurements have been in use in sedimentary rocks for more than thirty years since 1980s, originally in non-carbonate material such as loess and lacustrine sediments, later also in marine rocks. Their use is justified by the fact that sedimentary rocks are usually composed of diamagnetic (or paramagnetic) matrix because most of rock-forming silicate minerals have such properties. As a result, the identification of the Fe-, Fe–Mn-bearing phases or clay minerals, trapped as a form of impurity is easier in such medium. In pure media such as limestones, composed – under ideal circumstances – only of calcium carbonate, magnetic components can be easily revealed using MS. Their origin and provenance is a subject of scientific studies.

Acquired MS logs reflect stratigraphic variations in these impurities and can be interpreted in terms of environmental, tectonic, palaeoclimatic changes or sea level fluctuations (Crick et al., 1997a; Ellwood et al., 2000). High MS values are generally postulated to be connected with low sea levels with enhanced erosional activity when terrestrial weathering products are delivered to the sea in high amounts. In contrast, low values are connected with high sea levels with reduced fluxes of land-derived detrital particles. Also, biological production must be taken into account as well as changes in accumulations of organic carbon because MS belongs among parameters which are concentration-dependent. Most of the papers deal with the Mesozoic but also Palaeozoic and particularly Devonian limestones and MS logs (Crick et al., 1997a, 2000, 2001, 2002; da Silva et al., 2009; Ellwood et al., 2008; Riquier et al., 2007; Hladil et al., 2006, 2009 etc.). Despite the premises concerning sea-level fluctuations and MS values, inverse MS logs have been recorded during several important Devonian events marked by transgression such as the Kačák, Lower Kellwasser, Lower *pumilio* or *mid-punctata* events where high MS values were recorded in the critical interval (Crick et al., 1997b, 2002; Hladil & Pruner, 2001; Hladil, 2002; Hladil et al., 2006; Koptíková, 2011). The role of atmospheric dust delivered into depositional environment is an underestimated factor: in fact, it turned out to be important in many case studies published during the last decade (Hladil, 2002; Hladil et al., 2006, 2009, 2010a, Koptíková et al., 2010a).

MS signal in sediments can be sourced from the following phases: minerals with ferrimagnetic and antiferromagnetic characteristics such as Fe-oxides (magnetite, hematite, maghemite, ilmenite) or Fe-sulphides (pyrrhotite, greigite), Fe-oxyhydroxides (goethite, ferrihydrite or lepidocrocite), mineral phases with paramagnetic behaviour such as clay minerals (particularly chlorite, illite, smectite), micas (glauconite), Fe-carbonates (siderite, ankerite), Fe-sulphides (pyrite, marcasite), Fe-Mg silicates such as biotite, amphiboles, pyroxenes. Minerals with diamagnetic characteristics with weak and negative MS values (quartz, calcite, feldspars etc… generally minerals with no Fe, Cr or Ni) can also contribute to the resulting MS record and become dominant when ferrimagnetic or paramagnetic concentrations are less than 0.001 % and 10 %, respectively (Tarling & Hrouda, 1993).

All laboratory MS measurements were carried out by L. Koptíková at the GLI AS CR, v. v. i. in Prague using kappabridge KLY-2 device (Agico Ltd., Czech Republic), magnetic field intensity of 300 $A.m^{-1}$, operating frequency of 920 Hz, sensitivity for specimen 4×10^{-8} SI. Raw and normalized data on mass specific MS expressed in $m^3.kg^{-1} \times 10^{-9}$ were plotted and calculated from dimensionless total MS $\times 10^{-6}$ acquired using the KLY-2 device. The error of measurement due to stabilizing, shape parameters and orientation of the sample during the repeated measurements did not exceed ±2 %.

In total, more than 3 800 fresh rock samples ideally without calcite veins or dissolution seams (approximately 15–45 g in weight) were sampled and measured (Czech Republic, Portugal, USA – Nevada, Uzbekistan). The vertical intervals of bed-by-bed sampling established for each section separately were chosen with the respect to the character of sediment, sedimentation rate or thickness of the section, see Table 2.

Table 2. Sampling intervals in the studied sections [cm].

Sections	**Lochkovian**	**Pragian**	**Emsian – Eifelian**
Požár 3	10	5	10
Pod Barrandovem	-	20	-
Prastav Quarry	-	-	5
Na Škrábku Quarry	-	-	5
Červený Quarry (Suchomasty)	-	-	5–10
Nevada (USA)	-	-	20
Uzbekistan	-	-	10
Portugal	-	-	10 (Eifelian – Givetian?)

3.2 GRS

Gamma radiation is electromagnetic radiation induced by photons with great energy, no mass and charge; it is expressed in keV or MeV). Three sources of gamma radiation are generally involved in rocks: radioactive elements of the Th family, U-Ra family and single isotope of ^{40}K (Adams & Weaver, 1958). All these mentioned elements have very long half-lives (U and Th are primordial radionuclides – they have existed in their current form since before Earth was formed), they occur in the Earth's crust in significant amounts, have been still in the process of decay and can be thus measured (Rider & Kennedy, 2011). A contribution of these elements to the overall radioactivity of the sediments is more or less on the same order of magnitude. Potassium is much more abundant than Th and U but the contribution of ^{40}K isotope is low due to its scarcity. On the other hand, Th and U are considered trace elements in sediments but have a considerable effect on the overall radioactivity (Rider & Kennedy, 2011) – see IAEA (1989) for a conversion of the concentrations of K (in %), Th and U (in ppm) to the specific activity of the isotopes in the rock. Spontaneously emitting gamma rays of ^{40}K are distinct and reach an energy value of 1.46 MeV, the energy of Th and U varies but characteristics peaks of daughter decay products occur typically at higher energy levels (2.62 MeV for Th and 1.76 MeV for U; Rider & Kennedy, 2011). Another characteristic feature of gamma rays is Compton scattering: a consequence of the interaction of electrons and gamma rays when passing through material. It influences the energy: the higher the density of material, the stronger the attenuation of energy. When two or more radioactive elements occur, their contributions to the overall spectrum are mixed. Also, higher temperature when detector is heated can make the spectrum fuzzy (Rider & Kennedy, 2011).

Potassium is present in minerals such as feldspars (orthoclase, microcline – 14 and 16 wt. % K), micas and clay minerals (glauconite, muscovite, biotite, illite, kaolinite or smectite – illite contains by far the highest amounts of K in contrast to kaolinite or smectites where K concentrations are low), halide minerals (sylvite, carnallite, polyhalite – they contain 10 to 50 wt. % K; Rider & Kennedy, 2011).

The principal source of U is represented by acid igneous rocks (average 4.65 ppm U; Rider & Kennedy, 2011). This element forms soluble salts – uranyle form U^{6+} (stable under oxic conditions) which is transported as UO_2^{2+} in river water, and also U^{4+} (uranyle ion) – a less abundant form stable under reducing conditions. Sea water with the average concentration of 3 ppb U represents a reservoir of this element. There are generally 3 processes how U is being incorporated into sediments: a) chemical precipitation under acid, reducing conditions – such conditions are typical for stagnant, anoxic water and environments with slow sedimentation rate and black shale production; b) adsorption by organic matter (Adams & Weaver, 1958; Jones & Manning, 1994) which is the most common way where uranyl ions UO_2^{2+} – due to their large size and high charge density of uranium – can be bonded to organic particles, urano-organic complexes may form coatings on these particles or be scattered in the sediment; c) chemical reactions in phosphorites where U^{4+} is substituted for Ca in carbonate fluorapatite in marine phosphorites. It has to be taken in account that U shows different behaviour than K or Th because it is not chemically bonded to any mineral such as K in clay minerals: it has only loose associations with secondary components (organic matter etc.) and may be therefore scattered very irregularly in the sediment. This is also supported by its tendency to be easily leached and redeposited (Rider & Kennedy, 2011).

Acid and intermediate igneous rocks are the main source of Th. In contrast to U, Th is very stable, and so are all Th-bearing heavy detrital minerals – zircon, thorite, monazite, epidote or sphene but also apatite, epidote, bauxite, minerals of clay-mica group such as kaolinite, illite, muscovite, smectite, glauconite (Rider & Kennedy, 2011). Therefore, Th is transported by water and associated with clay-sized fraction and linked rather to terrestrial than marine material (Rider & Kennedy, 2011). In coarse detrital sediments, Th minerals are mostly associated with silt-sized fractions. Th is generally considered to be linked with siliciclastic components (Doveton, 1994; Ehrenberg & Svana, 2001; Fabricius et al., 2003; Fiet & Gorin, 2000).

Pure carbonates are not radioactive in fact (the same situation as with MS) but show U activity in several cases: where U is bound to organic matter (on stylolites or scattered in matrix), or where U enrichment is associated with slow sedimentation, erosional surfaces, palaeosols, karst exposures, sequence boundaries or connected with dolomitization. K and Th concentrations are considered to be associated with clay content in shaly carbonates or mixed shale-carbonate sediments (Pawellek & Aigner, 2003; Aigner et al., 1995; Ehrenberg & Svana, 2001).

Field GRS measurements as the second most effective method (low-cost, fast, non-destructive method for acquisition of large data sets) are used as a principal tool for correlations using K, Th and U concentrations (Rider & Kennedy, 2011). The outcrop GRS logging – measurements of sediment gamma-ray activity – was originally developed in 1960s. Since then, it has been used in well logging for basin-wide correlations and identification of shale beds with the highest gamma-ray activity (e.g., Lowder et al., 1964; Rider & Kennedy, 2011). GRS measurements are now included in almost all well logs to identify lithology, facies, interpret important stratigraphic surfaces (flooding surfaces, sequence boundaries, condensed intervals), to indicate the dominant clay mineral material and thus reveal possible source rocks (Rider & Kennedy, 2011; Ehrenberg & Svana, 2001). Recently, this method started to be used for the same purpose as MS stratigraphy in palaeoenvironmental studies and high-resolution stratigraphy in pure limestones (Aigner et al., 1995; Fiet & Gorin, 2000; Ruffell & Worden, 2000; Hladil, 2002; Raddadi et al., 2005; Hladil et al., 2000, 2006, 2009; Bábek et al., 2007, 2010; Kalvoda et al., 2011).

The Th/U ratio has been used as an indicator of redox conditions in the depositional environment (Adams & Weaver, 1958; Jones & Manning, 1994). High ratios >7 are regarded as reflecting oxidizing depositional environments while low ratios <2 are indicative of reducing conditions (Adams & Weaver, 1958; Doveton, 1994). The most frequent values are usually around 2–3, as reported by e.g., Ruffell & Worden, 2000 or Slavik et al., 2004 from the Prague Synform. But Hladil et al. (2006) and further citations ibidem reported inverse values (low Th/U ratio close to 0.5) for GRS records across the Upper Devonian in the Moravian Karst and modern Bahama Islands limestones. In the Great Bahama Bank, in a very shallow environment but with normal oceanic character, this inversion is explained by embedding of African dust rich in Fe but depleted in K and not as the effect of euxinic waters. In the Moravian Karst, the role of atmospheric dust trapped as impurities in the platform limestones should be taken into account; therefore the Th/U ratio must be interpreted carefully.

GRS measurements were performed using GR-320 enviSPEC portable spectrometer with a 3×3 inch NaI(Tl) scintillation detector (Exploranium, Canada). Counts per seconds in selected energy windows were directly converted to the concentrations of K (%), U (ppm), Th (ppm) and total GRS (ppm). Readings were taken in 120s period at each logging point, perpendicular to the section wall and at full contact with the rock. Hemispheric effective rock volume with a 100cm radius represents approximately a mass of 100 kg. A combined error from conditions, instrument and repeated measurements is estimated to be less than about ±7.5 % for the K, U and Th element concentrations.

In total, 641 measurements were performed in the field (Prague Synform and Nevada, USA). Vertical intervals of measurements established for each section separately were chosen with the respect to the character of sediment, sedimentation rate or thickness of the section, see Table 3.

Table 3. Vertical intervals of GRS measurements [m].

Section	**Lochkovian**	**Pragian**	**Emsian–Eifelian**
Požár 3	0.5	0.25	0.5
Pod Barrandovem*			
Prastav Quarry	-	-	0.25
Na Škrábku Quarry	-	-	0.25
Červený Quarry (Suchomasty)	-	-	0.25
Nevada (USA)	-	-	1
Uzbekistan**			

* measurements already taken by Slavik et al. (2000)

** GRS measurements were not performed due to administrative and security difficulties with equipment transport

3.3 Lithological characteristics and facies analyses

Both polished and covered thin sections (sampling interval represents each 0.5 to 2 m of the sections) were studied by optical microscopy and SEM-EMPA. Data on carbonate composition and grain size were processed using a routine grain-size distribution analysis (Wentworth, 1922; Flügel, 2004). Acquired data represent semiquantitative sets of information on grain-size distributions of carbonate material along lines across each thin section. Categories significant (≥20 %) and accessory (≥5 %) were used, quantities below 0.25 % were ignored (this classification was used in Paper 1 and Paper 2). Textural criteria of the classification generally followed Dunham (1962) and Embry & Klovan (1971).

3.4 Mineralogical characteristics and whole-rock geochemistry

3.4.1 Insoluble residues – light and heavy fraction assemblages

Mineralogical characteristics of insoluble residues were studied on samples obtained by treatment in 10% acetic or hydrochloric acid (all samples treated by L. Koptíková). In total, 38 samples (average weight 2 kg) from the Požár 3 section (across the Lochkovian up to the lower Emsian), 10 from the Prastav Quarry, 10 from the Na Škrábku Quarry and 10 from the Červený Quarry near Suchomasty (the last 3 represent the Emsian–Eifelian boundary). Light and heavy fraction assemblages were obtained by separation in heavy liquid (bromoform with the density of 2.83 g.cm^{-3}) using a Chirana centrifuge with 3000 rounds per minute and analysed using the SEM-EMPA, EDX, XRD. Additional 8 samples from the Požár 3 section (30–70 kg) were processed as fine-crushed whole-rock samples without acid dissolution and using gravitational, flotation, density and electromagnetic techniques to obtain higher amount of heavy fractions for studies on barite and detrital zircons (a Wilfley table, a Chirana centrifuge, a magnetic separator using current of 0.2 to 10 A, separation in acethylene tetrabromide and methylene iodide heavy liquids). Three sets of samples from the Požár 3 section were additionally used for experimental study using 3 different acid leaching techniques (acetic, hydrochloric and formic acid) to reveal the effect of the acids and technique used on magnetic properties of these insoluble residues.

3.4.2 SEM-EMPA

SEM-EMPA using Cameca SX 100 at the GLI AS CR, v. v. i. (A. Langrová, V. Böhmová, Z. Korbelová) was applied to identify mineral phases. Both polished sections of the grains, matrix, aggregates and loose grains or aggregates were analysed and documented.

3.4.3 INAA

Multielemental (40 elements) INAA analyses were realized at the NPI AS CR, v. v. i. in Řež (J. Frána, Z. Řanda) and applied to obtain whole-rock geochemical data sets. See Řanda & Kreisinger (1983) or Řanda et al. (2007) for detailed methodology and technical aspects of this method. Numbers of samples and sampling points were identical with those for insoluble residues. The results were normalized on the PAAS and Lu on the REE group.

3.4.4 X-ray techniques

X-ray techniques EDX (JEOL JXA-50A) and XRD (Phillips X'PERT PW3020) were applied to identify mineral phases – in light and heavy fractions separately and in whole-rock samples for comparisons. All analyses were performed at the GLI AS CR, v. v. i. in the Laboratory of Analytical Methods (R. Skála, J. Dobrovolný). Also the identification of clay minerals in the light fraction of the experimental study on different acid-treated samples using Phillips X'PERT PW3020 was performed by M. Šťastný in the same laboratory (standard treatment using saturation in ethylene glycol at 80 °C and then heating at 550 °C for 1 hour).

3.4.5 TOC and $CaCO_3$ content

TOC and $CaCO_3$ concentrations were obtained from selected MS samples, ground to fine powder to pass the 70µm size sieve. Homogenized samples 0.05 g in weight were dissolved in hydrochloric and phosphoric acid, then dried at 105 °C temperature, dry-combusted in stream of pure oxygen up to a 1000 °C temperature and analysed using Strohlein C-mat 5500 non-dispersive infrared carbon analysers. The statistical error was kept at ±4 % TOC. Measurements were realized at the Geological Institute, Slovak Academy of Sciences in the Laboratory of Organic Geochemistry in Banská Bystrica (A. Svitáčová, A. Biroň).

4 Results

The overall results are arranged in accordance to the papers attached (1–7). Their relation to the individual tasks of the thesis (Task 1–4) is discussed at the end of each chapter of relevant paper. Also unpublished data or data published only in an abstract form and presented at international conferences as preliminary results on additional studies produced during the thesis solution are discussed and cited here.

Papers 1–3 are commented here thoroughly (in contrast to the papers 4–7) because they solve crucial questions and tasks of the thesis, L. Koptíková is the only author or the first author and her own contribution is the highest.

4. 1 Paper 1

Fine-grained non-carbonate particulates embedded in neritic to pelagic limestones (Lochkovian to Emsian, Prague Synform, Czech Republic): composition, provenance and links to magnetic susceptibility and gamma-ray logs

Koptíková, L., Hladil, J., Slavík, L., Čejchan, P. & Bábek, O., 2010.

Geologica Belgica, 13, 4: 407-430.

MS and GRS logs in combination with the detailed analysis of stratigraphic variations in the compositions of detrital grain assemblages of fine-grained non-carbonate impurities embedded in the limestones were established in the Požár 3 section (125m-thick uninterrupted stratal succession). This active quarry encompasses almost the entire Lochkovian (represented generally by the Lochkov Fm. which surpasses to the lowermost Pragian, Pragian which is according to Emsian GSSP in Kitab in Uzbekistan reduced to one third of the thickness here and now most of the traditional Pragian *sensu* Chlupáč et al. (1998) belongs to the Emsian. The Praha Fm. is represented by the succession of the “false“ Koněprusy Lmst., Slivenec Lmst., Loděnice Lmst., Řeporyje Lmst. and Dvorce-Prokop Lmst. Lower parts of the Emsian are represented here by the Zlíchov Fm. and Zlíchov Lmst. These logs were then plotted against the background lithological characteristics and geochemical data as a control. Different assemblages, trends and patterns are encountered for the Lochkovian, Pragian and lower Emsian.

MS and GRS logs

The lowermost part of the Lochkov Fm. is characterized by elevated values both in MS and GRS and lithologically differs from the rest of the formation. Reddish and pinkish calcirudites and calcarenites with wavy lamination and higher proportion of shallow water bioclasts than the overlying Radotín Lmst. (typically spiculites and dark-grey calcisiltites) suggest deposition on the upper or middle parts of the slope in channelized environment. This segment of the section was distinguished and named Průhon lithofacies due to its above mentioned specific characteristics. But major changes in MS and GRS logs, mineralogy of insoluble residues (based on analyses of 38 samples; 2 kg/sample) are concentrated to the proximity of the Lochkovian-Pragian boundary which roughly corresponds to the Lochkov-Praha Fm. boundary. The Praha Fm. provides a stable pattern of elevated values in MS (4 to 5 fold higher than in the underlying Lochkov Fm. with mean value 15.7 vs. 3.6; Koptíková et al., 2009a) and high-amplitude oscillations. Also GRS data show elevated Th and K concentrations (mean value 3.7 ppm for Th, Th/U ratio close to 4, mean value for K 0.8 %; Koptíková et al., 2009a) and total GRS signal is driven by dominant concentrations of Th whereas the GRS records of the underlying Lochkov Fm. as well as overlying Zlíchov Fm. are dominated by U concentrations (mean value for K is 0.45 % in the Lochkov Fm., Th/U ratio around or below 1; Koptíková et al., 2009a). Approximate amounts of non-carbonate impurities if K concentrations are stechiometrically calculated to illite are 6.81 % for the Lochkov Fm., 13 % for the Praha Fm. and 9.94 % for the Zlíchov Fm (Koptíková et al., 2009a). Total amounts of impurities reach the maximum in the Praha Fm. around from 81.7 up to 87.45 metre marks in the section (Slivenec Lmst. and Slivenec–Loděnice Lmst. transition), the same is true for MS, Th and K (1.47 %).

Ba-K enrichment

Also elevated concentrations of Ba (maximum of 136 ppm at 87.45 metre mark in the Loděnice Lmst.) and barite grain accumulations are concentrated to the level of MS, K, Th maxima. This coincides with a deceleration of sedimentation rate, decreased carbonate productivity (lowest concentrations of $CaCO_3$ content) and condensation which is supported also by Slavík et al., (in print) who reported strongly condensed conodont biozones at this level and possible hiatuses.

Interpretation of MS, K, Th, Ba maxima around 87.45 metre mark in terms of environmental change – climatic changes and possible changes in atmospheric circulation

We interpret this level as the change in the delivery and increase in the flux of non-carbonate impurities (mostly of paramagnetic character). It might reflect a major change in the atmospheric circulation (changes in wind directions or intensities). Also global climate change cannot be excluded because the Lochkovian–Pragian sea level fall is documented worldwide (see citation in the paper 1). A difference between the Lochkovian and Pragian character of depositional environment is significant. But unfortunately there is a discrepancy in the interpretation of climate in the Lochkovian and Pragian. Hladil et al. (2008) proposed the Pragian and as period with very low sea level and hot and humid climate whereas Buggisch & Joachimski (2006) interpreted the Pragian as the period with cooler climate than the Lochkovian.

Mineral assemblages

The proportions of minerals which are responsible for MS signal – with paramagnetic and ferromagnetic characteristics – vary along the section. Fe-oxides and oxyhydroxides (such as magnetite or hematite, often with high contents of Ti), pyrrhotite, ilmenite, pyroxene, amphibole, olivine, chlorite, glauconite, clay minerals (illite, kaolinite, montmorillonite), ankerite, Fe-rich dolomite, pyrite, chalcopyrite, epidote were identified in insoluble residues. Quartz, muscovite, dolomite, feldspars (orthoclase, microcline, albite), zircon, barite, apatite, rutile were identified as diamagnetic phases.

Paramagnetic minerals as major carriers of MS signal

Grains of ferromagnetic properties occur both in the Lochkov, Praha and Zlíchov Fm. As we know that MS values are 4 to 5 fold higher in the Praha Fm. than in the other ones, elevated values in the entire unit and maxima in K and Th concentrations (as proxies for amounts of siliciclastic components) at the base of the Praha Fm., we can assume that the MS signal is rather driven by minerals of paramagnetic properties.

Pyrite–pyrrhotite assemblages in the Lochkov Fm. vs. Fe-oxides dominant assemblages in the Praha Fm.

The Lochkov Fm. and to a certain extent also the Zlíchov Fm. is characterized by a higher abundance of pyrite–pyrrhotite assemblages and low abundance of Fe-oxides (mostly goethite than hematite or magnetite) whereas the Praha Fm. is dominated by Fe-oxides. The presence of Fe-oxides is typical for the Praha Fm. (Slivenec, Loděnice or Řeporyje Lmst.) with their red or pink colour hues. It is indicative of higher oxygenation of sea water column which is supported also by high Th/U ratio and increase in the infestation of microborers (based on optical microscopy of thin sections) points to slower rates of sedimentation. This shift from suboxic conditions in the Lochkov Fm. with low-carbonated background sedimentation of grey calciturbidites (Zlíchov Fm. is very similar) to oxic conditions in the Praha Fm. might explain a preferential formation of Fe-oxides and oxyhydroxides in the Praha Fm. and pyrite and pyrrhotite in the Lochkov Fm. The origin of pyrrhotite in sediments is also discussed: it can be either detrital or authigenic (see citations in the paper). Authors who reported pyrrhotite of detrital origin argued for a very slow velocity of pyrrhotite formation below ~180 °C. As the studies on fluid inclusions of calcite veins in the Prague Synform suggest temperatures between 127 to 167 °C (Halavínová et al., 2008) we tend to prefer the authigenic origin of pyrrhotite in the Lochkov Fm.

Pyrite morphology – a further case study

Another very interesting feature which needs to be solved in detail is the contrasting pyrite morphology in the Lochkov, Zlíchov and Praha Fm. Euhedral grains occur in all formations but the most abundant form in the Lochkov and to some extent also in the Zlíchov Fm. is spherical or framboidal shape, whereas bipyramidal crystals dominate in the Praha Fm. Framboidal shapes of pyrite crystals are considered to be of microbial origin (Folk, 2005; Gong et al., 2008) and might indicate redox conditions in depositional settings (Wilkin et al., 1996). Our observations are in accordance with these interpretations because the distribution of framboidal pyrite shapes coincides with the suboxic conditions in the Lochkov and Zlíchov Fm. (suggested by low Th/U ratios – close or below 1). Conditions of bipyramidal pyrite crystals formation in the Praha Fm. or a study of isotopic composition of S are the question for further studies.

$\delta^{34}S$ and $\delta^{18}O$ isotopic data of barite grains – a case study in progress (unpublished)

Isotopic composition of barite was analysed at the Stable Isotope Laboratory of the Czech Geological Survey (K. Žák):

$\delta^{34}S$ = +29.8 ‰ (CDT) with the error of ±0.3 ‰

$\delta^{18}O$ = +20.0 ‰ (V-SMOW) with the error of ±0.5 ‰

Both values are obviously higher than the values for the Lower Devonian marine sulphate which is typically around ~ +16 up to +20 ‰ for $\delta^{34}S$ and ~ +14 up to +17 ‰ for $\delta^{18}O$ (Claypool et al., 1980). Hydrothermal origin of this barite can be excluded because $\delta^{18}O$ values of hydrothermal barites do not reach such high values (based on approximately 100 analysed hydrothermal barites from the Czech Republic and Slovakia; K. Žák, pers. comm., 2011). Barite was formed during early diagenesis in the sediments still rich in the pore water where Ba was transported in the reducing solution, part of the residual sulphate reduced by bacterial activity (which caused isotopic change in the $\delta^{34}S$ values, typically 3 or 4 fold higher in the $\delta^{34}S$ than in the $\delta^{18}O$; Claypool et al., 1980) penetrated in pore solution from the sea bottom.

Possible aeolian source of impurities – the REE concentrations and detrital zircon assemblages

REE concentrations and their distribution patterns

Geochemical data on the REE distributions of whole-rock samples (INAA) are indicative of the aeolian origin of the impurities in the Lochkovian to lower Emsian. Correlation coefficients of all studied samples plotted against 4 general patterns for fluxes of impurities into marine environment postulated by Nozaki (2001) – aeolian, riverine, sea water solutes and remineralization patterns. There is a strong positive correlation (0.57 to 0.9) for the aeolian pattern. A weak correlation for riverine pattern exists in the Lochkov Fm. (maximum 0.38) vanishing toward the Praha Fm. and increasing again toward the Zlíchov Fm. from the upper part of the Praha Fm. A pattern typical for remineralization fully corresponds to the lithology.

Detrital zircon assemblages – U-Pb ages and provenance (a case study in progress, unpublished)

Detrital zircons were identified at 6 stratigraphic levels in all 3 stages. The most unusual occurrence and also richest level is in the “false” Koněprusy Lmst. in whitish, light grey crinoidal calcarenites–calcirudites. Their morphology and different habitus (from perfectly oval recycled grains to long prismatic crystals max. 200 µm in size) suggest that several populations of different source and different age can be expected. These long prismatic crystals are non-fractured which is indicative that they might be of aeolian origin rather than of fluvial origin. There are no macroscopic observations of either volcanic ash layers or admixtures in the rocks.

Very preliminary results on the age distributions of these zircons show differences between the Lochkovian and Pragian. This might suggest a change in the flux and provenance of material delivered by oceanic currents but in the form of atmospheric dust. Hladil & Bek (1998, 1999) and Vavrdová (1989) reported plant spores assemblages from the Lower–Middle Devonian limestones in the Prague Synform with the affinities to Ardenne–Rhenish–Moravian–Eastern Canada regions, i.e., with links rather to Laurussia than to Gondwana. This is in contrast to Lower Devonian marine benthic fauna with Gondwana affinities. Moreover, Vavrdová (1989) reported these miospores from the Dvorce-Prokop Lmst. in the neighbouring Požár 2 quarry. Unfortunately, relevant data both on spores and zircon ages and provenance are still missing in the underlying rocks such as Silurian rocks or rocks around the Silurian–Devonian boundary, so it is still in debate where to put this change of affinities and source of the material.

Experimental study on the effects of different acid leaching methods on magnetic properties of insoluble residues with control of whole-rock sample analyses

Magnetic properties of insoluble residues of the Lochkovian beds of the Požár 3 section were assessed after the dissolution in three different acids (acetic, formic and hydrochloric) to test the influence these acid solution methods on the resulting composition of these residues. To characterize the light and heavy fractions of the residues, a large array of methods and techniques was used: MS measurements, temperature, field and frequency dependence of MS, IRM, together with XRD identification of clay minerals, or the SEM-EMPA of non-carbonate particles. The results obtained on residues were compared with those that were obtained using the whole-rock samples. The results (Koptíková et al., 2010c, 2011) revealed the neoformation of Fe-oxides (mostly magnetite) during the rinsing of acid after the dissolution of limestones and replacement by distilled water. Also dissolution of Fe-oxides during acid treatment was observed, e.g., hematite was identified in one untreated sample but during the measurements of temperature dependent MS of treated insoluble residue only magnetite and pyrrhotite appeared. Magnetite dominates in most of samples (based on IRM), no grains of superparamagnetic properties occur, only grains above 10 nm and pyrrhotite also occurs. It seems that hydrochloric acid is most destructive – it influences not only Fe-oxides and oxyhydroxides dissolution and neoformation after the dissolution but also total amounts of clay minerals and micas (based on the XRD and clay mineral analyses). Formic acid seems to be very gentle and suitable (fast enough due to its short molecule chain) for the extraction of insoluble residues of limestones despite the fact that there is some risk of insoluble calcium formates formation.

Tasks 1–3 were completed. Both MS and GRS logs were established, carriers of MS and GRS signal and their stratigraphic variations were identified, interpretations of palaeoclimatic, environmental changes and changes in depositional environment were outlined and interpreted.

Data were presented by L. Koptíková at 5 international conferences:

Field workshop 2008 IGCP 499-UNESCO "Devonian Land-Sea Interaction, Evolution of Ecosystems and Climate" (DEVEC), Libyan Petroleum Institute, April 23–30, 2008, Tripoli, Libya

Koptikova L., Hladil, J., Slavik, L., Frana, J. & Vacek, F., 2008b. Evidence of a significant change between Lochkovian and Pragian: detailed lithological, geophysical, geochemical and mineralogical aspects (Pozary 3 section in Prague Synform). *Abstracts*: 10-14.

Regional Devonian Workshop Prague & Graz, May 25–27, 2009, Prague, Czech Republic

Koptíková L., Hladil J. & Slavík L., 2009a. Lochkovian–Pragian boundary in the Prague Synform: lithological, mineralogical, geophysical and geochemical aspects as results of sea-level fall. *Berichte der Geologischen Bundesanstalt*, 79: 28-31.

First IGCP 580 Meeting, Magnetic susceptibility, correlations and paleoenvironments, December 2–6, 2009,Liège University, Liège, Belgium

Koptíková, L., Hladil, J., Slavík, L. & Frána, J., 2009b. Mineralogy of fine-grained non-carbonate particulates embedded in neritic to pelagic limestones, and connection to magnetic susceptibility and gamma-ray signals: a case study based on Lochkovian, Pragian and lower Emsian strata from the Pozar-3 section. *Abstract Book*: 34-35.

2010 IGCP 580 Meeting Applications of Magnetic Susceptibility on Paleozoic Rocks, November 28–December 4, 2010, Guilin, China

Koptíková, L., Schnabl, P., Skála, R., Vacek, F., Šlechta, S., Böhmová, V. & Šťastný, M., 2010. The effect of different acid dissolution methods on magnetic properties of insoluble residues of limestones. *Meeting Programme and Abstracts*: 9-10.

IGCP 596 Opening Meeting, Karl-Franzens-Universität Graz, September 19–24, 2011, Graz, Austria

Koptíková, L., Hladil, J., Schnabl, P., Skála, R., Slavík, L., Šlechta, S., Böhmová, V. & Šťastný, M., 2011. The influence of different acid dissolution methods on insoluble residues of limestones and their magnetic properties and mineralogical composition. *Berichte des Institutes für Erdwissenschaften*, 16: 58-59.

4.2 Paper 2

Stratigraphic significance and resolution of spectral reflectance logs in Lower Devonian carbonates of the Barrandian area, Czech Republic; a correlation with magnetic susceptibility and gamma-ray logs

Koptíková, L., Bábek, O., Hladil, J., Kalvoda, J. & Slavík, L., 2010.
Sedimentary Geology, 225: 83-98.

Much like paper 1, this study presents MS and GRS logs across the entire Lochkovian (Lochkov Fm.), Pragian (Praha Fm.) up to the lower parts of the Emsian (Zlíchov Fm.) from the same section Požár 3, MS and GRS carriers, but all from different point of view and using novel techniques such as SR in the background of MS, GRS, TOC, $CaCO_3$ data and detailed facies analysis. The aim of this paper was to test what information mostly on sequence stratigraphy or cyclostratigraphic patterns can bring SR along other petrophysical method, focusing also on sea level fluctuations through the studied interval.

SR is a technique used as a proxy for organic carbon content and siliciclastic input into carbonate sediments, applied mostly on cores and using visible-light, for the estimation of chromophore concentrations – minerals – such as hematite, goethite or chlorite (Mandarino, 1967; Deaton & Balsam, 1991; Mix et al., 1995), often used as palaeoclimatic proxies (Ji et al., 2001; Debret et al., 2006; Grygar et al., 2006). Chromophores such as $CaCO_3$, organic carbon, dolomite and hematite are considered to control the rock colour. Colour Scale CIE L*a*b* was introduced by CIE (Commission Internationale d'Eclairage) in 1976. It employs parameter lightness L, and values a, b for colour-opponent dimensions. According to Nederbragt et al. (2006), L* value is often related to organic carbon and $CaCO_3$ content. A more complicated situation is in coloured carbonates – yellow, red or pinkish ones where more chromophores play a role. The red colour is considered to be related to early diagenetic hematite and it is often indicative of bottom oxygenation in shallow-water environments (Wang et al., 2005) or bacterial activity in pelagic settings with lower oxygenation level (Préat et al., 1999; Mamet & Préat, 2006). The peaks on the first derivative of the SR curve are used for semiquantitative estimates on goethite and hematite concentrations (Barranco et al., 1989; Deaton & Balsam, 1991; Ji et al., 2001).

Interpretation of facies and facies associations

Seven facies types were distinguished (F1 to F7) across the distal ramp and slope carbonate section outcropped in the Požár 3 Quarry. Major part of the facies is interpreted as carbonate turbidites. Facies were into grouped into 4 facies associations (A1 to A4). A1 represents the lower parts of the Lochkov Fm. – Průhon lithofacies (for details see paper 1) – thicker and amalgamated beds interlayed by thin marl laminae, wavy laminations, probably representing storm deposits, A2 represents the rest of the Lochkov Fm. (and basal part of the Praha Fm.) – cyclic alternations of turibidites, deep-subtidal deposits and hemipelagic deposits showing upward coarsening and thinning of the beds. A3 comprises the entire Praha Fm. succession and basal parts of the Zlíchov Fm. – a mix of the shallow-water benthic allochems and hemipelagic material at the basal parts of the A3 and (hemi)pelagic nodular deposits with multimodal grain-size distribution in the upper parts. A4 comprises the rest of the Zlíchov Fm. exposed in the quarry and is characterized by a coarsening-upward succession from calcilutites to fine-grained calciturbidites.

GRS log

Facies associations A1 and A2 show low K (0.4 and 0.5 %) and Th average concentrations (2.4 and 1.8 ppm), relatively high U concentrations (4.1 and 4.2 ppm) and low Th/U ratios (0.8 and 0.5). Minima in K and Th concentrations are linked with coarse-grained turibidites and K and Th statistically correlate through sections ($R^2 = 0.639$). In addition, these maxima in K and Th concentrations coincide with the minima in the $CaCO_3$ content, so we can assume that this reflects fine-grained siliclastic input (alumosilicates such as clay minerals, feldspars, micas; Rider & Kennedy, 2011; Fiet & Gorin, 2003; Fabricius et al., 2003). Th and K variations through the section reflect the effect of dilution of these fine-grained siliclastic particles due to variation on carbonate productivity and changes in the volume of delivered particles. They are interpreted in terms of transgressive and regressive cycles and point to third-order eustatic sea level fluctuations – landwards and basinwards facies shifts.

Facies association A3 shows a different type of GRS pattern – K and Th is significantly elevated (0.9 % and 3.8 ppm) and U depressed (1.2 ppm). The elevated Th/U ratio (4.2) indicates a higher terrigenous input and well oxygenated environment – maximum of this increase is between 80–87 metre marks and is followed by a sudden drop. This drop correlates with the level of the Emsian GSSP in the Kitab State Geological Reserve in Uzbekistan (87–90 metre marks). The overlying hemipelagic nodular limestones show a uniform pattern of high K, Th concentrations and high Th/U. A gradual decreasing trend starts between 113 and 118 metre marks with two anomalous peaks in K, Th and also U concentrations. A peak at 113 m is associated with the so-called graptolite event (Hladil et al., 1996; Chlupáč et al., 1998) close to the base of the Zlíchov Fm. Facies association A4 at the top of the section has again low average concentrations on K (0.6 %), Th (2.5 ppm) and U (2.3 ppm), Th/U ratio is 1.1.

MS log

Facies association A1 and the base of A2 is characterized by relatively high values (average 6.5), A2 by lower values (2.7) and 5 cycles can be distinguished here. A weak statistical correlation exists between the MS and K and Th logs (for MS and K: $R^2 = 0.46$; for MS and Th: $R^2 = 0.37$), data are not correlated with $CaCO_3$ and TOC. Two factors are probable cause of these low correlative coefficients: different sampling interval and volume of sampled material of both methods (GRS and MS) and the effect of diagenesis and formation of diagenetic minerals which join the fine-grained siliciclastic material due to relative sea level fluctuations. A3 segment is characterized by very high MS values (average 18.0). They are interpreted in terms of slower sedimentation rates (based on lithological observations, GRS log). In the upper part MS values decrease again toward the graptolite event interval. Upper parts of the A3 and A4 are marked by decreasing trend (average values 9.35) followed by increase in MS values, similar trend as in the K and Th concentrations.

SR log

The CIE L*a*b* log is closely connected with facies associations (A1–A4) and also MS and GRS log. A1 has high values on the CIE L* and yellow to orange hues which are associated with elevated concentrations of goethite (also indicated by the first derivative curve of the reflectance spectra). An A1-A2 boundary is marked by rapid decrease in the SR parameters, the colour of limestones is darker and limestones are less coloured (corresponds to greyscale) than the underlying A1. Lochkovian-Pragian stage boundary at the 75 metre mark is not marked by SR. But above this boundary (from 76 metre mark) there is sharp increase to positive values in the CIE L* a* and b* up to the top of the A2 and this shift roughly coincides with the Lochkov and Praha Fm. boundary in the light grey limestones with yellow-to-yellow-orange hues (slightly below A2-A3 boundary). A2-A3 boundary is characterized by increase ion reflectance in blue and green band and decreased CIE L*a*b* values (low L*, yellow and very low red values). The colour of limestones is grey to dark grey. A shift to red limestones begins between 92 and 93 metre marks, where approximately 20 m thick band of red coloured limestones occurs (92.5 to 112.5 m) – they are characterized by lower L* values, high average CIE a* and b* values and a peak associated with hematite. The rest of A3 are light grey limestones with high values on L* and lower CIE a* and b* values. The graptolite event interval is marked by decreased L* values. A4 is darker coloured which has effect on lower values of L* and CIE b* and lower reflectance in green and yellow bands.

The colour of limestones does not correlate with the T-R trends (description below) but important lithological boundaries are marked by CIE L*a*b* parameters. MS and SR logs show cyclic patterns, as we know that the CIE L* parameter is partly correlated with TOC and $CaCO_3$ content but MS is not, so we can interpret and prove that MS is significantly influenced by the diagenetic minerals and we can conclude that the MS method should not be used independently – always in combination with other methods and knowledge of the background geological characteristics including lithology, GRS, $CaCO_3$ or TOC data and other. CIE L*a*b* parameters mark sensitively the peaks on regressions of the T-R cycles (see subchapter on sea level fluctuations).

SR – identification of subvertical faults and alteration zones

4 zones of faded colours – 37 to 43, 49 to 54, 60 to 68 and 97 to 104 metre marks characterized by high values (peaks) on CIE L*, CIE b* parameters and yellow band of reflectance spectra were identified and interpreted as subvertical faults, yellow coloured “leaching zones“. The first derivative curve revealed the occurrence of the goethite absorbance band. The colour changes are related to post-depositional alteration along subvertical faults. Surprisingly, this fault-related alteration has only little influence on the MS signal.

Carriers of colour in limestones suggested by the SR

Data on brightness in the A1 and A2 are poorly positively correlated with the $CaCO_3$ content and negatively with the TOC content. A higher correlation coefficients exist in the A3, A4 for SR and $CaCO_3$ but slightly worse for SR and TOC. This might be due to higher content of $CaCO_3$ and low values of TOC in the A3 and A4. There is no correlation between MS and $CaCO_3$ contents; it can be therefore assumed that for our data CIE L* parameter can be used as a better proxy for siliciclastic components in the limestones than the MS. L* and MS can be influenced by the occurrence of diagenetic minerals. As it was outlined in paper 1 (Koptíková et al., 2010a) that the Lochkov Fm. is characterized by higher abundance of pyrite and pyrrhotite assemblages, low concentrations of Fe-oxides, these minerals can contribute to low L* values, high MS values with no regard to $CaCO_3$ content. Moreover, a drop and rise of L* coinciding with the red limestones boundaries in the Praha Fm. is influenced by the occurrence of diagenetic hematite.

Red pelagic limestones of the Praha Fm. and interpretation of their colour

A 20 m thick band of red coloured limestones between 92.5 to 112.5 metre marks is characterized by sharp boundaries shows no facies changes (no changes in allochem composition etc.) or changes in K, Th or MS values. The only prominent and significant change is in the Th/U ratio and the change to high positive values (3 to 10) which is reflecting changing bottom oxygenation and subsurface redox gradients during early diagenesis. It means a turnover to oxic bottom conditions. The SR data, on the background of GRS, MS and $CaCO_3$ data, indicate that the red colour in the Praha Fm. hemipelagic limestones originated from early diagenetic hematite precipitation under the conditions of an oxygenated ocean floor. Moreover, Fe-bearing detrital supply from the continent can be excluded as the main cause of red coloration. Such change in bottom oxygenation and shifts from anoxic/suboxic to oxic conditions is regarded in Phanerozoic marine beds as an important palaeoceanographic process (Hu et al., 2005). Red pelagic limestones e.g., of Late Cretaceous or Upper Jurassic age can be correlated even globally (Wang et al., 2005; Li et al., 2005).

Sea level fluctuations through the Lochkov, Praha and Zlíchov Fm. – implications from the combination of the MS, GRS and SR logs

Facies arrangements, GRS log and $CaCO_3$ data are indicative of decametre-scale T-R trends and these trends have interregional context in the third-order eustatic sea level fluctuations.

CIE L*a*b* parameters mark sensitively the peaks on regressions of the T-R cycles. There is a general transgressive trend for the Lochkov and Praha Fm. At the base of A1 there is a high input of shallow-water detrital material, low values of K and high CIE L*. K and Th reach the local maxima between 25 and 40 metre marks, $CaCO_3$ content reaches here the local minimum. This is interpreted as the landward facies shift and A2 is represented by more deeper-water facies. Then, K and Th concentrations decrease (between 55 and 80 metre marks, upper and uppermost parts of the Lochkov Fm., basal parts of the Praha Fm.), facies prograde toward slope with a maximum between 78 and 80 metre marks at the base of the Praha Fm. (K and Th are low, $CaCO_3$ content is high). Early to Middle Lochkovian transgressive trend and the significant regression during the Basal Pragian Event (close above the Lochkovian-Pragian boundary) have been reported both from the Prague Synform and Morocco (Chlupáč et al., 1998; Hladíková et al., 2000; Crick et al., 2001; Lubeseder, 2008). This level is marked by a positive excursion in the $\delta^{13}C$ isotope curve from neighbouring section Požár 1 and Požár 2, Carnic Alps in Austria, Cantabrian Mountains in Spain and interpreted as the regression starting point (Hladíková et al., 1997; Buggisch & Mann, 2004). Moreover this level can be correlated with the sea level fall (below Ia cycle *sensu* Johnson et al., 1985) in the Euramerican craton. The most significant changes appear in the basal parts of the Praha Fm. (~80 m). K, Th, MS and the Th/U ratio rapidly increase, $CaCO_3$ and L* values decrease, which is indicative of landward facies shift between 80–87.5 m. This is also the level of maximum enrichment in barite (see paper 1). Transgression at this level is also marked by aggradation in the nearby Koněprusy reef complex located approximately 20 km to the SW from the Požár 3 section (Chlupáč et al., 1998; Hladíková et al., 2000) which was the source of shallow-water detrital material delivered down the slope (Chlupáč et al., 1998). It can be also correlated with the sea level rise Ia in Euramerican craton (Johnson et al., 1985), point of reversal to oxic conditions in Morocco (Lubeseder, 2008). In the upper part of the Praha Fm. (112–118 m) close below the Zlíchov Fm. base at the graptolite event interval K, Th, Th/U ratio, MS start to decrease whereas L* values increase and this is interpreted as a regression. This can be correlated with the top of the Pragian Ia cycle in Euramerica (Johnson et al., 1985). The Koněprusy reef complex is eroded at the same time due to sea level fall as reported by Janoušek et al. (2000). A regressive trend continues to the Zlíchov Fm. characterized by a return to turbidite sedimentation on the slope from (hemi)pelagic character of deposition in the Praha Fm.

All 4 tasks of the thesis were successfully completed – MS and GRS logs were established, data on the SR data were correlated with petrophysical ones and also with additional geochemical data sets (data on TOC and $CaCO_3$ contents), carriers of MS and SR signals were identified, their stratigraphic variations were revealed. Facies shifts and interpretations in terms of the T-R cycles were established separately for the Lochkov, Praha and Zlíchov Fm. Potential for interregional and global correlation of these eustatic sea level falls was outlined, T-R cycles were correlated with the Euramerican craton. The origin of red coloration of pelagic limestones in the Praha Fm. was discussed and interpreted.

4.3 Paper 3

Precise position of the Basal Choteč Event and evolution of sedimentary environments near the Lower-Middle Devonian boundary: The magnetic susceptibility, gamma-ray spectrometric, lithological, and geochemical record of the Prague Synform (Czech Republic)

Koptíková, L., 2011.

In: Brett, C.E., Schindler, E., P. & Königshof, P. (Eds), Sea-level cyclicity, climate change, and bioevents in Middle Devonian marine and terrestrial environments.

Palaeogeography, Palaeoclimatology, Palaeoecology, 304, 1-2: 96-112.

This paper summarizes the first study on the anatomy of the BCE interval close above the Emsian–Eifelian boundary in the Prague Synform using high-resolution stratigraphic tools (MS and GRS logging) in combination with geochemical methods (INAA and mineral assemblages in insoluble residues) together with microfacies analysis. MS sampling was realized as a part of the MSc. thesis in the Prastav Quarry near Prague-Holyně (parastratotype of the Eifelian GSSP), Na Škrábku Quarry near Choteč and Červený Quarry near Suchomasty (Koptíková, 2004). The latter 2 represent a relatively deeper-water environment with slope facies (partly separated from open sea by sea-floor elevations or archipelagos) and the last one shallow-water environment on the shelf or upper part of the slope exposed to the open sea. This is also reflected in the lithostratigraphical scheme. BCE base represents a sharp transition between light grey Třebotov Lmst. (Daleje-Třebotov Fm.) and dark grey and blackish Choteč Lmst. (Choteč Fm.) in the deeper-water environment and gradual change between the Suchomasty and Acanthopyge Lmst. in the shallow-water environment marked by a shift to from reddish and pinkish to more intense grey colour hues. All GRS measurements and study on mineral assemblages of insoluble residues were performed within the frame of this thesis. Also the sampled interval in the Koněprusy Area was later extended to the entire exposed Emsian strata (Suchomasty Lmst.) in the Červený Quarry (unpublished but here commented data) down to the contact of the Koněprusy and Suchomasty Lmst. (Suchomasty Lmst. unit overlies the Koněprusy Lmst. after a hiatus).

BCE interval – increase in environmental dynamics

A detailed study of the BCE interval revealed an increase in dynamics of the environment, decrease in amount of delivered pelagic component and increase in calciturbidite or distal storm activity, increase in the flux of recycled and altered lithoclastic-skeletal detritus material of shallow-water origin. It starts in the upper part of the Třebotov Lmst. composed of calcisiltite material from distal turbidite currents and alternating with hemipelagic material. Bouma sequences were identified in the Choteč Lmst. A more proximal environment is recorded in the Na Škrábku Quarry in comparison to the Prastav Quarry. Similar trend occurs in the Červený Quarry and shallow-water equivalents.

MS and GRS carriers – light and heavy mineral assemblages

Study on the light and heavy fraction mineral assemblages revealed the dominance of the diamagnetic and paramagnetic non-carbonate impurities – it turned out that the resulting MS record is driven rather by paramagnetic (chlorite, pyroxene, amphiboles, pyrite) than ferromagnetic phases (Fe-oxides and oxyhydroxides – hematite, goethite). Quartz followed by muscovite, feldspars (albite), clay minerals (kaolinite) and chlorite belongs to the most common light fraction phases. GRS-U peak yielded abundant prismatic authigenic quartz crystals (~ 100 µm) and XRD has detected also kaolinite, muscovite and chlorite. Barite, apatite, rutile were also identified in heavy fraction assemblages as well as Fe-oxides and oxyhydroxides (often rich in Ti up to several percent). Apatite-rich beds coincide with the position of GRS-U peak and overlying beds contain also scattered grains of amphiboles/pyroxene, pyrite and also barite. There are also lateral variations in amounts of Fe-oxides and oxyhydroxides and barite grains. Diagenetic precipitates rich in authigenic apatite at the GRS-U peak and barite grains 1.5 m above this peak were identified only in the Prastav Quarry and are almost absent in the Na Škrábku Quarry. Here, Fe-oxides and oxyhydroxides dominate in the heavy fractions assemblage and the content is exceptionally high – up to 90 %.

MS and GRS record – intrabasin correlative patterns and sea level fluctuations

MS log shows a smooth curve below the first BCE beds in the Třebotov and Suchomasty Lmst. Then a drop in MS values appears at the very event datum (base of the Choteč and Acanthopyge Lmst.) being followed by long elevation on MS values and high-amplitude and magnitude oscillations which characterize the interval above the BCE base. The significant drop is clearly identified in the deeper-water but missing in the shallow-water section where minor gaps are identified. It is interpreted as a minor sea level drop before the main pulse of the sea level rise at the BCE level.

Unpublished data on MS of complete Suchomasty Lmst. exposed in the Červený Quarry show 15 to 20 fold higher values in the lower parts of the Suchomasty Lmst. (overlying Koněprusy Lmst.) with 4 quasicyclic patterns of elevated values. Toward the BCE level, the values are rapidly decreasing to zero or to negative values with one positive peak just before the event datum. Then values stay very low and oscillate. Such high MS values are probably due to red hematite pigments and grains occurring in the Suchomasty Lmst. which were precipitated by bacteria. Filaments, crystals and hematite grains were identified in thin sections as coatings of bioclasts or fillings of bored clasts.

GRS record provides a stable significant pattern with typical feature of the point of reversal in the Th/U ratio at the event base from Th/U>>1 to Th/U<<1 both in the deeper- and shallow-water environment regardless to the lithology. It means that the total GRS record in the Třebotov and Suchomasty Lmst. is driven by Th concentrations while U concentrations are low; the opposite is true for the Choteč and Acanthopyge Lmst. This reversal signifies a shift from well-oxygenated environment to suboxic environment at the event datum. This is also supported by the occurrence of monospecific *Chondrites* isp. assemblage in the Choteč Lmst. which may indicate decreased oxygen content. Joint Th and U GRS maxima (so-called GRS-U peak) occur above the first event related beds and its stable position regardless to lithology (notably in the Červený Quarry where lithological boundary between the Suchomasty and Acanthopyge Lmst. is not distinct) is very significant (1.25, 0.25–0.5 and 1 m above in the Prastav Quarry, Na Škrábku Quarry and Červený Quarry respectively). The position of this GRS-U peak could be interpreted here as the maximum flooding surface or early highstand (GRS maxima and enrichment in the U concentrations are considered to reflect maximum flooding surface e.g., Raddadi et al., 2005). The occurrence of barite above this level can be indicative of upwelling process with the maximum above the GRS-U peak. A prasinophyte bloom and enhancement in nutrient load at the BCE datum is also reported by Berkyová et al. (2009). To sum up, if the BCE is interpreted here as the transgressive pulse connected with upwelling, MS pattern is the inverse to the premises that during transgressions MS values are low and *vice versa* during regression. It was also earlier reported for the Kačák, Lower Kellwasser, Lower *pumilio* or *mid-punctata* events where high values of MS (inverse patterns) were recorded through the critical interval (Crick et al., 1997b, 2002; Hladil & Pruner, 2001; Hladil, 2002; Hladil et al., 2006; Koptíková, 2011). So, the BCE MS log joins these important Devonian events. This might be a consequence of not only impurities delivered into the oceans *via* oceanic currents but also in the form of atmospheric dust; these inverse patterns might record the changes in the atmospheric dynamics (see also subchapter on REE distributions across the BCE).

REE distributions and aeolian origin of impurities

PAAS and Lu-normalized data on the REE and their distributions show very uniform patterns both in the deeper-water facies and shallow-water open ocean facies, indicative of their origin by aeolian atmospheric deposition according to 4 general patterns introduced by Nozaki (2001) for fluxes into recent oceans. There is a strong positive correlation to this aeolian pattern with stable correlative coefficients from 0.60 up to 0.80 across the BCE interval in the Prastav Quarry, 0.52 up to 0.82 for the Na Škrábku Quarry and slightly lower for the Červený Quarry (0.64 up to 0.70 with one anomalous negative value in the upper part of the Suchomasty Lmst.). There are also some effects of sea water solutes (with typical depletion in the LREE, mostly in Ce) and remineralization pattern. Riverine pattern is almost absent here.

All 4 tasks were completed in this paper: MS and GRS logs were established, carriers of MS and GRS signal were identified, interpretations of environmental changes and changes in depositional environment were postulated, and sea level fluctuations were suggested. Regional correlations within one sedimentary basin were successfully tested and proved.

Data were presented by L. Koptíková at 2 international conferences:

International Conference Global Alignments of Lower Devonian Carbonate and Clastic Sequences, SDS/IGCP Project 499 joint field meeting, August 25 – September 3, 2008, State Committee of the Republic of Uzbekistan on Geology and Resources, Kitab State Geological Reserve, Uzbekistan

Koptikova, L., Berkyova, S., Hladil, J., Slavik, L., Schnabl, P., Frana, J. & Bohmova, V., 2008b. Long-distance correlation of Basal Chotec Event sections using magnetic susceptibility (Barrandian – vs. – Nevada) and lateral and vertical variations in fine-grained non-carbonate mineral phases. *In*: Kim, A.I., Salimova, F.A. & Meshchankina, N.A. (Eds), International Conference Global Alignments of Lower Devonian Carbonate and Clastic Sequences, SDS/IGCP Project 499 joint field meeting, August 25 – September 3, 2008, State Committee of the Republic of

Uzbekistan on Geology and Resources, Kitab State Geological Reserve, Tashkent, Uzbekistan. Contributions: pp. 60-62.

Subcommission on Devonian Stratigraphy and IGCP 499 Devonian Land Sea Interaction, Eureka, NV, 2007, San Diego State University & SUNY-Geneseo, September 9–18, Eureka, Nevada, USA

Koptikova, L., Hladil, J., Slavik, L. & Frana, J., 2007. The precise position and structure of the Basal Choteč Event: lithological, MS-and-GRS and geochemical characterization of the Emsian-Eifelian carbonate stratal successions in the Prague Syncline (Teplá-Barrandian unit, Central Europe). *In*: Over, D.J. & Morrow, J. (Eds), Subcommission on Devonian Stratigraphy and IGCP 499 Devonian Land Sea Interaction, Eureka, NV, 2007, San Diego State University & SUNY-Geneseo, September 9–18, 2007, Eureka, Nevada, USA. SDS & IGCP 499 Eureka NV 2007 Program and Abstracts: pp. 55-57.

4.4 Paper 4

Stratigraphy of the Middle Devonian boundary: Formal definition of the susceptibility magnetostratotype in Germany with comparisons to sections in the Czech Republic, Morocco and Spain

Ellwood, B.B., García-Alcalde, J.L., El Hassani, A., Hladil, J., Soto, F.M., Truyóls-Massoni, M., Weddige, K. & **Koptikova, L.**, 2006.

Tectonophysics, 418, 1-2: 31-49.

First data on MS from the Emsian–Eifelian boundary interval in the Prague Synform were published. MS logs of two sections including the parastratotype of the Emsian-Eifelian boundary in the Prastav Quarry near Praha-Holyně and Red Quarry near Suchomasty (= Červený Quarry section commented in the paper 3 were compared, and correlative patterns for interregional correlation were established. These data were confronted with logs from the GSSP section of this boundary in the Eifel Mountains in Germany (near Wetteldorf-Schönecken), two sections in Morocco (Mech Irdane and Jbel Issoumour) and El Puerto section in the Cantabrian Mountains in Spain. Utility of the MS stratigraphy as a tool for interregional correlations and refining the biostratigraphic resolution was confirmed. A magnetostratotype at the GSSP in Wetteldorf-Schönecken was established at this paper and all later sampled sections (including Prague Synform) were linked to this stratotype section. MSEC method (Crick et al., 1997a) was applied. Raw data on MS were smoothed using a fine spline. MSEC subchrons were defined using the high-frequency smoothed curve and MSEC chrons were established using the low-frequency smoothed curve.

A comparison of the sections with well-established conodont zonation (the boundary is defined by FAD of the conodont species *Polygnathus costatus partitus* and the base of the P. c. partitus conodont Zone) with the sections with poor control on conodont zonation but well-defined by brachiopods – GSSP in Germany, 2 sections in the Morocco (Mech Irdane and Jbel Issoumour) and 2 sections in the Prague Synform with the section in Spain (El Puerto Creek) where (poor conodont biostratigraphy). The Emsian–Eifelian boundary represents the boundary between the MSEC chrons EMΩ-1 (the last Emsian chron) and E I-1 (the first Eifelian chron). In the Prastav Quarry it is the level approximately 1.5 m below the boundary of the Třebotov and Choteč Lmst. (a BCE interval treated in the paper 3), in the Red Quarry less than 1 m below the boundary of the Suchomasty and Acanthopyge Lmst. (shallow-water lithostratigraphic equivalents).

The results and conclusions of the paper were indicative that this method allows the identification of the Emsian–Eifelian boundary if the section with poorly defined biostratigraphic scales is compared with those with well-established zonation.

Discussion on the results (a state in 2006) under a recent knowledge (a state in 2012) and reassessment of the conodont scale in the Prastav Quarry

The only point for discussion on the results is the precision, reliability and up-to-date state of the biostratigraphic data and scales used for the comparisons and correlations. It turned out that this method is greatly dependent on the resolution of sampling and thus on the FAD levels of species (conodonts in our case). Berkyová (2009) moved the base of the P.c. partitus Conodont Zone (Emsian–Eifelian boundary) to the level of 4.8 m below the BCE interval (it means 2 metres below the original Emsian–Eifelian boundary presented in paper 4). Also the use of a smoothed data can be very risky and tricky and sometimes can remove characteristic peaks or patterns of MS. In later papers, L. Koptíková preferred to use raw data or data treated by the DTW method or methods sensitive to the data sets which represent signal varying in time and speed.

Task 4 was completed in this paper. MS logs of two Emsian–Eifelian sections in the Prague Synform – the Prastav Quarry (GSSP of the Eifelian stage) and the Red Quarry (= Červený Quarry) – were linked to the GSSP of the Eifelian in Germany (Wetteldorf-Schönecken), to 2 sections in Morocco (Mech Irdane and Jebel Issoumour) and 1 in Spain (El Puerto Creek).

4.5 Paper 5

The dynamic time-warping approach to comparison of magnetic susceptibility logs and application to Lower Devonian calciturbidites (Prague Synform, Bohemian Massif)

Hladil, J., Vondra, M., Cejchan, P., Vich, R., **Koptikova, L.** & Slavik, L., 2010.

Geologica Belgica, 13, 4: 385-406.

The use of novel methods in geology for the alignment of logs (for the first time for MS log comparisons) was tested in this paper: algorithm DTW – dynamic time warping which analyses sequences varying in time and speed. A quite new method primarily developed for speech recognition (Sakoe & Chiba, 1978) is based on the comparisons of signals (in this case MS logs) which may vary in time and speed – this is very important factor in any geological material and all records, especially in old sediments (generally as far as you go in time back, it is more difficult to interpret primary signal). In geology, these variations in time and speed can be translated as different sedimentation rates, different amounts of material delivered into depositional environment or the occurrence of gaps. A justification for the use of the DTW method for log comparisons was the problem that data sets are very often used treated and smoothed (recently Ellwood et al., 2011 and many others), and the resulting logs are transformed, “a noise“ is eliminated but very often some characteristic peaks are omitted or joined together. Also the Fourier transform analysis is applied (Ellwood et al., 2007). The main problem of these techniques when applied to the geological material is that they are based on the data sets representing sediments and expecting no gaps and a constant sedimentation rate.

DTW is an algorithm which allows the finding of optimum alignment between two numerical sequences, a similarity between them is measured, variation in speed and distortion or missing sequences from the logs are detected.

Two sections in the Praha Fm. were selected – Požár 3 and Pod Barrandovem sections. They represent major and the most complete parts of the Pragian stage and the precision of the correlation is backed up by biostratigraphy (Slavik, 2004; Slavik et al., 2007). They are very well documented in detail (biostratigraphy, lithological, mineralogical, geochemical data, data on MS, GRS logs with the resolution of 0.25–1 m scale for GRS and 0.05–0.20 for MS; Koptíková et al., 2010a, b; Slavik et al., 2000, 2007) which can support the use of the DTW and help with the interpretation of results, they represent different depositional environments which is demonstrated in different lithostratigraphic members (see Melichar & Hladil, 1999; Chlupáč et al., 1998). Succession of beds in the Požár 3 is described in papers 1 and 2. MS segment for comparison covers the interval from the basal parts of the Slivenec Lmst. up to the upper parts of the Řeporyje Lmst. Total thickness of the segment is approximately 28 m. The Pod Barrandovem section is represented by the sequence of calciturbidites with elevated thickness (thickness of entire Pragian is approximately 180 m). Almost whole thickness of the limestones exposed here belongs to the Dvorce-Prokop Lmst. lithotype which is characterized by grey to yellow-brownish (if weathered) and pressure solution seams (Chlupáč et al., 1998). They contain calcimud, calcisiltite material with fine-lithoclastic components. Their depositional environment is interpreted as a fill of a depression or a thicker accumulation in a steep lower slope/toe-of-the-slope zone (Slavik et al., 2000) and the thickness of the studied interval equivalent to those in the Požár 3 Quarry is almost 4 fold higher.

An optimum concerning the requirements for input data was preliminary found for this paper (but extensive testing and further studies are necessary and crucial). Relevant points at each of the sections as the beginning and the end of the segment were set, the premise of a similar sampling interval (and thus similar resolution of data) was also met.

MS logs alignment – recognition of characteristic peaks and locations of major gaps

An alignment of the two logs and computing of warping function (can be understand as relative shortening or swelling if the logs are aligned to each other) when one log is apprehend as “unwarped standard“ to which the second one is calculated (and vice versa for the control) has revealed that the logs can be compared with the precision of several centimetres, characteristic peaks were found and fixed, the number of macroscopically hidden and here identified gaps, level of significant condensations (parts of the record missing in one compared log) is higher for the Požár 3 section than for the Pod Barrandovem section. Intervals with major gaps lie between 104.5 and 105.5 metre marks in the Požár 3 section and at the beginning of the Pod Barrandovem section at the height of 19 m. Upper parts of the Pod Barrandovem section proved thickening of the beds which was originally indicated in the lithological characteristics (homogenized beds, occurrence of the *Chondrites* and *Zoophycos* isp…).

Accuracy and increase in the resolution of compared parameters – MS logs and lithological characteristics

DTW results and alignment of the logs showed also similarities in the lithotypes which are well distinguished in the Požár 3 section (Slivenec, Loděnice and Řeporyje Lmst.) but not in the Pod Barrandovem section. Only Dvorce-Prokop Lmst. lithotype was reported here. But after a closer look to the compared logs and lithology, we can distinguish counterparts of the Praha Fm. lithotypes also in this section – of course shifted and with slight differences due to different depositional settings and local specifics as different sedimentation rate, diagenetic compaction etc.

The resolution of the DTW algorithm is about 2 orders of magnitude higher (with the resolution of few centimetres) if compared to biostratigraphical, chemostratigraphical or lithostratigraphical tools and techniques.

A study on the global correlation of the log in the Požár 3 section with the GSSP of the Emsian stage in Uzbekistan in Kitab is accepted.

Task 4 was completed in this paper: regional correlative patterns were identified using a novel DTW algorithm for the first time for MS logs comparisons. Resolution of 2 orders of magnitude higher than the correlative tools used before was proved with the resolution of several centimetres. These datasets are prepared now for global correlations (study on the Požár 3 log and the log of the Emsian GSSP in Uzbekistan which is accepted). Task 3 was also completed subordinately because the alignment of the MS logs revealed also delicate variations in the limestone lithotype of the Pod Barrandovem section and enabled subdivision.

4.6 Paper 6

An Emsian-Eifelian calciturbidite sequence and the possible correlatable pattern of the Basal Choteč event in Western Ossa-Morena Zone, Portugal (Odivelas Limestone)

Machado, G., Hladil, J., Slavík, L., **Koptíková, L.**, Moreira, N., Fonseca, M. & Fonseca, P., 2010.

Geologica Belgica, 13, 4: 431-446.

A study on carbonate-volcaniclastic sequence in the Covas Ruivas section in south-western Ossa-Morena Zone in the Iberian Massif in Portugal of the Emsian-Eifelian age was realized using also MS together with reef fauna and facies analyses. The age of the sequence was determined and assigned to the Polygnathus costatus patulus and Tortodus australis Conodont Zones (uppermost Emsian – middle late Eifelian) and record the BCE level. Detailed lithological characteristics point to the calciturbidite and debris-flow origin of the beds which are alternated with hemipelagic tuffites. Their depositional environment is suggested in the upper parts of the slope. It was a part of the reefal system developed on top of volcanic high. Despite the proximity of volcanic complex it seems that the environment was influenced by volcanic activity only weakly.

MS values across the studied interval are generally low (which is indicative that the contribution of volcanic-derived material is low). A very interesting feature is that the carbonate-rich massive beds which intercalated these tuffites show MS values of 1 or 2 orders of magnitude higher than the values of the tuffites. Analyses of insoluble residues revealed only scarce particles which might be of volcanic origin (non-determined black rounded micrograins). Pyrite grains are not abundant and occur in the levels with higher content of organic matter. Due to the fact that there is probably no relation between the amount of non-carbonate material (of both volcanic and non-volcanic origin) and MS values if compared MS values and the proportion of carbonate and non-carbonate particles (based on thin section analyses), it can be concluded that the primary signal is not masked by the coeval volcanic and sedimentary processes. Background sedimentation with only a minor contribution of the volcanic material (e.g., ultra-fine grained particles which can be missed in thin section analyses) might carry the MS signal. Thus a tentative interregional correlation using MS logs of the BCE interval is suggested with sections in Morocco (paper 4 – Ellwood et al., 2006), Nevada (Central Great Basin, USA; sampled in 2007, 2009, 2011) and Uzbekistan (Zeravshan-Gissar Mountain region in Tien-Shan Folded System, sampled in 2008).

The upper Emsian and lowermost Eifelian MS record shows alternation of periods of high-amplitude oscillations with highly oscillating intervals (0–10 and 20–30 m). Low values before the BCE datum reported by Koptikova et al. (2007, 2008b) from the Prague Synform, Central Great Basin (USA, Nevada), to some extent also from Uzbekistan, was not observed here but could correspond to a major gap or the first occurrence of skeletal debris (36–47 m). The onset of increased input of coarse-grained skeletal detritus material is other of typical features which mark the base or the proximity of the BCE level. A positive shift in MS values in the Covas Ruivas section (at the height of 47 m MS values again decrease) coincides with these first sets of calciclastics. Elevated average MS values follow (47–57 m) and then decreased MS values (~58 m). This interval of decreased MS values might represent the BCE start, but it is not as significant as the underlying first interval with decreased MS values. Also the amplitudes of the oscillations are higher (68–80 m).

Task 4 was completed. A correlative pattern for the BCE MS log was proposed here. Tentative global links of the MS patterns were suggested across different palaeogeographical settings between Portugal (Ossa-Morena Zone), Czech Republic (Prague Synform), USA (Nevada, Central Great Basin), Morocco (Anti-Atlas) and Uzbekistan (Zeravshan-Gissar Mountain Region).

4.7 Paper 7

The Odivelas Limestone: evidence for a Middle Devonian reef system in western Ossa-Morena Zone (Portugal)

Machado, G., Hladil, J., **Koptíková, L.**, Fonseca, P.E., Rocha, F.T. & Galle, A., 2009.

Geologica Carpathica, 60, 2: 121-137.

Even though this paper deals with the Middle Devonian sequences in the Ossa-Morena Zone in the Iberian Massif in Portugal, it matched the original assignment of this thesis which was focused on entire Devonian in the Prague Synform and potential correlations elsewhere. This paper was published before the theme of the thesis modification in 2009. Despite the fact that the MS log was finally linked to the Devonian of the Moravian Karst, the use of MS logging was tested for the interregional correlations in the combination of detailed analyses of lithological and palaeontological content, geochemical properties.

Data on reefal fauna (crinoids, rugose and tabulate corals, brachiopods), palynomorphs and acritarchs revealed the Middle Devonian age of the Odivelas Lmst., one of the few records of such age in the Ossa-Morena Zone in Portugal. Despite the fact that the rocks were deformed and metamorphosed, abundance of the fauna allowed the precise dating as late Eifelian–early Givetian and with Rhenish facies affinities.

MS logging was performed at one small outcrop of thin-bedded crinoidal calciturbidites and bioherm beds (total thickness of 2.4 m). Data were tentatively (due to limited exposure and the effects of metamorphic processes) assigned to the upper parts of the Eifelian of the reference section in the Moravian Karst (Hladil et al., 2006). This position was suggested and based on the extremely low magnitudes and medium amplitude MS patterns and might point to the Polygnathus ensensis or P. hemiansatus conodont zones (Hladil et al., 2006).

Fine-grained, mostly altered volcanic admixture (redeposited and altered ?volcanic ash or recycled detrital material) is considered to affect the MS signal, as well as black prismatic crystals (needles) of undetermined mineral. Their envelopes show by several orders higher MS values than the inner parts (7.9 vs. 84.6 $m^3.kg^{-1}\times10^{-9}$). Diagenetic trapping of Fe by pyrite and consequent weathering to Fe-oxyhydroxides may also influence the primary MS signal here which could be also modified by metamorphism during Variscan Orogeny in this area. To sum up, lithological, geochemical analyses, field observations are indicative of a very narrow relationship of the reef system and volcanic structures in the Beja Igneous Complex in the Ossa-Morena Zone.

Task 4 was completed. The MS log of the limited exposures of the Odivelas Lmst. in the Ossa-Morena Zone in Portugal was finally and tentatively linked to the MS pattern of late Eifelian–early Givetian in the Moravian Karst.

5 Conclusions

The composite reference section in the Lower Devonian succession of the Barrandian Area was established using the MS and GRS logs from 5 sections representing both deep- and shallow-water environment of carbonate slope systems: Požár 3 section (Lochkovian to Emsian: Lochkov Fm., Praha Fm., lowermost part of Zlíchov Fm.), Pod Barrandovem section (Pragian to lower Emsian: Praha Fm.), Prastav Quarry, Na Škrábku Quarry and Červený Quarry (Emsian–Eifelian: Daleje-Třebotov – Choteč Fm.). Both background data and data across the boundaries of geological units or event intervals were acquired with the emphasis on obtaining continuous data series as complete as possible. Such a complex, detailed and multidisciplinary data set has never been collected in the Prague Synform.

The data sets of petrophysical, lithological, mineralogical and geochemical parameters of the Lower Devonian succession in the Prague Synform were linked to the existing biostratigraphical scales and offer complex information for interregional and global correlations now with the precision of a few centimetres, which is a resolution 10 to 100 fold higher than in any established biostratigraphic scale in the Devonian of the Prague Synform. This type of elaboration is highly topical because of the number of GSSP which occur here and, therefore, the reference section must conform to the modern stratigraphic requirements.

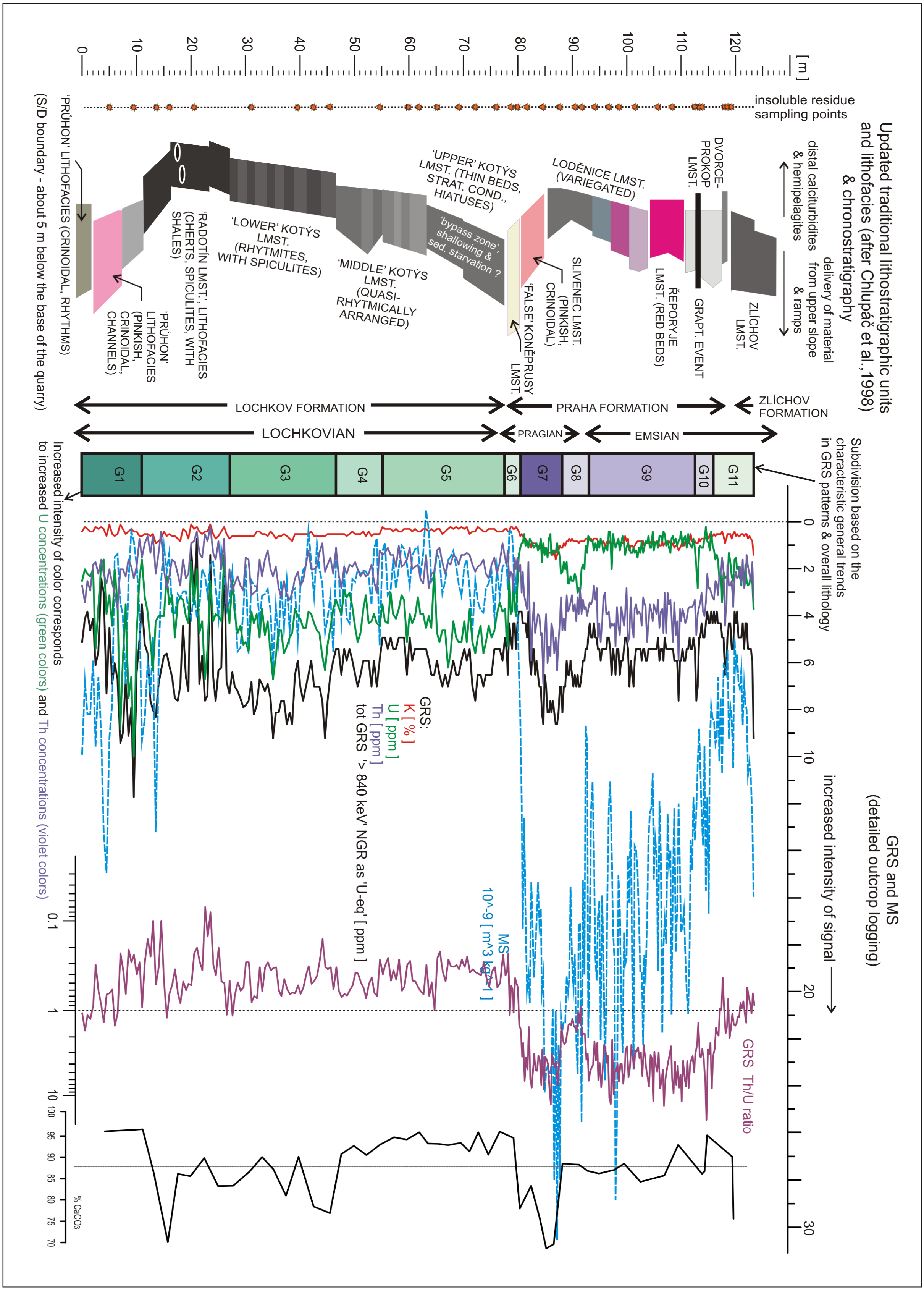
Major changes in the MS, GRS logs and mineralogy concentrate to the proximity of the Lochkov and Praha Fm. boundary (see Figure 2 for entire logs). The Praha Fm. provides a stable pattern of elevated MS and GRS values compared to those in the underlying Lochkov Fm. and the overlying Zlíchov Fm. At this level, a reversal point in Th/U ratios is observed (dominant Th concentrations in the Praha Fm. vs. dominant U concentrations in the underlying Lochkov Fm. and overlying Zlíchov Fm.). Facies arrangements, GRS logs along with $CaCO_3$ data are indicative of a general transgressive trend for the Lochkov and Praha Fm. followed by a significant regression close to the Lochkovian–Pragian boundary. K, Th, MS values and Th/U ratios increase, while $CaCO_3$ contents decrease between 80–87.5 m (Požár 3 section), indicating a 3rd-order transgressive pulse which can be correlatable in the Euramerican craton, a drop in sedimentation rate and a decrease in carbonate productivity. K, Th, MS maxima and barite enrichment around 87.45 metre mark in the Praha Fm. (Požár 3 section) is interpreted here as a change in the delivery and increase in the flux of non-carbonate impurities (mostly of paramagnetic character). It might reflect a major change in the atmospheric circulation (changes in wind directions or intensities). In the upper part of the Praha Fm., K and Th concentrations, Th/U ratios and MS values start to decrease again; this is interpreted as a regression which continues to the Zlíchov Fm.

Proportions of minerals which can carry MS signal vary along the composite section. Fe-oxides and oxyhydroxides (such as magnetite, hematite often with high Ti contents of several percent, or goethite), pyrrhotite, ilmenite, pyroxene, amphibole, olivine, chlorite, biotite, glauconite, clay minerals (illite, kaolinite, montmorillonite), ankerite, Fe-rich dolomite, pyrite, chalcopyrite, epidote were identified in insoluble residues. Quartz, muscovite, dolomite, feldspars (orthoclase, microcline, albite), zircon, barite, apatite, rutile were identified as diamagnetic phases. To sum up, minerals with paramagnetic characteristics were revealed as dominant MS carriers. For SEM images of the identified mineral phases, see Figures 4 and 5. The Lochkov Fm. and to a certain extent also the Zlíchov Fm. are characterized by an elevated abundance of pyrite–pyrrhotite assemblages and a low abundance of Fe-oxides (goethite prevailing over hematite or magnetite) whereas the Praha Fm. is dominated by Fe-oxides. The presence of Fe-oxides is typical for the Praha Fm. (reddish or pinkish Slivenec, Loděnice and particularly Řeporyje Lmst.), indicating higher oxygenation of the sea water column (high Th/U ratio). The SR logging suggested their early diagenetic origin. This shift from suboxic conditions in the Lochkov Fm. (and very similar in the Zlíchov Fm.) to oxic conditions in the Praha Fm. might explain the preferential formation of Fe-oxides and oxyhydroxides in the Praha Fm. and pyrite and pyrrhotite in the Lochkov Fm.

Geochemical parameters (mostly the REE distributions) show very uniform patterns across the entire reference composite section, and are indicative of the limestone impurities origin by aeolian atmospheric deposition.

The studies presented here emphasize that MS–GRS method of correlation has a great potential, providing new and effective solutions. It has been demonstrated mainly for the BCE interval. The correlative MS and GRS pattern structure through the Emsian–Eifelian successions were found regionally but also on very distant places around the world. A smooth curve below the first BCE beds is followed by a drop in MS values at the very event datum, followed by a long elevation in MS values and high-amplitude/high-magnitude oscillations in the interval above the BCE base. Tentative global links of this MS pattern were outlined across different palaeogeographical settings between Portugal (Ossa-Morena Zone), Czech Republic (Prague Synform), USA (Nevada, Central Great Basin), Morocco (Anti-Atlas) and Uzbekistan (Zeravshan-Gissar Mountain Region). GRS record across this interval provides a stable significant pattern with typical feature of the point of reversal in the Th/U ratios at the BCE base from Th/U>>1 to Th/U<<1 both in the deeper- and shallow-water environments regardless of lithology (Figure 3). This point of reversal signifies a shift from well-oxygenated environment to suboxic environment at the event datum. The GRS-U peak (joint Th and U maxima; Figure 3) occurs above the first event-related beds and its stable position regardless of lithology is very significant. The position of this GRS-U peak is interpreted here as the maximum flooding surface or an early highstand and the BCE interval as a transgressive pulse connected with upwelling. The observed MS patterns contradict the premises that MS values are low during transgressions and high during regressions. This might be a consequence of the fact that impurities are delivered into the oceans not only by oceanic currents but also in the form of atmospheric dust.

A similar strength for regional and interregional correlations has also been indicated for other parts of this Lochkovian–Eifelian reference section where my own and other studies will benefit of this integrated data set.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insoluble residue sampling points
Updated traditional lithostratigraphic units and lithofacies (after Chlupáč et al.,1998) & chronostratigraphy
distal calciturbidites & hemipelagites
delivery of material from upper slope & ramps
DVORCE-PROKOP LMST.
ZLÍCHOV LMST.
GRAPT. EVENT
ŘEPORYJE LMST. (RED BEDS)
LODĚNICE LMST. (VARIEGATED)
SLIVENEC LMST. (PINKISH, CRINOIDAL)
'FALSE' KONĚPRUSY LMST.
'UPPER' KOTÝS LMST. (THIN BEDS, STRAT. COND., HIATUSES)
'bypass zone', shallowing & sed. starvation ?
'MIDDLE' KOTÝS LMST. (QUASI-RHYTMICALLY ARRANGED)
'LOWER' KOTÝS LMST. (RHYTMITES, WITH SPICULITES)
'RADOTÍN LMST.' LITHOFACIES (CHERTS, SPICULITES, WITH SHALES)
'PRŮHON' LITHOFACIES (PINKISH, CRINOIDAL, CHANNELS)
'PRŮHON' LITHOFACIES (CRINOIDAL, RHYTHMS)
(S/D boundary - about 5 m below the base of the quarry)
LOCHKOV FORMATION
PRAHA FORMATION
ZLÍCHOV FORMATION
LOCHKOVIAN
PRAGIAN
EMSIAN
G1
G2
G3
G4
G5
G6
G7
G8
G9
G10
G11
Subdivision based on the characteristic general trends in GRS patterns & overall lithology
GRS and MS (detailed outcrop logging)
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0
2
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8
10
20
30
GRS:
K [%]
U [ppm]
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tot GRS '> 840 keV' NGR as 'U-eq' [ppm]
MS 10^-9 [m^3 kg^-1]
GRS Th/U ratio
0.1
1
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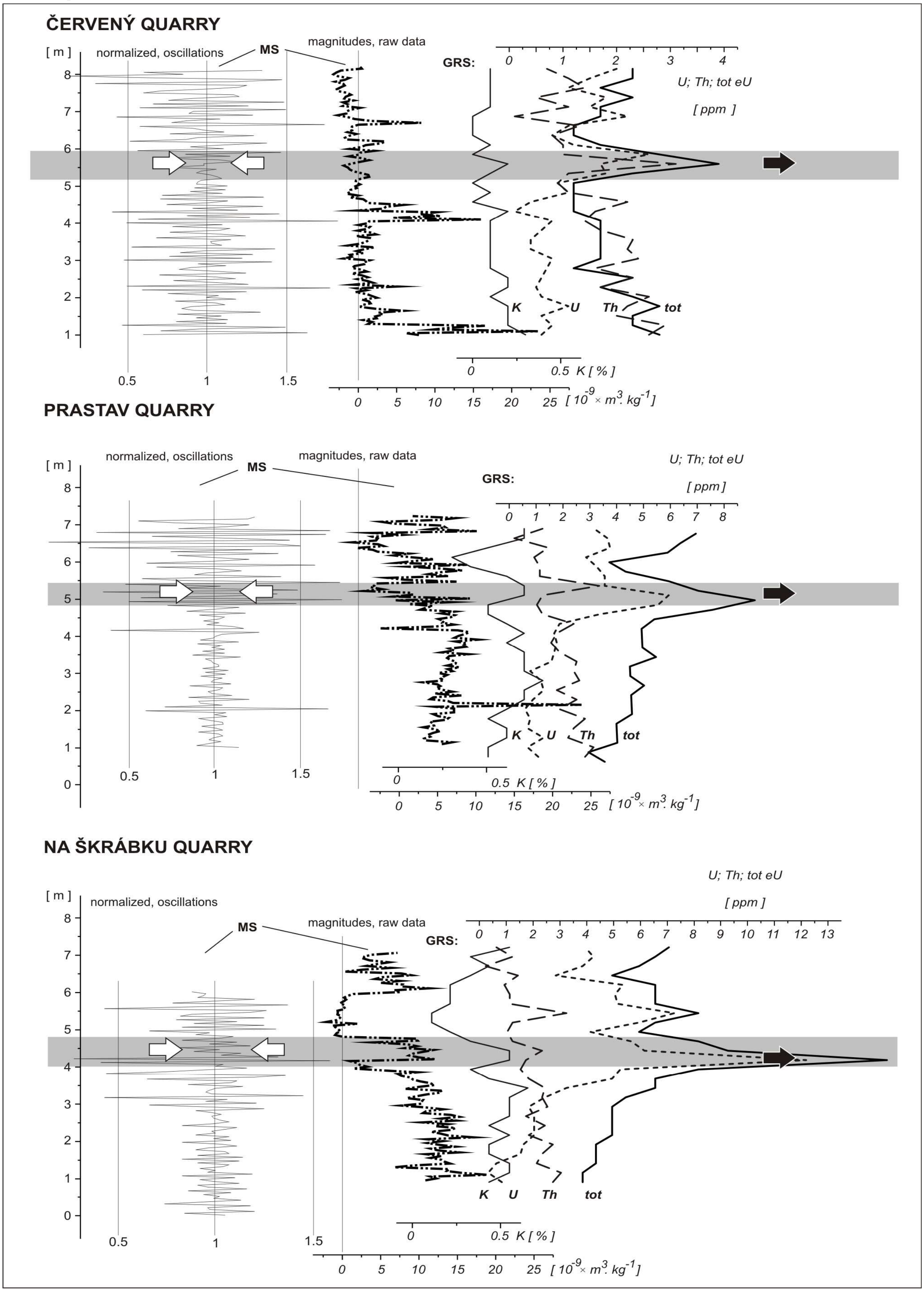
% CaCO3
Increased intensity of color corresponds to increased U concentrations (green colors) and Th concentrations (violet colors)

Figure 2.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PRASTAV QUARRY
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K
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0 0.5 K [%]
0 5 10 15 20 25 [$10^{-9} \times m^3 \cdot kg^{-1}$]
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Figure 3.

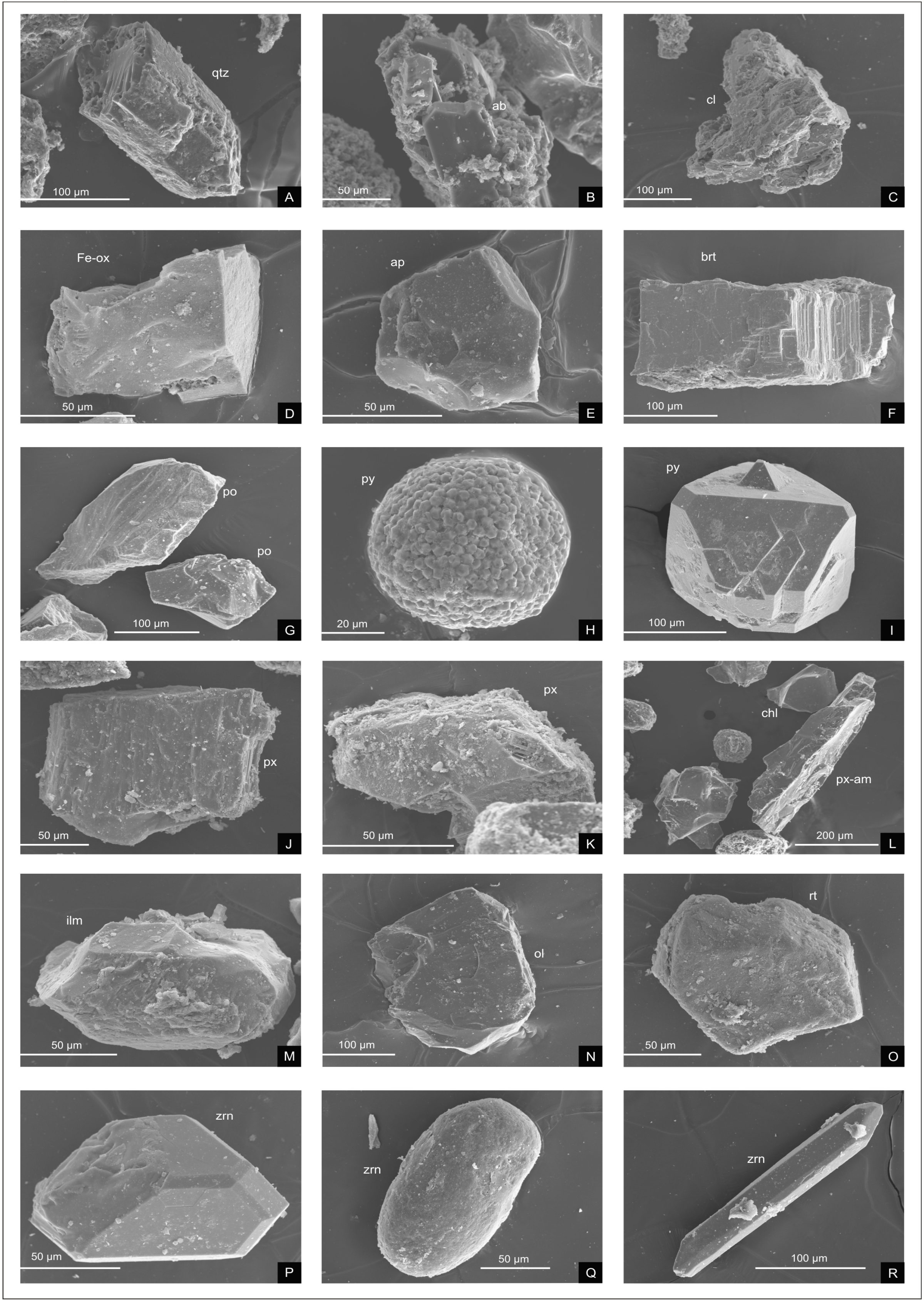
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Figure 4.

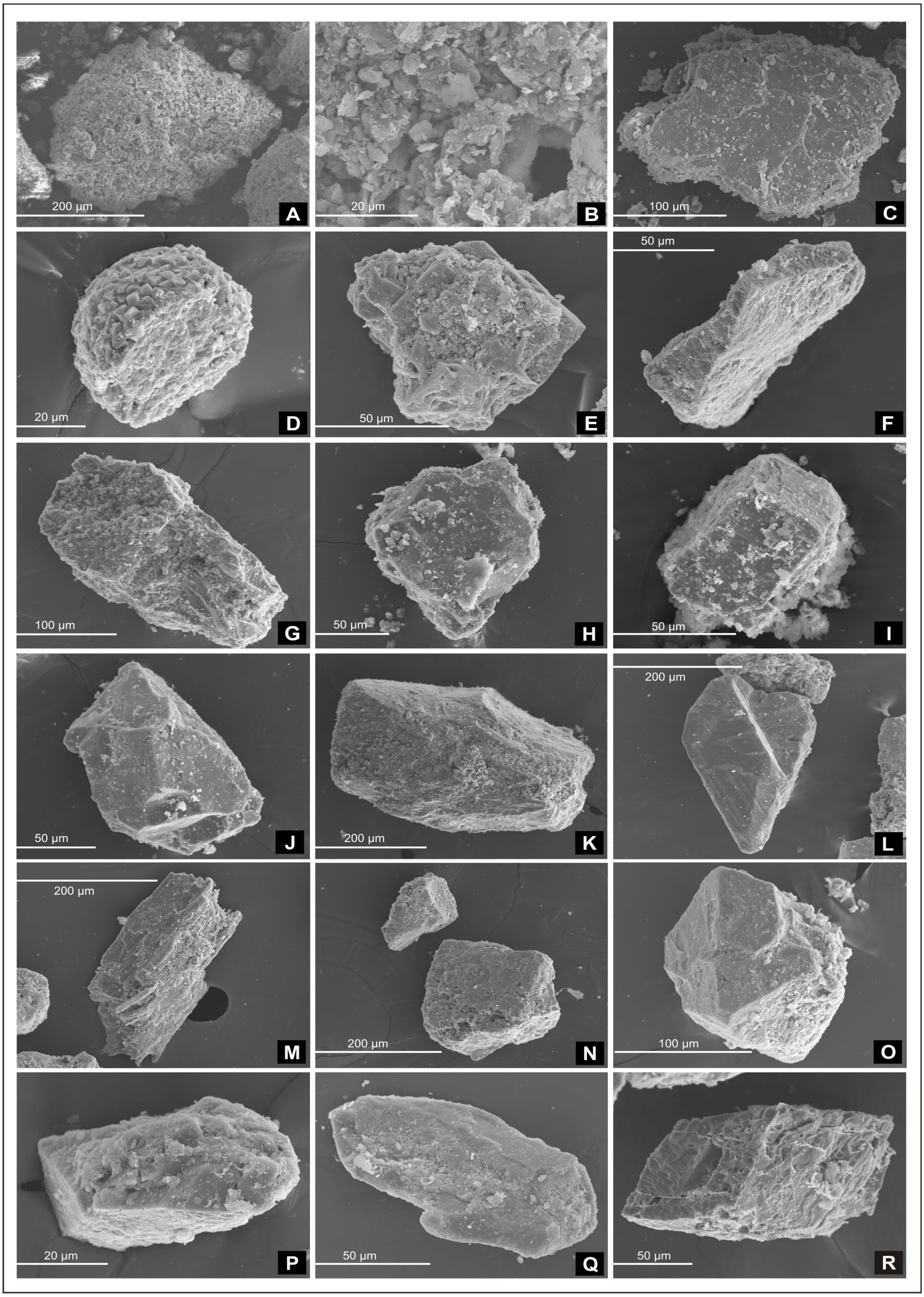
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Figure 5.

Figure 2. A composite section of the overall MS and GRS logs across the Lochkovian to the lower Emsian succession in the Požár 3 section plotted against limestone lithotypes (lithostratigraphic units and biostratigraphy after Chlupáč et al., 1998; herein refined and modified – Kotýs Limestone, Průhon lithofacies in the basal parts of the Lochkovian – defined here for the first time and distinguished by its special MS and GRS patterns compared to the rest of the Lochkovian beds). Green and violet colours highlight variations in U and Th concentrations (reversals in the Th/U ratio). For their mean values and statistical characteristics, see Table 2 in Koptíková et al., 2010a. From Koptíková et al., 2010a.

Figure 3. MS logs plotted against the GRS logs, and a correlatable pattern across the BCE interval. The event datum is marked by a drop in MS values (missing in the shallow-water environment represented by the Červený Quarry due to probable hiatus), by the point of Th/U ratio reversal and by a subsequent steep rise in MS values with high-amplitude and high-magnitude oscillations. A GRS-U peak interpreted as the maximum flooding surface lies 0.25–0.5 m, 1 m and 1.25 m above the event boundary in the Na Škrábku Quarry, the Červený Quarry and the Prastav Quarry, respectively. Slightly modified after Koptíková (2011).

Figure 4. SEM images of light and heavy mineral assemblages in the insoluble residues in the Požár 3 section (Lochkovian to lower Emsian). A–I: minerals of authigenic, diagenetic or possible detrital origin, J–R grains of pure detrital origin. C, D, G, H, I–N: MS carriers. A – quartz (69 m), B – albite (31.1 m), C – clay mineral (20.5 m), D – undetermined iron oxide – oxyhydroxide (20.5 m), E – apatite (9.7 m), F – barite (87.45 m), G – pyrrhotite (79.7 m), H – framboidal pyrite (69 m), I – bipyramidal pyrite (87.45 m), J – pyroxene – augite (112.7 m), K – pyroxene (9.7 m), L – grain of pyroxene/amphibole elemental composition, chlorite and pyrite framboid (45.5 m), M – ilmenite (98.5 m), N – olivine (54.7 m), O – rutile (9.7 m), P – zircon (98.5 m), Q – zircon (65 m), R – zircon (79.7 m). From Koptíková et al., 2010a.

Figure 5. SEM images of light and heavy mineral assemblages in insoluble residues across the BCE interval. The images document typical light and heavy mineral assemblages and MS carriers (D, G, H, J, M–P, R). A–I: the Prastav Quarry, J–N: the Na Škrábku Quarry, O–R: the Červený Quarry. A, B – ultra-fine porous mixture of mineral phases found in all specimens across the whole studied interval and all lithotypes, B – porous matrix in detail, C – albite, upper part of the Třebotov Lmst., D – Fe-oxyhydroxide, note spherical shape, Choteč Lmst., GRS-U peak level, E, F – apatites, Choteč Lmst. (GRS-U peak level), G, H – grains with the elemental composition of pyroxene/amphibole, Choteč Lmst. (1.5 m above the GRS-U peak level), I – barite, Choteč Lmst. (1.5 m above the GRS-U peak level), J – grains with the elemental composition of pyroxene/amphibole, upper part of the Třebotov Lmst., K – quartz, upper parts of the Třebotov Lmst., L – quartz, Choteč Lmst. (GRS-U peak level), M – grains with the elemental composition of pyroxene/amphibole, Choteč Lmst. (GRS-U peak level), N – Fe-oxyhydroxides, Choteč Lmst. (GRS-U peak level), O – pyrite, upper part of the Suchomasty Lmst., P – Fe-oxyhydroxide, Acanthopyge Lmst. (GRS-U peak level), Q – quartz, Acanthopyge Lmst. (GRS-U peak level), R – oxidized pyrite, Acanthopyge Lmst. From Koptíková (2011).

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8 Appendices