FACIES AND SEDIMENTARY ENVIRONMENT OF THE CARBONATE-DOMINATED CARPATHIAN KEUPER FROM THE TATRICUM DOMAIN: RESULTS FROM THE DOLINA SMYTNIA VALLEY (TATRA MTS, SOUTHERN POLAND)

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Abstract: The paper focuses on an interpretation of sedimentary and early diagenetic environment in the carbonate-dominated uppermost Ladinian–Norian succession from the Tatricum domain of the Tatra Mountains as well as its controlling factors. Limestones with cherts are the product of pedogenic processes, formed during long-term exposures of carbonate substrate. Chalcedony cherts were formed during relatively early diagenesis of pedogenic limestones. Dolostones and dolomitic mudstones were deposited in a kind of salt marshes. Pseudomorphs after sulfates and absence of benthic fauna indicate increased salinity and intensive evaporation. Additionally, low TOC concentration suggests a low productivity in the basin. On the contrary, stable isotope signals indicate that the sedimentary environment was strongly affected by meteoric water. Moreover, $\delta^{18}O$ and concentration of Sr suggest that dolostones were formed under the influence of both marine and meteoric waters. Dolomitic mudstones could be deposited in a salt-marsh environment fed by distal sheet floods. Components of palynological material and organic compounds in black dolomitic mudstones indicate the terrestrial origin of organic matter. Dolomitic regoliths were formed as the result of subaerial exposure and karstification of dolostones. Coarse-grained siliciclastics and variegated mudstone are interpreted, respectively, as a fluvial channel and flood plain facies of ephemeral fluvial environment. Sedimentary environment of the Keuper sediments was controlled by two main factors: synsedimentary tectonic movements and climate changes. In the latest Ladinian, the Middle Triassic carbonate platform was emerged, what resulted in the development of palaeosols. Block tectonic movements affected the Tatricum Basin in Keuper time. Horsts were emerged, whereas troughs were filled with fluvial or salt marsh sediments. Intensive tectonic movements are suggested by seismic-generated slumps and abrupt facies changes. More intensive chemical weathering and intensive contribution of pure siliciclastics suggest climate pluvialization in late Ladinian–early Carnian time. On the contrary, domination of physical weathering indicates the aridization of climate in late Carnian?–Norian time. The upper Carnian?–Norian succession was formed in hot and semi-arid climate conditions. Long-term climate changes was masked by short-term climate fluctuations. Geochemical indicators suggest that dolostones represent more humid periods, whereas dolomitic mudstones relatively dry periods.

Key words: tectonics, climate, dolostones, palaeosols, uppermost Ladinian–Norian, High-Tatric Unit, Western Carpathians.

INTRODUCTION

By the end of the Ladinian, fundamental facies changes occured in the Tatricum Basin. The Middle Triassic carbonate platform was emerged, and underwent erosion and pedogenic processes. In the Carnian–Norian period, sediments of the so called Carpathian Keuper were deposited. The sediments of this period developed in two lithofacies: continental clastics (red beds type) and shallow marine carbonates. For instance, the seqence of Dolina Smytnia valley represents the succession with carbonate sediment dominance.

Sedimentary and diagenetic environment of the Carpathian Keuper were subject to research by several authors, but they have mostly been focused on the Fatricum Basin (Al-Juboury & Durovič, 1992, 1996; Rychliński, 2008). So far, there were no sedimentological analyses conducted for analogous deposits from the Tatricum domain, although
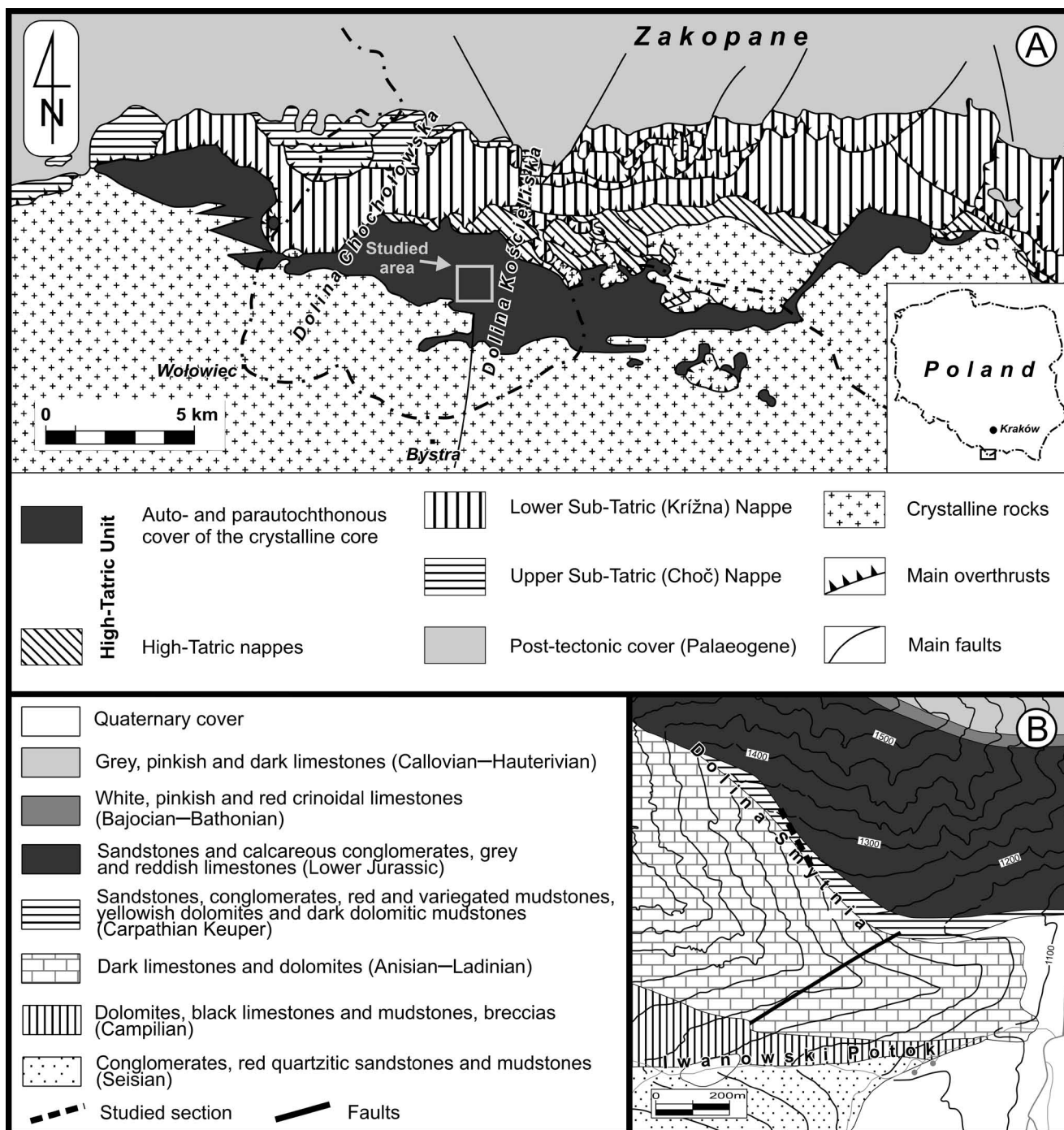
Fig. 1. Location of the studied section (after: Bac-Moszaszwili *et al.*, 1979; modified). **A.** Location of the Dolina Smytnia valley region in the tectonic-sketch map of the Tatra Mts **B.** Location of the studied section in the geological map of the Dolina Smytnia valley region

some mineralogical and petrographic as well as stratigraphical investigations have been carried out (Turnau-Morawska, 1953; Kotański, 1956b). Scarce occurrence of the discussed sediments was caused by the erosion after Old Cimmerian tectonic movements at the Triassic/Jurassic boundary (Kotański, 1956a, 1959a, 1961) and general high susceptibility of rocks to the weathering.

The main goal of this publication is an interpretation of sedimentary environment, and its controlling factors in the carbonate-dominated uppermost Ladinian–Norian succession from the Tatricum domain in the Tatra Mts. In addition,

further assessment of conditions during dolomitization and silicification of carbonates is presented.

GENERAL SETTING

The Tatra Mts are the highest and farthest north-located massif of the Central Western Carpathians. It comprises the Variscan crystalline core and strongly deformed Lower Triassic–mid Cretaceous rocks. Crystalline basement is covered by subsequent autochthonous (locally parautochtho-

nous; Dumont *et al.*, 1996) rocks and local overthrust of Czerwone Wierchy (lower) and Giewont (upper) nappes (Kotański, 1961, 1979b; Passendorfer, 1961). The above mentioned tectonic elements form the High-Tatric Unit which is covered by the lower (Krížna) and upper (Choč) Sub-Tatric nappes (Fig. 1A).

Sediments of the High-Tatric Unit were deposited in the Tatricum Basin (Andrusov *et al.*, 1973; Kotański, 1979b) that during the Triassic was confined to the northern part of the Carpathian segment of the Western Tethys and situated on the southern edge of the North-European Platform (Kozur, 1991; Michalík, 1993, 1994).

Occurrence of the Upper Triassic sediments of the High-Tatric Unit is limited to the autochthonus cover. The Carpathian Keuper succession is developed in two facies: siliciclastic and carbonate. Some sequences are developed in clastic facies, whereas in other sections the Carpathian Keuper is developed as a complex of dolostones (Turnau-Morawska, 1953; Kotański, 1956b, 1959a, c, 1979a; Wójcik, 1959), occasionally, as in the Dolina Smytnia valley, with several metre-thick intercalations of siliciclastics within dolostones (Fig. 2).

Keuper sediments are devoid of any index fossils. Therefore, it is difficult to establish their age precisely. Carbonate sediments from the Dolina Smytnia valley section are considered as equivalent to the Carpathian Keuper siliciclastics (Kotański, 1956b). Kotański (1956b) assigned carbonate-clastics and dolostones to the Carnian and Norian, respectively (Fig. 2).

Deposition of the Keuper sediments was preceded by emergence of the Middle Triassic restricted carbonate ramp, developed in dry and hot climate conditions (Jaglarz & Szulc, 2003). Emergence of the carbonate ramp was accompanied by erosion and palaeosol formation (Jaglarz & Rychliński, 2005; Jaglarz, 2007). Jaglarz (2007) proved that palaeosols (see below) from the base of the Dolina Smytnia valley sequence may be of the latest Ladinian or the earliest Carnian age (Fig. 2).

Sediments of various ages overlie the Keuper deposits. In the Czerwone Żlebki area, red bed siliciclastics are replaced by continental sediments of the Tomanová Formation (upper Norian–Rhaetian) consisting of plant-bearing dark mudstones and quartzitic sandstones (Raciborski, 1891; Kotański, 1959a, c; Michalík *et al.*, 1976, 1988; Fijałkowska & Uchman, 1993). In the Dolina Chochołowska area, the Rhaetian neritic sediments, composed of black mudstones and organodetritic limestones with *Rhaetina gregaria*, rests on siliciclastics (southern slope of Bobrowiec Mt) or dolostones and clastics (Przełęcz w Kulawcu pass) of the Keuper (Kotański, 1959c, 1979a; Radwański, 1968). Lower Jurassic marine sediments rest on the erosively truncated Norian dolostones in the Dolina Smytnia area (Kotański, 1956b; Radwański, 1959).

MATERIALS AND METHODS

Investigations encompass the uppermost Ladinian–Norian succession of the High-Tatric Unit from the Dolina Smytnia valley in the Western Tatra Mts (Fig. 1). Detailed sedimentological field studies were supplemented by microfacies observations. The respective values of $\delta^{13}C$ and $\delta^{18}O$ were determined using measurements made with mass spectrometer SUMY, at the Institute of Geological Sciences, Academy of Sciences of Belarus at Minsk. The samples were treated with 100% orthophosphoric acid. Carbon dioxide was then collected in a trap with liquid nitrogen and purified in vacuum. Measurement error was ±0.2‰. Stable isotope ratios in carbonate samples are presented in this paper in reference to the PDB standard.

Main elements were analyzed with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-ES) method. For this purpose, selected rock samples (0.2 g in weight) were mixed with $LiBO_2$ and heated. The mixture was then cooled down and dissolved in HNO_3 (5%). Composition of the solution was analyzed with ICP-ES spectrometer. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used for strontium analyses. Preparation of samples were analogous to the ICP-ES method. Subsequently, compositions of solutions were analyzed by mass spectrometer. Analyses of main and trace elements were carried out at the Acme Analytical Laboratories Ltd. (Vancouver, Canada).

For total organic carbon (TOC) content, 10 g rock samples were analysed with the Leco method. Organic carbon content is the difference between total carbon and graphite contents. Total carbon content was measured with the Leco method and graphite content was established by roasting the samples at a temperature of 600 °C and washing them out with hydrochloric acid (HCl). Analyses were carried out at the Acme Analytical Laboratories Ltd. (Vancouver, Canada). One sample of black mudstone was analysed by the Rock Eval method at the Petroleum Geochemistry Laboratory, University of Science and Technology (Kraków, Poland).

A sample of about 100 g was subject to organic geochemical analyses. It underwent 24 h extraction using Soxhlet's apparatus with dichloromethane (DCM) and methanol (7.5:1, v/v). The solvents were then evaporated from the extracts to dryness with a rotary, vacuum evaporator. Organic compounds were initially fractioned according to a procedure described by Rospondek *et al.* (1994). The residues were dissolved in a small volume of dichloromethane (DCM). The DCM was then evaporated and the extract was weig- hed, and then fractionated by adsorptive chromatography column (Bochwic, 1975). The column (80×5 mm) was packed with Al_2O_3 (activated for 2 h at 130 °C) and washed with *n*-hexane before use. The mixture was introduced to the column, after drying on a small quantity of Al_2O_3. The extract was separated into two fractions: aliphatic (satura- ted) hydrocarbons eluting with *n*-hexane, and aromatic hydrocarbons eluting with *n*-hexane/DCM (9:1, v/v). After solvents removal, the fractions were weighed.

Composition of aliphatic and aromatic hydrocarbon fractions was analysed by the Gas Chromatography-Mas Spectroscopy (GC-MS) method. The GC-MS analysis was carried out on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 Network with mass selective detector (MSD) in the Department of Geochemistry, Mineralogy and Petrography, University of Silesia (Sosnowiec, Poland) according to a procedure presented by Rospondek *et al.* (2009).
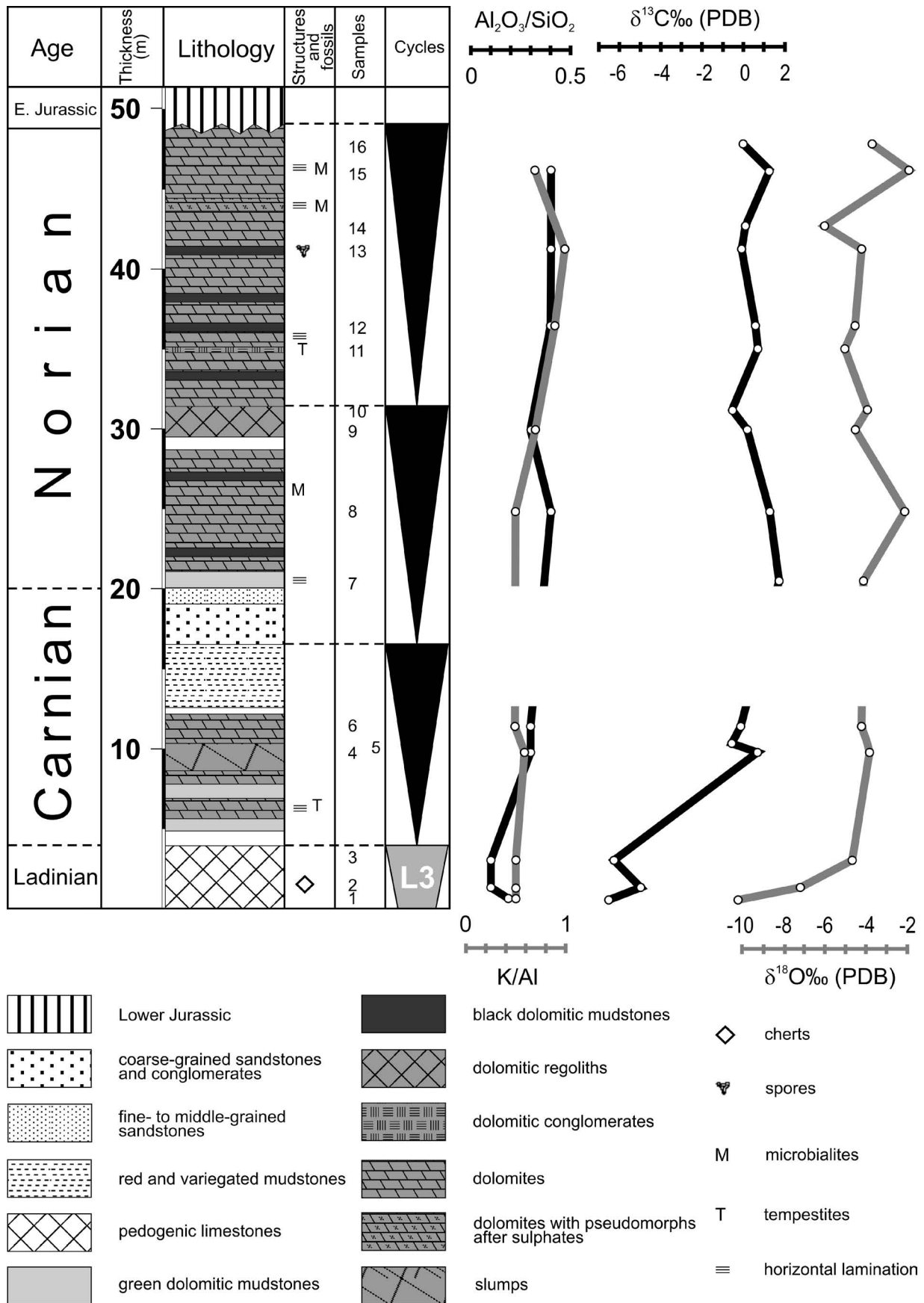
Fig. 2. Uppermost Ladinian–Norian sequence from the Dolina Smytnia valley. Tectonically-controlled shallowing-upward cycles (dark triangles) and selected chemical indicators. Chronostratigraphy after Kotański (1956b), modified by Jaglarz (2007). L3 – 3rd order depositional sequence at the top of Ladinian succession

DOLINA SMYTNIA VALLEY SECTION

The Dolina Smytnia valley section was mentioned by Zejszner (1852) and Uhlig (1897) who considered it as "lower Triassic". Later it was investigated by Turnau-Morawska (1953) and Kotański (1956b, 1959b).

The discussed section is located in the eastern part of the Kominiarski Wierch massif, at 1250–1300 m above sea level (Fig. 1B). The section is reversed and inclined to the south-west (angle of inclination is about 65°). The investigated sequence is about 50 m thick (Fig. 2).

Limestones with cherts (4 m thick), forming the top of the Ladinian sequence, occur in the lower part of the succession, and deposits dominated by alternated dolostones and dolomitic mudstones, in the upper part of the sequence. Conglomerate, sandstones and variegated mudstones of few meter-thick occur in the middle part of dolostone-mudstones complex. The top of the Upper Triassic sequence is eroded and covered by Lower Jurassic sediments (Radwański, 1959; Łuczyński, 2001).

RESULTS
LITHOFACIES

The lithofacies described below can be grouped into several facies associations. Dolostones, green and black dolomitic mudstones and dolomitic regoliths are considered as a salt marsh facies. Limestones with cherts are classified as pedogenic facies, linked with long-term exposure of the Middle Triassic carbonate platform. Pure siliciclastic deposits in turn, represent continental red bed type sediments.

Dolostones

Dark to light-grey dolostones are generally well bedded. Bed thicknesses are from 8 to 70 cm. Only dolostones from the lower part of the seqence are faintly bedded. The dolostones are often laminated; dark laminae are alternated with light laminae containing dispersed dolomite crystals. Laminae are often plastically deformed (Fig. 3A, B). Micrites and microsparites dominate among dolo- stones (Fig. 3D). Fenestral structures are distinctive for dolostones from the upper part of the succession (Fig. 3C).

Grain-supported dolomitic conglomerate (few dozen of centimetres thick) with well-rounded clasts (2 to 10 mm in diameter) and erosive basic surface occur in the dolostone succession (Fig. 4C). Horizons of breccias were also found (Fig. 5).

Dolostones are alternated with green or black mudstones (Fig. 4A). The thickness of dolostone beds is greater than mudstone beds, and boundaries between them are usually sharp.

Interpretation

Laminated dolostones are interpreted as stromatolites. Dispersed dolomite crystals are considered as fine pseudomorphs after sulfates (Fig. 3A–B). Some laminae deformations in the described rocks are considered as enterolithic-like structures (Fig. 3A). Formation of such structures resulted from recurrent hydratation and dehydratation of Ca-sulfates in the process of alternate capillary rise and fall of brines (cf. Álvaro *et al.*, 2000; Schreiber & El Tabakh, 2000).

Dolostones with fenestral structures are recognized as thrombolites. Fenestral structures are a result of drying or decaying microbialites (Shinn, 1968). Decay of microbialites is more probable because of chaotic arrangement and irregular shape of fenestra, although their shape modification by evaporites cannot be excluded.

Dolomitic conglomerates with erosive bottom surface, identified in the upper part of the sequence (Fig. 4C), are a result of redeposition of eroded sediments during high-energy event. Most of intraclasts were probably derived from desiccated sediments during an episode of emersion (cf. Platt, 1989; Muir *et al.*, 1980).

Dolostones were presumably deposited in a periodically emerged shallow-marine environment. It was probably a kind of backshore marsh. Pseudomorphs after sulfates, absence of fauna and bioturbational structures indicate an intensive evaporation and increased salinity.

Green and black dolomitic mudstones

Laminated dolomitic mudstones are green and black (Fig. 4B). They are composed of siliciclastics dominated by quartz and dolomitic matrix. Green dolomitic mudstones are up to 3 cm thick, and black dolomitic mudstones are up to 20 cm thick. Black dolomitic mudstones occur in the upper part of the sequence (Fig. 2). Opaque phytoclasts and sporomorphs were distinguished among palynological components of black dolomitic mudstones (Annette Götz, pers. commun., 2006).
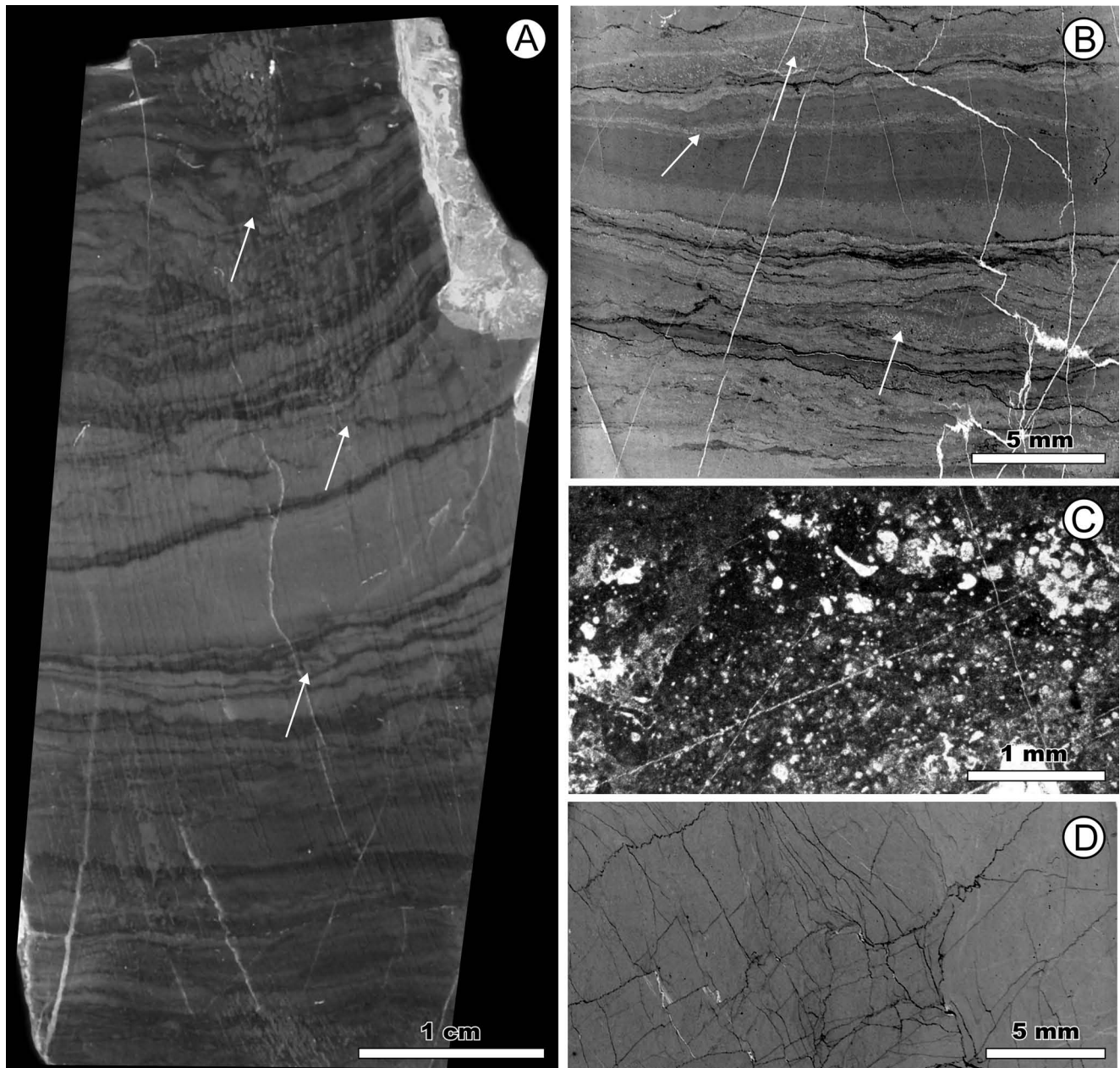
Interpretation

Green and black dolomitic mudstones alternating dolostone beds (Fig. 4A) are connected with periodic input of terrestrial clastics. Green colour of mudstones dominating in the lower part of the sequence suggests reductive conditions in the sedimentary environment (McBride, 1974). This, in turn, is an indicator of frequent flooding or high level of groundwater (Turner, 1980; Aigner & Bachmann, 1989). Black colour of mudstones from the upper part of the sequence indicates the presence of non-decomposed organic matter deposited in subaqueous environment (McBride, 1974). Dolomitic mudstones are probably the effect of sedimentation by distal sheet floods caused by sporadic, intensive rainfalls. However, aeolian deposition of siliciclastic components of dolomitic mudstones cannot be excluded (cf. Aigner & Bachmann, 1989; Reinhardt & Ricken, 2000).

Dolomitic regoliths

Dolomitic regoliths (about 2 m thick) rest on the rough surface of the host dolostones. They consist of yellow claystones (several to 20 mm thick) alternating with beds, lenses and rounded clasts of dolostones (Fig. 6).

Interpretation

Dolostones with flasers of yellow dolomitic claystones are interpreted as regoliths, and rest on karstified surface of the host dolostones (Fig. 6). They comprise clay minerals enriched in oxidized ferric compounds, which represent kars- tic residuum after dissolved carbonates. Dolomitic

Fig. 3. Dolostones. **A.** Laminated dololutite, dark laminae are microbial in origin. Sediment deformations in the upper part (arrows) interpreted as enterolithic-like structure. **B.** Details of A. Dark laminae microbial in origin, light laminae including dolomite crystals interpreted as pseudomorphs after evaporites (arrows); thin section. **C.** Thrombolites with fenestral structures, which were caused by decay of microbialites; thin section. **D.** Dololutite with stylolites; thin section

clasts within clayey-carbonate matrix display rounded edges, what is a proof of their partial dissolution during initial pedogenic processes (Wright & Wilson, 1987). Dolomitic regoliths were formed as the result of subaerial exposure and karstification of dolostones.

Limestones with cherts

Limestones with cherts include grey and grey-yellow sandy limestones and sandy dolomitic limestones. Limestones with cherts are composed of rounded clasts and nodules of limestones, sandy limestones and dolomitic sandy limestones and matrix consisting of carbonate micrites or microsparites. Carbonate nodules display blurred boundary with matrix (Fig. 7A, B). Mono- and polycrystalline quartz grains (up to about 30%) are dispersed in the matrix (Fig. 7C, E). Quartz grains are rounded. Chalcedony cherts and crystalline forms of ferric oxides and hydroxides commonly occur (Fig. 7A, D). Limestones with cherts are bioturbated (Fig. 7D, E). Bioturbational structures (rhizoids) are often filled with sparry calcite, cherts or with matrix sediment (Fig. 7E).

Interpretation

Limestones with cherts are interpreted as palaeosol. Limestone and dolomitic clasts represent fragments of host rocks, which repeatedly underwent weathering and pedoge-
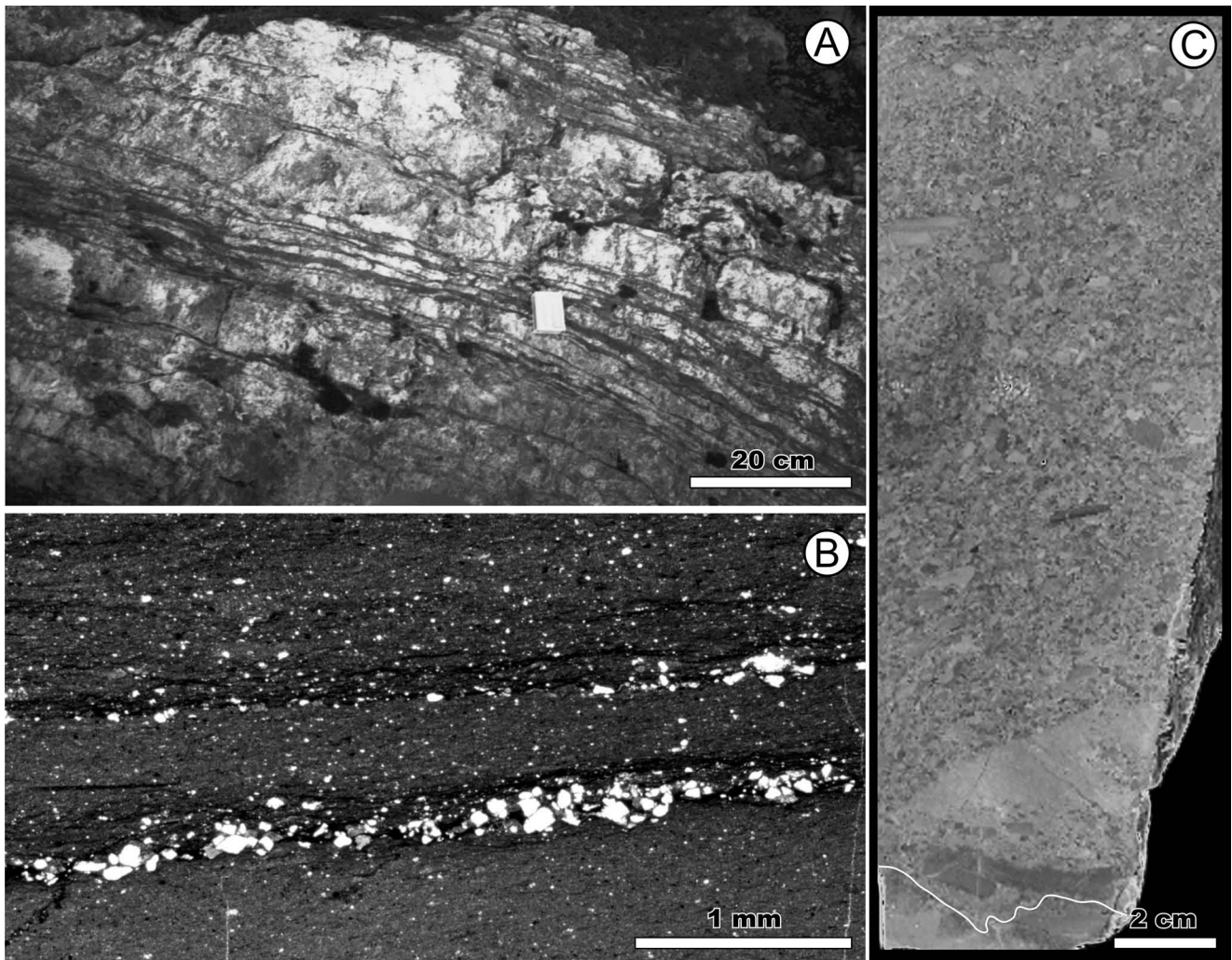
Fig. 4. Dolostone-dolomitic mudstone complex. **A.** Dolostones alternated with black dolomitic mudstones. **B.** Laminated dolomitic mudstone. Light laminae enriched with quartz grains; thin section. **C.** Dolomitic conglomerates. Erosive surface marked by white line
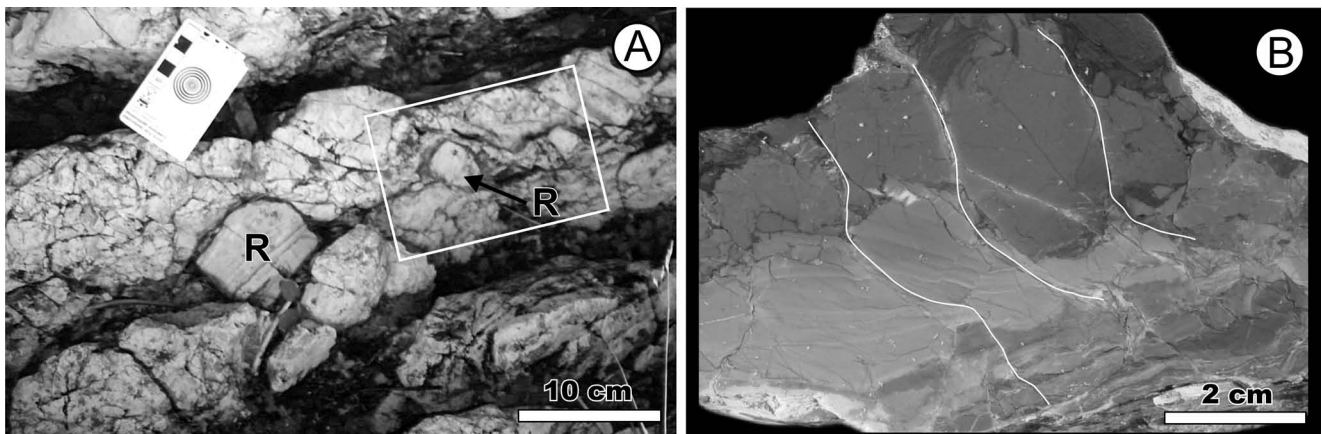
Fig. 5. Seismically-generated structures. **A.** Seismically-generated slump breccia in dolostone and dolomitic mudstone complex. Rotated blocks (R). White rectangle shown in Fig. 5B. **B.** Slab of seismic-generated breccia marked with white rectangle in Fig. 5A. Shear surfaces are marked with white lines

nesis (Fig. 7B). Roundness of carbonate clasts is interpreted as their partial dissolution in vadose zone (Wright & Wilson, 1987). Similarly, lime nodules are recognized as the effect of dissolution and re-precipitation of calcium carbonate

(Fig. 7A, B). Matrix-supported framework clasts and grains are the effect of pedoturbation (Fig. 7B, E). Bioturbations were caused by the root activity. Rhizoids are the most significant features indicating pedogenic origin of the dis-
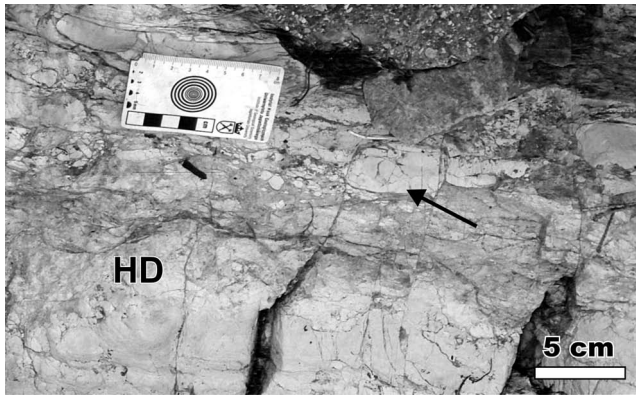
Fig. 6. Dolomitic regoliths. Karstified host dolostones (HD). Dolomitic clasts within clayey-carbonate matrix display rounded edges (arrow)

cussed deposits (Fig. 7D, E). Limestones with cherts were formed by pedogenic processes during long-term exposure of carbonate substrate.

Conglomerates, sandstones and variegated mudstones

Grain-supported quartz conglomerates (grains several millimetres across) and coarse-grained sandstones are light-grey or pinkish. Grains are well-rounded and their sorting is poor to medium. Matrix is siliceous or clayey. Fine-grained red sandstones are quartzitic wackes and arenites with siliceous-clayey-ferrigenous matrix. Variegated mudstones are quartzitic mudstones and very fine-grained wackes with clayey-siliceous-ferrigenous matrix.
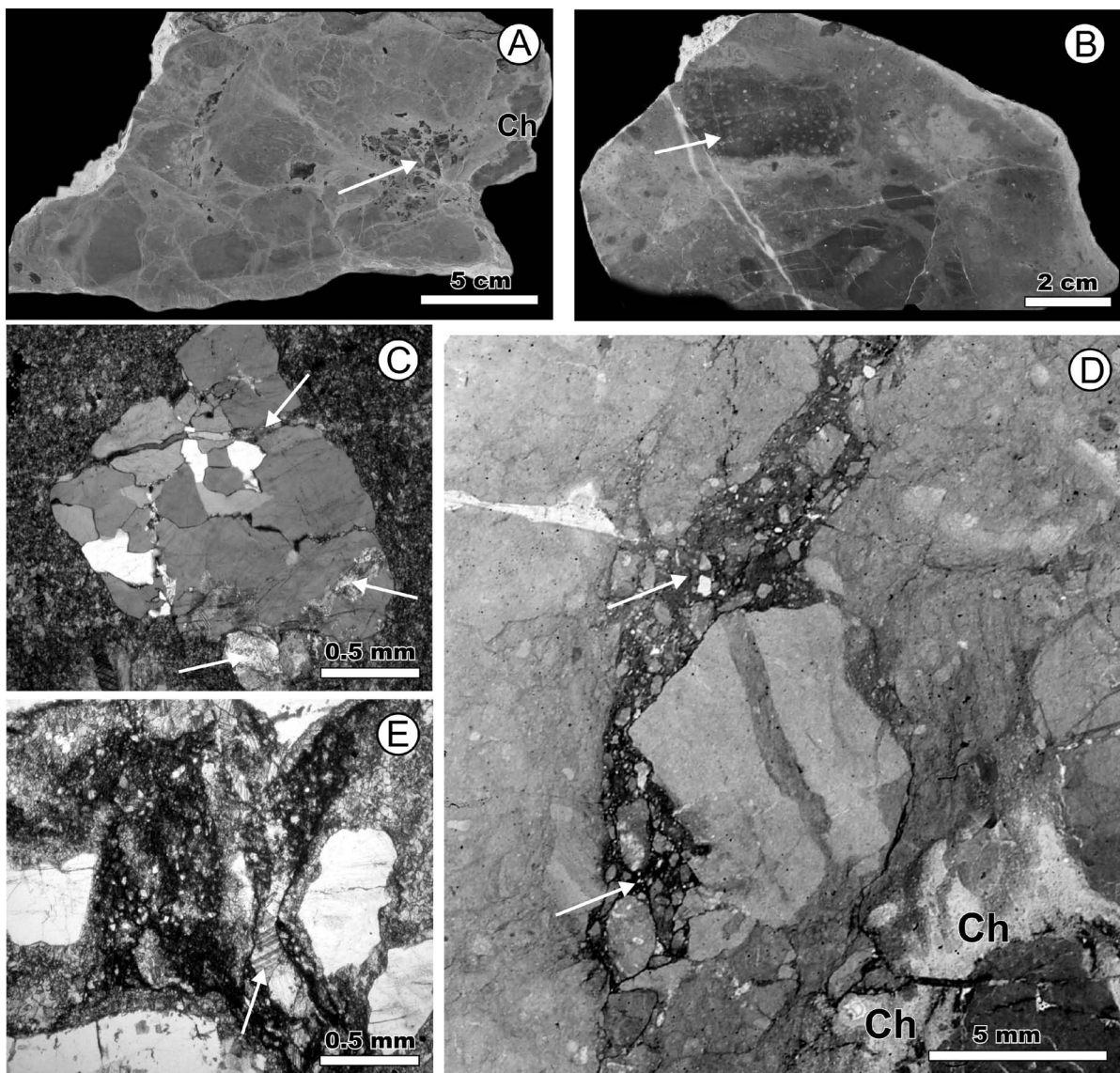
Fig. 7. Pedogenic limestones with cherts. **A.** Nodular pedogenic limestone with reddish cherts (Ch). Cherts are locally crushed (arrow). **B.** Nodular pedogenic sandy limestone. The parts of clasts have faint limits with matrix (arrow). Matrix-supported clasts interpreted as the result of root penetration. **C.** Corrosion traces – polycrystalline quartz grain replaced by carbonates (arrows; thin section, x nicols). **D.** Biodeformed pedogenic limestone with cherts (Ch). Rhizoid filled with the surrounding sediments (arrows); thin section. **E.** Biodeformed pedogenic limestone. Light grains (quartz) are dispersed in the result of the activity of roots. Bioturbation structures filled with sparite calcite cements (arrow); thin section

Concentration of selected elements and value of geochemical indicators in the Dolina Smytnia valley sequence

Samples	SiO_2 (%)	MgO (%)	Si (%)	Al (%)	K (%)	Ti (ppm)	Sr (ppm)	Al_2O_3/SiO_2	K/Al	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18}O_{PDB}$ (‰)	TOC (%)
1(W)	3.50	8.43	1.64	0.37	0.17	180	426	0.20	0.47	-6.5	-10.1	0.03
2(W)	6.54	2.78	3.06	0.31	0.15	180	641	0.09	0.49	-5.0	-7.1	0.03
3(W)	15.07	4.51	7.05	0.78	0.42	420	357	0.10	0.54	-6.2	-4.7	0.03
4(D)	5.21	19.65	2.44	0.95	0.56	480	71	0.34	0.60	0.7	-3.8	0.03
5(D)	-	-	-	-	-	-	-	-	-	-0.6	-3.9	-
6(D)	2.87	20.22	1.34	0.51	0.27	240	92	0.33	0.54	-0.1	-4.2	0.04
7(GM)	-	-	-	-	-	-	-	-	-	1.8	-4.1	-
8(D)	1.82	20.70	0.85	0.42	0.22	180	106	0.43	0.54	1.3	-2.1	0.03
9(R)	5.57	19.26	2.60	1.03	0.72	420	134	0.35	0.70	0.2	-4.5	0.03
10(R)	-	-	-	-	-	-	-	-	-	-0.6	-3.9	-
11(D)	-	-	-	-	-	-	-	-	-	0.7	-5.0	-
12(BM)	26.38	12.83	12.33	5.22	4.48	2578	76	0.37	0.86	0.6	-4.5	0.33
13(BM)	18.36	13.45	8.64	3.60	3.43	2000	92	0.37	0.95	-0.1	-4.2	2.92
14(D)	-	-	-	-	-	-	-	-	-	0.1	-6.0	-
15(D)	1.84	19.92	0.86	0.39	0.28	180	143	0.40	0.72	1.3	-1.9	0.04
16(D)	-	-	-	-	-	-	-	-	-	0.0	-3.7	-

Limestones with cherts (W), dolostones (D), green dolomitic mudstones (GM), dolomitic regoliths (R), black dolomitic mudstones (BM)

Interpretation

Pure siliciclastics are interpreted as the ephemeral fluvial red bed-type facies (see Jaglarz, 2007). Coarse-grained siliciclastics are interpreted as fluvial channel deposits. Fine-grained red arenites, wackes and variegated mudstones can be considered as overbank deposits. Arenites and wackes probably represent crevasses whereas variegated mudstones flood plains.

GEOCHEMICAL DATA

Magnesium oxide (MgO) content in dolostones ranges from 19.7 to 20.7 wt.%. For regoliths and limestones with cherts the content is 19.3% and 2.8 to 8.4 wt.% of MgO, respectively. The contents of SiO_2 in dolostones, dolomitic mudstones, dolomitic regoliths and limestones with cherts, are 1.8 to 5.2%, 18.4 to 26.4%, 5.6 and 3.5 to 15.1 wt.%, respectively (Table 1). Average content of Sr in dolostones is 103±30 ppm and varies between 71 and 143 ppm.

The values of $\delta^{13}C$ and $\delta^{18}O$ for dolostones fall in the range of –0.6 to 1.3‰ (average 0.4±0.7‰) and –6.0 to –1.9‰ (average –3.8±1.4‰), respectively. $\delta^{13}C$ in black and green dolomitic mudstones are –0.1 to 0.6‰ and 1.8‰ respectively, $\delta^{18}O$ were defined on –4.5 to –4.2‰ and –4.1‰, respectively. The $\delta^{13}C$ and $\delta^{18}O$ of dolomitic regoliths are –0.6 to 0.2‰ and –4.5 to –3.9‰, respectively. Finally, $\delta^{13}C$ and $\delta^{18}O$ limestone with cherts are –6.5 to –5.0‰ (average –5.9±0.8‰) and –10.1 do –4.7‰ (average –7.3±2.7‰), respectively (Table 1).

TOC content in dolostones, dolomitic regoliths and limestones with cherts does not exceed 0.04 wt.%, but reaches 2.92 wt.% in black dolomitic mudstones (Table 1).

Elementary sulphur is the main component of apolar (saturated) fraction of organic substance in black dolomitic mudstones. Aliphatic hydrocarbons were also identified with chain length ranging from C_{18} to C_{30}, with maximum of n-C_{25}. Phytane, pristane and nor-pristane are also present in significant amounts (Fig. 8). Phenantren and methylophenantren predominated in the aromatic hydrocarbon fraction.

DISCUSSION

STABLE ISOTOPE SIGNALS

The presence of fresh-water during deposition of the discussed sediments is considered as the main reason of $\delta^{13}C$ decreases, because fresh-water is enriched in light carbon isotopes of organic origin (Scholle *et al.*, 1992; Peryt & Scholle, 1996; Chafetz & Zhang, 1998).

Influence of temperature and evaporation is very low in the case of carbon stable isotope fractionation (Moore & Druckman, 1981; Tucker & Wright, 1990, p. 384). Therefore, $\delta^{13}C$ is much better indicator of marine *versus* meteoric water contribution than $\delta^{18}O$ in the sedimentary environment (Szulc, 2000). Enrichment of deposits in heavy stable isotope of oxygen is the effect of evaporation, whereas enrichment in light isotope is the result of fresh-water influence or increase of fluids temperature (*cf.* Hudson, 1977; Peryt & Magaritz, 1990; Lintnerová & Hladíková, 1992).

Pedogenic limestones show negative values of $\delta^{13}C$ (Table 1; Fig. 2). Negative $\delta^{13}C$ values are caused by fresh water enriched in isotopically-light, soil-derived CO_2 (*cf.* Platt, 1989; Aziz *et al.*, 2003). Probably, the upper part of
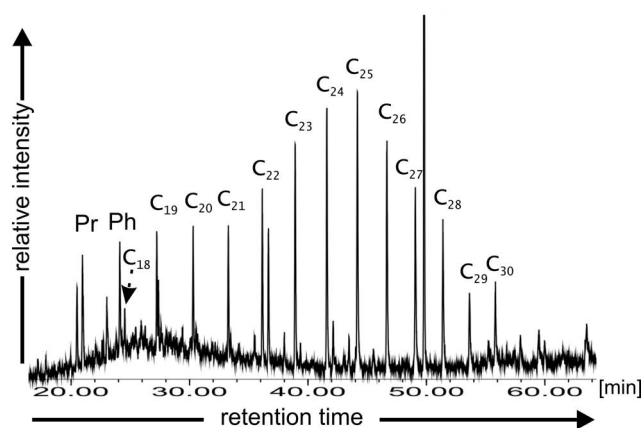
Fig. 8. Gas chromatogram of the aliphatic hydrocarbon fraction. Organic matter from black dolomitic mudstones. C_{18}–C_{30}: alkanes; pristane (Pr), phytane (Ph)

pedogenic limestones is enriched in heavy oxygen isotope as a result of intensive evaporation in the top of soil profile (Liu *et al.*, 1996). Divergence of $\delta^{13}C$ and $\delta^{18}O$ curves in the top of dolomitic regoliths can be similarly interpreted (Fig. 2).

Values of $\delta^{13}C$ in dolostones and dolomitic mudstones vary between –0.6 to 1.8‰ (Fig. 2). The $\delta^{13}C$ value of marine water amounts to over 0‰ (see Hoefs, 1997, p. 156; Tucker & Wright, 1990, p. 384), but in Upper Triassic rocks it was between 1.5 to 3.5‰ (Korte *et al.*, 2005). Thus, the discussed dolostones seem to be enriched in light carbon isotopes. Dolomitization causes insignificant modifications in original composition of stable carbon isotopes (cf. Tucker & Wright, 1990, p. 384). Based on that, it can be stated that dolostones enrichment in light stable carbon isotope reflects the influence of fresh-water during deposition of host sediments. It seems that original composition of stable carbon isotope was preserved. Late diagenetic processes (*e.g.*, recrystalization, calcification) would probably result in more homogeneous isotopic value in dolostones.

EARLY DIAGENESIS

Dolomitization

Early diagenetic dolomitization is indicated by the preservation of original sedimentary structures (*e.g.*, lamination, bedding), fine grains, high concentration of siliciclastics, the presence of pseudomorphs after sulfates and the absence of fauna in dolostones (Sarin, 1962; Veizer, 1970; Peryt & Scholle, 1996). All the above features, slump breccias, conglomerates and regoliths containing dolostone clasts suggest that the investigated dolostones are early-diagenetic.

Generally, among early diagenetic dolostones products of hypersaline or mixed-water can be distinguished (Folk & Land, 1975; Hardie, 1987). Hypersaline dolostones contain higher concentration of strontium (Sr) than those formed in mixed zone (Tucker & Wright, 1990, p. 380). In general, concentration of Sr in the discussed dolostones (Table 1) is lower than Sr content in early diagenetic dolostones of hypersaline environments (100–600 ppm according to Veizer

& Demovič, 1974). Moreover, the discussed dolostones contain much less of Sr than dolostones of comparable age from other parts of the Central Carpathians (145–1010 ppm; Al-Juboury & Durovič, 1996).

Dolomitization modifies the stable oxygen isotope composition. It depends on the temperature of precipitation and isotopic composition of dolomitizing solutions (Tucker & Wright, 1990, p. 384). Enrichment of sediments in heavy oxygen isotope reflects intensive evaporation whereas enrichment in light oxygen isotope is the result of the influence of meteoric waters during dolomitization (Ward & Halley, 1985; Peryt & Magaritz, 1990; Spötl & Burns, 1991). Broad range of $\delta^{18}O$ indicates that dolostones were formed under the influence of both meteoric and marine waters (Table 1; Fig. 2). Sedimentary features, concentration of Sr, and $\delta^{18}O$ indicate that the discussed dolostones were formed during early diagenesis in hypersaline environment with periodic influx of fresh-water. Salt marshes are a very probable environment of dolomitization.

Silicification

Chalcedony cherts occur only within pedogenic limestones. Corrosion of detrital quartz grains suggests that silica originated from dissolution of those grains (Fig. 7C), although clay minerals could also be the source of silica. Dissolution of silica occurs in strongly alkaline environment (pH>9; Friedman & Shukla, 1980; Sonnenfeld, 1992). This phenomena is common in calcrete (*e.g.*, Summerfield, 1983). Currently, chalcedony replaces carbonate matrix (Fig. 7A, D). Silica precipitation probably occurred when pH of the environment decreased by weathering and oxidation of ferrous sulfides (*cf.* Chafetz & Zhang, 1998). It is confirmed by the occurrence of ferric oxides and hydroxides in the discussed deposits. Ferrous sulfides were probably formed as a result of reduction of sulfates in contact with organic carbon compounds (*cf.* Palmer, 1995). Presence of organic carbon in the studied pedogenic limestones is indirectly confirmed by low $\delta^{13}C$ value (Table 1; Fig. 2).

SYNSEDIMENTARY TECTONICS

Seismically-generated structures

Seismic shocks in carbonates, which are distinguished by the progressive lithification, are recorded by the tiering of deformations (Szulc, 1993). The earlier, lithified sediments underwent brittle deformations (*e.g.*, synsedimentary faults) whereas the younger ones underwent plastic deformations or homogenization. Intra-formation breccias, interpreted as slump breccias occur within dolostones. In mentioned breccias, plastic material was alocated along shear while blocks of earlier lithified sediment were rotated (Fig. 5).

Tectonically-controlled cycles and facies-diversity

Three shallowing upward cycles were distinguished in the Dolina Smytnia valley sequence (Jaglarz, 2007). The top of pedogenic limestones forming the uppermost part of the Ladinian depositional L3 sequence makes the boundary of the first cycle (Fig. 2). The first cycle is composed of al-
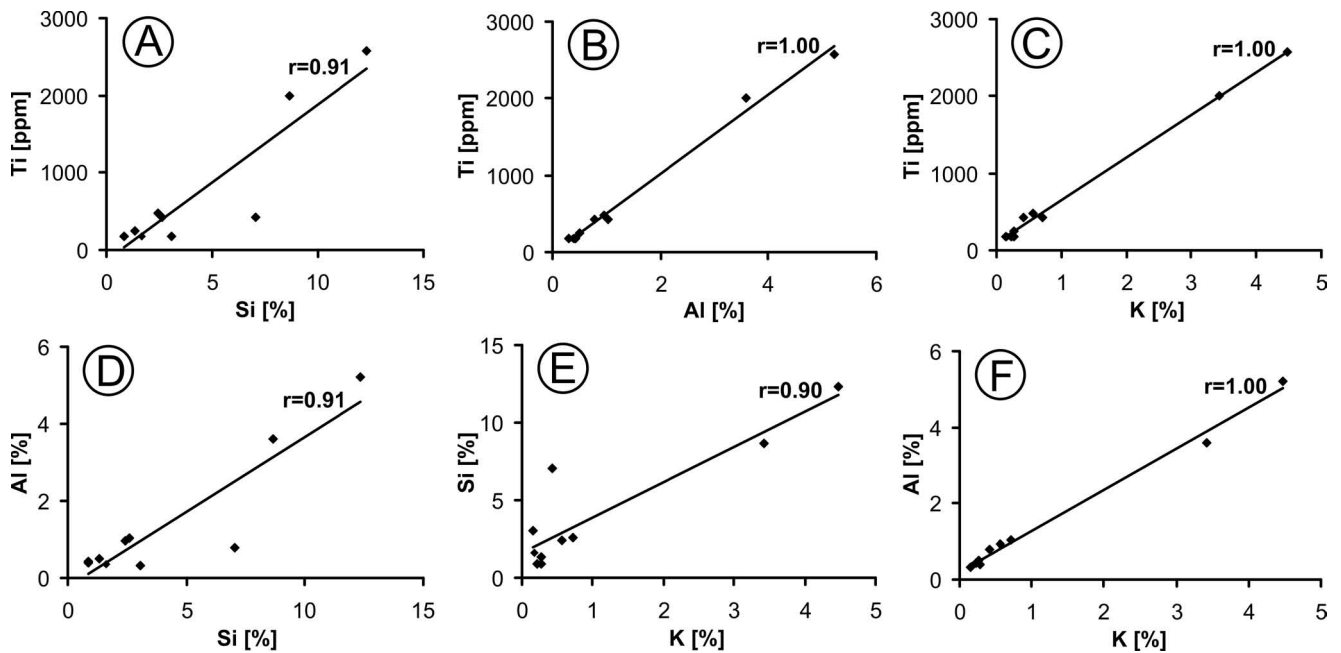
Fig. 9. Correlative graphs of concentration of selected main elements in the Dolina Smytnia valley sequence. High correlation coefficients indicate continental origin of siliciclastic components. **A.** Ti *versus* Si. **B.** Ti *versus* Al. **C.** Ti *versus* K. **D.** Al *versus* Si. **E.** Si *versus* K. **F.** Al *versus* K

ternating dolostones and green dolomitic mudstones passing upward into faintly bedded dolostones. Seismically-induced slumps were recognized within this complex (Fig. 5). Variegated mudstones form the uppermost part of the cycle. The thickness of the first cycle is 12 m. Eroded top of the variegated mudstones makes the boundary of the second cycle. Fine- grained conglomerates, coarse-grained and red fine-grained sandstones begin the second cycle. Siliciclastics pass upward to alternating dolostones and black dolomitic mudstones. The top of the dolomitic complex is karstified forming dolomitic regoliths. The second cycle is 15 m thick. The top of dolomitic regoliths makes the boundary of the third cycle. Alternating dolostones and black dolomitic mudstones form the third cycle, which is 17 m thick. The Upper Triassic deposits are eroded and covered by the Lower Jurassic sediments (Fig. 2; Kotański, 1956b).

Both abrupt facies changes and seismically-generated slumps indicate that sedimentary environment in the Tatricum Basin in the latest Ladinian–Norian time was controlled by block tectonic movements. It corresponds to tectonic movements of the Labinian phase (Kotański, 1956b, 1961). Horsts were eroded or exposed to pedogenic processes while in troughs red bed or salt-marsh sediments were deposited. Rise of tectonic blocks was caused by disintegration of the southern edge of the North-European Platform due to existence of mega-shear faults zone in the Penninic Rift (Michalík, 1993, 1994).

PRODUCTIVITY AND SOURCE OF ORGANIC MATTER

Both low TOC concentration (below 0.04 wt.%) and absence of a skeletal fauna in carbonates suggest low productivity in the basin. Only black dolomitic mudstones do

have higher concentration of TOC (to 3 wt.%; Table 1). Palyno- logical material suggests terrestrial origin of organic matter (Annette Götz, pers. commun., 2006).

The content of elementary sulphur suggests the presence of original sedimentary pyrite. Absence of short-chain alkanes can be an effect of the biodegradation of organic matter (Marynowski *et al.*, 2001). Domination of long-chain alkanes with uneven number of C atoms indicates that they were probably derived from land plants (Tissot & Welte 1984; Meyers, 1997; Marynowski *et al.*, 2001). This feature points to the terrestrial origin of organic matter. Moreover, pristane *versus* phytane ratio, about 1, supports this conclusion (Fig. 8; Waleńczak, 1987). The exclusive presence of aromatic hydrocarbons like phenanthrene and methylophenanthrene and absence of steranes and hopanes are an indicators of high thermal maturity of the organic matter. It is additionally confirmed by strong thermal degradation of palynological material (Annette Götz, pers. commun., 2006).

CLIMATE CONDITIONS

Geochemical indicators based on the ratio of main elements in siliciclastic components of carbonate rocks inform about palaeoclimate changes. Titanium (Ti) in sedimentary rocks is exclusively terrigenous. Therefore, correlation coefficients of Ti against silica (Si), aluminium (Al) and potassium (K) amounting from 0.91 to 1.00 as well as between Si, Al and K amounting from 0.90 to 1.00 (Fig. 9) indicate continental origin of siliciclastic components.

Al_2O_3/SiO_2 ratio informs about concentration levels of quartz *versus* clay minerals. When the value of this parameter is below 0.1 it indicates quartz-dominated siliciclastic components, whereas the value over 0.3 marks domination

of clay minerals (Lintnerová *et al.*, 1988). In the case of dolostones, dolomitic mudstones and dolomitic regoliths, Al_2O_3/SiO_2 is >0.3. The value of discussed indicator in pedogenic limestones does not exceed 0.2 what suggests more intensive contribution of siliciclastics (Fig. 2).

Potassium and aluminium occur in clay minerals structure. Illite, clay mineral of Si and K, is formed in hot and dry climate with physical-dominated weathering (*cf.* Leeder, 1985; Chamley, 1989). On the other hand, kaolinite (clay mineral of Al and Si) is considered as a mineral formed during pluvialization in hot and humid climate conditions (*cf.* Keller, 1970; Chamley *et al.*, 1997; Środoń, 1999). Therefore, fluctuation of K/Al ratio reflects changes of climate humidity. K/Al indicator is higher, when the climate is drier (Reinhardt & Ricken, 2000). K/Al indicator for pedogenic limestones is higher by about 0.2 if compared with the Middle Triassic carbonates (see Jaglarz, 2007). It indicates a climate pluvialization during the latest Ladinian and early Carnian time. The increased value of K/Al indicator in the upper part of the Dolina Smytnia sequence suggests climate arididity.

Long-lasting climate changes were masked by the short-term climate fluctuations. Particularly high were differences of K/Al value for dolostones and dolomitic mudstones (Table 1). Alternation of dolomitic mudstones and dolostones was caused by periodic fluctuations of climate humidity under hot and semi-arid climate conditions. Dolostones were formed during periods of more intensive chemical weathering, whereas terrigenous sediments were deposited during relatively dry periods. Relationship of dolomitic mudstones with dry periods can suggest aeolian origin of their terrigenous components.

The Middle Triassic carbonate platform was emerged in the late Ladinian what brought significant changes in facies development. Development of carbonate palaeosols containing quartz-dominated siliciclastics and intensive chemical weathering suggest climate pluvialization at the Ladinian/Carnian boundary. Climate pluvialization (Partnach event) was caused by the volcanic activity noted in the Alpine-Carpathian domain during the late Ladinian time (*cf.* Szulc, 2000). Volcanic activity can be also confirmed by the existence of tuffites in the top of underlying sediments (see Gaździcki & Lefeld, 1997).

The beginning of pure siliciclastic sedimentation of the Carpathian Keuper should be linked with climate pluvialization period (Reingraben, Raibl or Lunz events) during early Carnian times. The Alpine-Carpathian area was covered by siliciclastic sediments at that time (see Lein, 1987; Kovács, 1984; Sauer *et al.*, 1992; Haas *et al.*, 1995; Rüffer & Bechstädt, 1998). After this period, the aridity of climate followed. Geochemical parameters indicate the return of physical weathering, which resulted in detrital components of carbonates. They are dominated by illite which is an indicator of arid climate conditions. Michalík (1993) and Haas *et al.* (1995) also postulated the climate aridization in late Carnian–Norian time. Arid climate conditions resulted in significant reduction of siliciclastic deposition in the southern parts of the Alpine-Carpathian region (see Kozur & Mock, 1997; Feist-Burkhardt *et al.*, 2008; Rychliński, 2008).

CONCLUSIONS

1. Sedimentation of the uppermost Ladinian–Norian deposits from the Dolina Smytnia valley was controlled by two basic factors: block tectonic movements and climate changes. Facies diversity of the Carpathian Keuper sediments resulted from synsedimentary block tectonic movements.

2. Pedogenic limestones (silicified during relatively early diagenesis) were formed at the Ladinian/Carnian boundary in the result of the emersion of the Middle Triassic carbonate platform. Formation of pedogenic limestones took place during the period of climate pluvialization in the latest Ladinian to early Carnian time.

3. Early-diagenetic dolostones and dolomitic mudstones were formed in salt marshes. Salt marshes were periodically emerged and intensively evaporated, but strongly influenced by fresh-water. Salt marshes were developed in troughs communicated with the sea. When troughs were isolated from the sea pure fluvial siliciclastics were deposited.

4. Dolostone-dolomitic mudstone complex from the upper part of Dolina Smytnia valley sequence was formed during long-lasting period of climate aridity in upper Carnian?–Norian time.

5. Dolostone and dolomitic mudstone couples represent short-term fluctuations of climate humidity. Dolostones were formed during relatively humid periods, whereas dolomitic mudstones during arid periods.

6. Both low TOC concentration and absence of a skeletal fauna suggest low productivity in the basin. In addition, components of palynological material and organic compounds indicate a terrestrial origin of the organic matter.

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