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A three component (organic carbon, pyritic sulphur, carbonate content) model as a tool for lithostratigraphic correlation of Carboniferous sediments in the Alpine-Carpathian-North Pannonian realm

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Abstract: The paleogeography of the Alpine-Carpathian-North Pannonian (ALCAPA) realm is still a matter of debate. In order to establish a tool for lithostratigraphic correlation, the total organic carbon content (TOC), the sulphur (S) content, and the carbonate content were measured in Carboniferous sediments of this realm. The presented database consists of 260 samples from Carboniferous sedimentary sequences in the Alpine-Carpathian-Pannonian realm. The TOC/S ratio in pelagic and continental environments is in accordance with the ratios observed in several studies. A high S-content in the Szabadbattyán Formation suggests an euxinic environment in an intra-shelf position. This is a distinctive feature to all other formations of the same depositional environment. Apart from the pelagic environment, sedimentary processes in the distinct basins result in composite TOC/carbonate relationships, which are indicative for a combination of an organically controlled with a carbonatic controlled deposition. The data of this study demonstrate that the analysed geochemical data can be interpreted in terms of the sedimentary environment. Therefore, the database can be used for a further research in the reconstruction of the Carboniferous paleogeography in this area.

Key words: Carboniferous, Variscan tectonofacies, black shales, TOC/S-carbonate ratio.

Introduction

The analysis of the organic fraction of clastic sediments gives rise to a better understanding of their sedimentary environment and subsequent thermal overprint. Sediments rich in organic matter are found in very specific depositional environments. Their actual quantity and quality is the final result of the ancient biological productivity, the preservation conditions (e.g. oxygen level during deposition), the sediment accumulation rate and the thermal history of the sedimentary basin.

To reconstruct the environmental conditions, the relationship between organically bound carbon (total organic carbon, TOC) and pyritically bound sulphur can be used to differentiate between normal marine sediments, freshwater sediments and marine euxinic sediments. This model was established by Berner (1970) for recent sediments and is now widely applied for all Phanerozoic sediments (e.g. Berner 1984).

The relationship between TOC and S in sediments is usually controlled by early-diagenetic processes: sedimentary pyrite is formed by the reaction of hydrogen sulphur (H_2S), which originates from the bacterial reduction of dissolved sulphate, with reactive able iron. To enable the reduction, organic matter is necessary as the reducing agent and energy source (Berner 1984). Prerequisite for the proceeding process is the existence of anoxic conditions, which are common below the sediment-water interface, but rare in the free water column.

In recent normal marine environments pyrite formation depends only on the availability of organic matter. The supply of sulphate and detrital iron minerals are usually sufficient. Normal marine sediments display therefore a positive correlation of TOC versus S with a TOC/S-ratio of about 2.8 (Berner 1970; Goldhaber & Kaplan 1974; Berner & Raiswell 1983). Such a positive correlation can usually not be established for freshwater sediments. Freshwater contains about 1 % of the seawater sulphate. The limiting factor for pyrite formation is therefore the supply of dissolved sulphate. Consequently, freshwater sediments often contain high amounts of organic carbon and low amounts of pyrite (Berner & Raiswell 1984). Euxinic deposits are characterized by the existence of hydrogen sulphur in the bottom water. Pyrite can form above or at the sediment-water interface. Accordingly, the correlation of TOC versus S displays a positive intercept on the S-axis (Leventhal 1983). The limiting factor for the pyrite formation is the supply of detrital iron minerals.

Russegger et al. (1997) demonstrated that the C/S-ratios observed in Paleozoic sediments of the Eastern and Southern

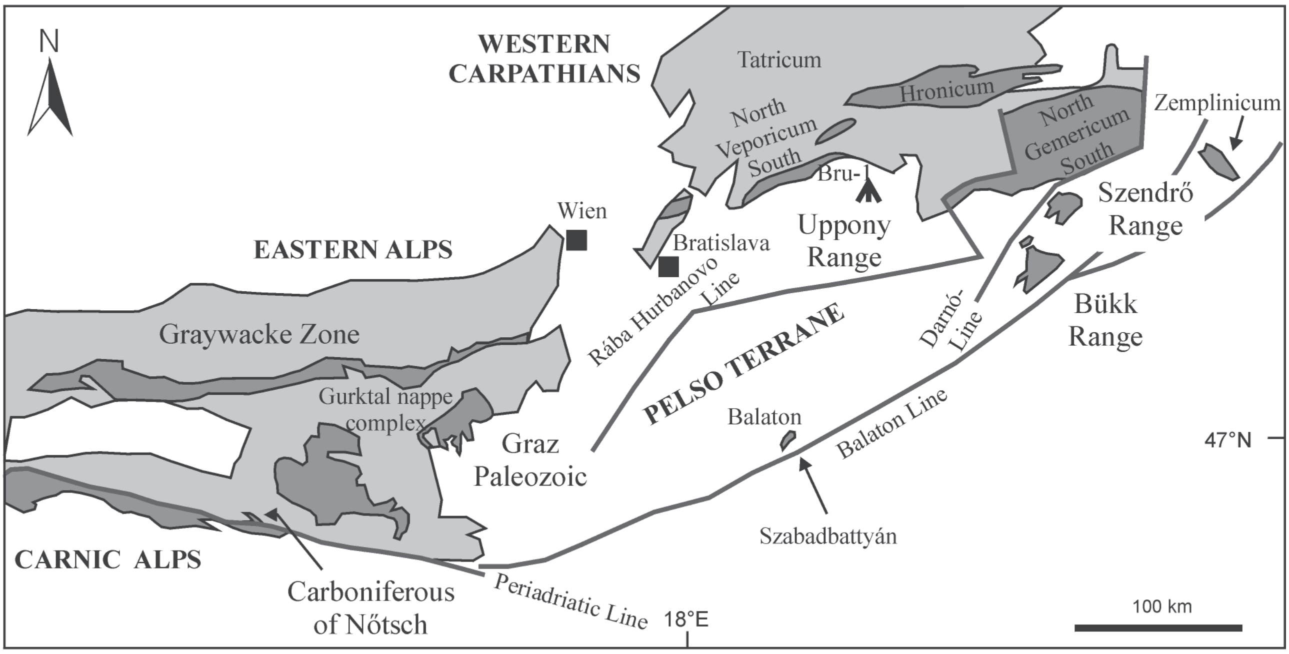

Fig. 1. Geological sketch map with the position of the investigated units (borehole Bru-1 — Brusnik Anticline).

Alps (Gurktal Nappe Complex, Carboniferous of Nötsch, Carnic Alps and Graz Paleozoic Nappe Complex) are in general agreement with the global data of Berner & Raiswell (1983). Locally, intra-basinal factors shift the values of the Eastern and Southern Alps from the global curve. Therefore, it is expected that TOC and S values can be used in the correlation of Paleozoic tectonostratigraphic units.

Due to the severe Alpine tectonics the paleogeography of the Alpine-Carpathian-Pannonian (ALCAPA) realm (Fig. 1) is still under intensive discussion (Vozárová & Vozár 1996, 1997; Ebner et al. 1997, 1998; Neubauer et al. 1997; Kovács et al. 2000). Therefore the aim of this contribution is the evaluation of TOC, S and carbonate content values measured in sediments of this realm in order to establish an additonal and novel tool for lithostratigraphic and paleogeographic correlation. We analyse here Carboniferous sediments which provide the opportunity to study syn- and post-tectonic sedimentary basins related to the Late Carboniferous (Variscan) collision of two continents (Neubauer & Vozárová 1990; Ebner 1991a,b,c, 1992; Ebner et al. 1991, 1998).

Geological setting

The evolution of Carboniferous sediments in the ALCAPA-domain (Eastern and Southern Alps, Western Carpathians, Transdanubian Range, Bükk Mt, Szendrő and Uppony Mts) was controlled by the Variscan continent-continent collisional event (Ebner et al. 1991; Ebner 1992). This domain was dissected subsequently during the Alpine (Cretaceous to Paleogene) collisional events, which were succeeded by orogen parallel strike-slip tectonics (Neubauer et al. 1997; Kovács et al. 1997; Vozárová & Vozár 1997). Tentatively, the Carboniferous tectonofacies zoning can be described as follows (Ebner et al. 1998) (Fig. 2):

Following Late Devonian–Early Carboniferous deformation, metamorphism and intrusion of granites, a synorogenic foredeep basin (Nötsch-Veitsch-Ochtiná Zone) evolved in the external segments of the rising Variscan orogen. Carboniferous marine carbonatic sediments exposed NE of Lake Balaton (Szabadbattyán Formation) may belong to this zone. Segments of the Carboniferous of Nötsch may belong to the transition from the shelf to the flysch basin (Krainer 1993).

Towards the south to southeast, a pelagic basin evolved. Remnants of this basin are exposed within the Graz Paleozoic Nappe Complex and the Szendrő–Uppony Range. In contrast, parts of the Gemer Paleozoic, the Noric Nappe of the Austroalpine Greywacke Zone, and the Paleozoic sequences of the Austroalpine Gurktal Nappe Complex are

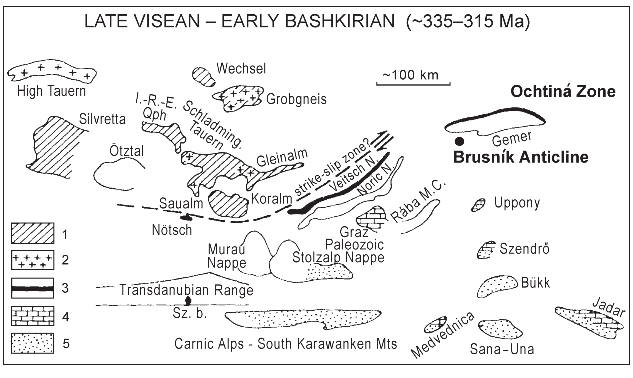

Fig. 2. Carboniferous paleogeography (1 — metamorphic domains, 2 — Variscan granitoids, 3 — synorogenic foredeep basins of the Nötsch–Veitsch–Ochtina Zone, 4 — pelagic carbonatic basins, 5 — flysch basins) of the investigated area (Ebner et al. 1998).

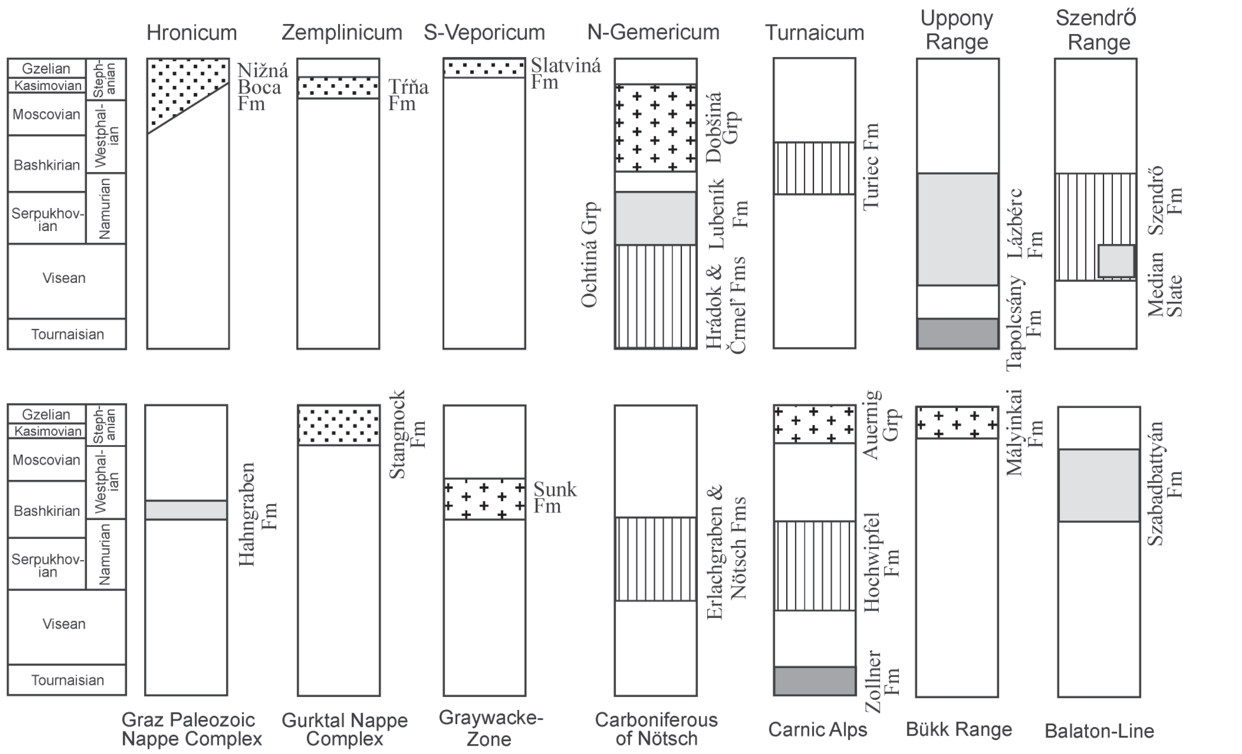

Fig. 3. Stratigraphy and depositional environment (point symbol — continental, cross symbol — paralic environment, vertical hatch — slope environment, light shading — neritic environment, dark shading — pelagic environment) of the investigated samples.

characterized by siliciclastic and volcaniclastic sediments. This carbonatic to siliciclastic shelf evolved into a flysch basin (exposed within the Carnic Alps, Szendrő and Bükk Mountains, and Brusník Anticline).

A Late Carboniferous (Variscan) angular unconformity separates this sequence from post-orogenic continental to cyclic shallow marine molasse sequences. In the pelagic shelf domain the climax of the Variscan event is indicated by karstified carbonatic horsts and the formation of conodont mixed faunas. In basinal siliciclastic flysch basins, this event is mirrored by disrupted carbonate platforms, submarine gravitational transported sediments, and basic volcanics (Ebner 1991a,b,c; 1992).

In the Gemeric units, the superposition of terrestrial clastic sediments above marine sediments (Dobšiná Group) indicates a tectonic event during Late Carboniferous times which succeeded an older tectonic event (Vozárová 1992, 1996). Similarly, a Variscan deformation cannot be proven within the Uppony–Szendrő Mountains. However, marine molasse sediments resemble the shallow-marine molasse sediments of the Southalpine Carnic Alps and suggest, therefore, a similar tectonofacies setting.

In the following section we characterize the investigated formations (Fig. 3) by the geological parameters which may influence the geochemical composition of the samples.

Western Carpathians

Tectono-facially, the investigated samples can be assigned to syn- and post-orogenic depositional environments. With respect to their position within the Variscan orogen, the investigated units are parts of three tectonic zones (Vozárová & Vozár 1997; Vozárová 1998):

The Central Western Carpathian Crystalline Zone belongs to the internal zone of the Variscan orogen. The Variscan units of this zone include the Tatra Terrane within the Alpine Tatric Unit and Northern Veporic Unit, the Kohút Terrane within the Southern Veporic Unit (with the sampled Slatviná Formation), the Byšta Terrane within the Zemplinic Unit (with the sampled Tŕňa Formation), and the suspected Ipoltica Terrane within the Hronic Unit (with the sampled Nižná Boca Formation). The Northern Gemeric Zone comprises relics of the Rakovec and Klátov Terranes with the synorogenic Hrádok and Črmeľ Formations of the Ochtiná Group and the postorogenic Rudňany, Zlatník and Hámor Formations of the Dobšiná Group. The Inner Western Carpathian Crystalline Zone belongs to the external zone of the Variscan orogen. Within the (sampled) Turnaic Nappe Unit the Turiec Formation overthrusts the Early Jurassic of the Meliatic Unit. This unit shows paleogeographic relations to the Szendrő Range and Carnic Alps (Vozárová 1992; Vozárová & Vozár 1992).

Nižná Boca Formation (Westphalian–Stephanian)

The 400 to 500 m thick, diagenetic (Vrána & Vozár 1969; Plašienka et al. 1989; Šucha 1989) Nižná Boca Formation (Sitár & Vozár 1973; Planderová 1979) is a fluvial–lacustrine sequence of a clastic delta, influenced by a dacitic volcanism. The sequence was deposited within an extensional retroarc basin (Vozárová 1996; 1998).

Tŕňa Formation (Early Stephanian)

The 800 to 1000 m thick Tŕňa Formation (Bouček & Přibyl 1959; Němejc 1947, 1953; Němejc & Obrhel 1958; Planderová et al. 1981) is subdivided into two several hundreds of meters thick cycles. The lower megacycle contains seven limnic-fluvial cyclothems with several cm up to 60 cm thick coal seams. The second megacycle is characterized by alluvial stream-channel sediments with some rhyolitic to dacitic volcaniclastic beds. The sequence was deposited with a retroarc basin (Vozárová 1996; 1998). The grade of metamorphism corresponds to the boundary between very low-grade to low-grade metamorphic conditions (Milička et al. 1991).

Slatviná Formation (Stephanian C)

The up to 800 m thick, low-grade metamorphic (Vozárová 1990) Slatviná Formation (Planderová & Vozárová 1978) comprises deltaic–lacustrine sediments of two regressive coarsening upward cycles of a retroarc basin (Vozárová & Vozár 1992; Vozárová 1996; 1998).

Hrádok and Črmeľ Formations (Upper Tournaisian–Visean) of the Ochtiná Group

The 1000 to 1200 m thick, low-grade metamorphic Hrádok and Črmeľ Formations (Planderová 1982; Bajaník & Planderová 1985; Sassi & Vozárová 1987; Vozárová 1996) comprise turbiditic sediments, intercalated with tholeiitic N-MORB volcanics. Rarely, lydites, siliceous metapelites, and laminated limestones were found in thin layers. The Hrádok Formation contains more frequently coarse-grained paraconglomerate turbidites and fragments of ultramafic rocks, whereas the Črmeľ Formation is distinguished by rare rhyolitic volcaniclastic turbidites. The depositional environment is interpreted as a synorogenic deep-water slope basin, filled mainly by siliciclastic turbidites, some ultrabasic olistoliths, and sediments transported by gravity currents (Vozárová 1996, 1998).

Lubeník Formation (uppermost Visean–Serpukhovian) of the Ochtiná Group

The less than 400 m thick Lubeník Formation (Bouček & Přibyl 1960; Kozur et al. 1976) consists of black slates, dolomitic slates, well-bedded dolomites and massive coarse-grained magnesite of a shallow-water, neritic and littoral environment. The grade of metamorphism corresponds to the boundary between very low-grade to low-grade metamorphic conditions (Vozárová 1996).

Rudňany Formation (Westphalian A–B) of the Dobšiná Group

The less than 200 m thick, low-grade metamorphic (Bajaník et al. 1981; Vozárová & Šucha unpubl. data) Rudňany Formation (Němejc 1947) is composed of coarse conglomerates with components of the underlying pre-Upper Carboniferous complexes (Klátov and Rakovec Terranes, Lower Carboniferous flysch sequence of Črmeľ Formation; Vozárová 1996; Vozárová & Vozár 1996), black slates and sandstones. The Rudňany Formation is interpreted as a delta-fan complex, which propagated into the shallow water littoral to neritic zone of a peripheral foreland basin (Vozárová 1996; Vozárová & Vozár 1996).

Zlatník Formation (Westphalian B–C) of the Dobšiná Group

The basal part of the 150 to 400 m thick Zlatník Formation (Rakusz 1932; Němejc 1947, 1953; Bouček & Přibyl 1960; Kozur & Mock 1977; Bajaník et al. 1981) is composed of organodetric limestone within fine-grained clastic metasediments. The upper part comprises fine-grained clastic metasediments and fine-grained basaltic volcaniclastics with scarce effusions of tholeiitic basalts. The grade of metamorphism corresponds to the boundary between very low-grade to low-grade metamorphic conditions. The depositional environment is interpreted as a littoral to neritic segment of a post-orogenic peripheral foreland basin (Vozárová 1996).

Hámor Formation (Westphalian D) of the Dobšiná Group

The 50 to 200 m thick, low-grade metamorphic (Bajaník et al. 1981; Plašienka et al. 1989) Hámor Formation is a regressive, paralic sequence of a deltaic sedimentary system within a post-orogenic peripheral foreland basin (Vozárová 1996). It is composed of coal-bearing, slates, sandstones, and conglomerates, which show a cyclic coarsening-upward trend.

Turiec Formation (Bashkirian) of the Brusník Anticline

The 600 m thick, low-grade metamorphic (Mazzoli & Vozárová 1989) Turiec Formation was deposited in a syn-orogenic deep-water slope basin which evolved after the collapse of a pre-flysch carbonate platform. It comprises a turbiditic sequence of black phyllites, metasiltstones and metasandstones with some Bashkirian (Ebner et al. 1990) slides and sediments transported by gravity currents (Vozárová 1992).

North Pannonian Domain

The units included in this study (Transdanubian Range, Bükk, Uppony and Szendrő Mts) form parts of the Pelsonia Composite Terrane, which represents the southern part of the "North Pannonian–Inner-Central West Carpathian" orogenic collage (Kovács et al. 1997, 2000).

Uppony Mountain

Tapolcsány Formation (Silurian?–Lower Carboniferous?)

The 300 to 400 m thick, very low-grade metamorphic (Árkai 1983; Árkai et al. 1995) Tapolcsány Formation comprises slates and black, radiolarian lydites, free of any carbonate content. The sequence was deposited within a pre-orogenic euxinic deep-water basin (Kovács 1992; Fülöp 1994; Ebner et al. 1998).

Lázbérc Formation (Late Visean–Bashkirian)

The 200–300 m thick, very low-grade metamorphic (Árkai 1983; Árkai et al. 1995) Lázbérc Formation is composed of limestone with calc-schist, slate, and sandstone intercalations. The depositional environment is interpreted as a pre- to syn-orogenic deep carbonate ramp which evolved synchronously with the flysch sediments of the Szendrő Phyllite Formation (Ebner et al. 1991, 1998; Kovács 1992; Fülöp 1994).

Szendrő Mountains

Szendrő Phyllite Formation (Late Visean–Bashkirian/Lower Moscovian?)

The 500 to 600 m thick, low-grade metamorphic (Árkai 1983; Árkai et al. 1995) Szendrő Phyllite Formation is composed of metasandstones, phyllites, and limestone olistoliths, comparable to the Szilvásvárad Formation of the Bükk Mountains (Árkai 1983). The "Median Slate Unit" is a tectonically separated unit of this sequence. The Szendrő Phyllite Formation was deposited within a syn-orogenic flysch basin, contemporaneous with the collapse of an Early Carboniferous carbonate platform (Ebner et al. 1991, 1998; Kovács 1992; Fülöp 1994).

Bükk Mountains

Mályinka Formation (Late Moscovian–Gzhelian)

The 400 m thick, diagenetic to very low-grade metamorphic (Árkai 1983; Árkai et al. 1995) Mályinka Formation is a fossiliferous carbonate-clastic sequence of a post-orogenic, marine molasse basin, which evolved continuously above the Szilvásvárad Formation (Ebner et al. 1991; Fülöp 1994; Haas et al. 2001; Filipovic et al. 2003; Pelikan et al. 2005). In the Szentlélek Zone, where the North Bükk Anticline becomes extremely narrow being overthrust by the Kisfennsik Nappe, the overprint reaches the low-grade zone.

Transdanubian Range

Szabadbattyán Formation

Upper Visean, dark grey to black slate, light to dark grey sandstone, black, fossiliferous limestone in about 100 m known thickness. Depositional environment: neritic, siliclastic-carbonatic ramp (Lelkes-Felvári 1978; Fülöp 1994; Ebner et al. 1991).

Eastern and Southern Alps

The investigated units of the Austro- and Southalpine units belong to the Noric Composite Terrane of Frisch & Neubauer (1989) and Neubauer et al. (1997) and to the Veitsch Nappe of the Greywacke Zone. The sampled formations involve pre- (Hahngraben Formation, Zollner Formation), syn- (Hochwipfel Formation) and post-orogenic sequences (Sunk Formation, Erlachgraben and Nötsch Formation, Stangnock Formation, Auernig Group). The group of the post-orogenic sequences may be related to early Variscan events (close to the Devonian/Carboniferous boundary: Sunk Formation in the Veitsch Nappe of the Greywacke Zone, and Erlachgraben/Nötsch Formation in the Carboniferous of Nötsch) or to the late Carboniferous orogeny (Stangnock Formation within the Gurktal Nappe Complex; Auernig Group within the Southern Alps).

Hahngraben Formation (Westphalian A) from the Rannach Nappe of the Austroalpine Graz Paleozoic Nappe Complex

The Hahngraben Formation comprises 50 m thick dark coloured slates with rare siltstones, sandstone, some olistolithic layers (with components of Visean flaser limestone), and graded bedded allodapic limestones of an undefinded marine clastic sedimentary basin (Ebner et al. 1991, 2000). In this unit, the sedimentary succession ends during the Westphalian A. Because of missing overstep sequences there is no evidence for a Variscan unconformity within the Graz Paleozoic Nappe Complex. The influx of detrital mica and gravitational transported sedimentary material in the Hahngraben Formation indicates a tectonic (Variscan) reorganization of the hinterland. The Rannach Nappe shows very low- to low-grade metamorphic conditions (Rantitsch et al. 2005).

Stangnock Formation (Stephanian) of the Austroalpine Gurktal Nappe Complex

The very low-grade metamorphic (Rantitsch & Russegger 2000) Stangnock Formation is a more than 400 m thick sequence of polymict conglomerates, immature coarse-grained sandstones and dark slates of a proximal fluvial system (Krainer 1993). This formation is interpreted as an intramontane molasse formed after Variscan deformation of the Paleozoic basement (Ebner et al. 1991).

Sunk Formation (Westphalian A–C) from the Veitsch Nappe of the Austroalpine Greywacke Zone

The low-grade metamorphic (Rantitsch et al. 2004) Sunk Formation comprises 50 to 150 m thick coarsening upward siliciclastic sediments with seams and lenses of graphite. The stratigraphic sequence of the Veitsch Nappe mirrors the evolution of a shallow shelf (which grades locally to a hypersalinar lagoon with some bioherms) to a regressive shore line with river dominated delta deposits (Sunk Formation; Ratschbacher 1984, 1987; Krainer 1993; Ebner & Prochaska 2001). Consequently, the Sunk Formation is part of a marine molasse sequence which evolved after the first tectonothermal peak of the Variscan orogenic stage (Flügel 1977; Schönlaub 1979; Neubauer & Vozárová 1990; Ebner 1992; Neubauer & Handler 2000).

Table 1: Analytic results of this study (S — sulphur, TOC — total organic carbon, C — carbonate content) from the Carpathians and Hungary. The results of 169 samples from the Eastern and Southern Alps are documented in Russegger et al. (1997).

Sample	Locality	Formation	Tectonic Unit	S	TOC	Ccarb.
S1	Nižná Boca	Nižná Boca Fm	Hronicum	0.011	0.10	0.1
S2	Malužiná Valley	Nižná Boca Fm	Hronicum	0.009	0.08	0.0
S3	Malužiná Valley	Nižná Boca Fm	Hronicum	0.010	0.10	0.0
S5	Ipoltica Valley	Nižná Boca Fm	Hronicum	0.009	0.13	0.1
S8	Dikula Valley	Nižná Boca Fm	Hronicum	0.008	0.12	0.0
TR59-1115	Tŕňa 59 well	Tŕňa Fm	Zemplinicum	0.008	0.22	0.2
TR59-1135	Tŕňa 59 well	Tŕňa Fm	Zemplinicum	0.023	0.33	5.7
TR59-890	Tŕňa 59 well	Tŕňa Fm	Zemplinicum	0.017	1.73	0.2
TR59-665	Tŕňa 59 well	Tŕňa Fm	Zemplinicum	0.023	2.64	1.2
TR59-270	Tŕňa 59 well	Tŕňa Fm	Zemplinicum	0.021	2.06	12.8
TR59-150	Tŕňa 59 well	Tŕňa Fm	Zemplinicum	0.029	3.10	23.9
V1	Krokava	Slatviná Fm	S-Veporicum	0.008	0.21	0.0
V2	Sušanský vrch	Slatviná Fm	S-Veporicum	0.005	0.06	0.0
V3	Turčok	Slatviná Fm	S-Veporicum	0.005	0.02	0.1
S13 A	Košické Hámre	Črmeľ Fm	N-Gemericum	0.007	1.41	0.5
S13 B	Košické Hámre	Črmeľ Fm	N-Gemericum	0.006	0.14	0.9
S14	Ružín	Črmeľ Fm	N-Gemericum	0.010	0.27	0.1
O2	Poproč	Hrádok Fm	N-Gemericum	0.008	0.79	0.1
O1	Sušanský vrch	Hrádok Fm	N-Gemericum	0.006	0.25	0.0
H7	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.007	0.90	0.1
H6	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.008	1.73	0.6
H5	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.007	0.79	0.1
H4	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.006	1.07	0.3
H3	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.006	0.96	0.0
H2	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.006	0.83	0.1
H1	Ochtiná-Magura	Hrádok Fm	N-Gemericum	0.006	0.19	0.0
S15	Košická Belá	Lubeník Fm	N-Gemericum	0.007	0.08	0.0
S19	Ochtiná	Lubeník Fm	N-Gemericum	0.009	0.51	8.5
S20	Ochtiná Quarry	Lubeník Fm	N-Gemericum	0.007	3.12	0.1
S21B	Poproč	Lubeník Fm	N-Gemericum	0.018	0.90	0.0
S21A	Poproč	Lubeník Fm	N-Gemericum	0.019	1.11	0.1
S10	Závadka	Rudňany Fm	N-Gemericum	0.005	0.05	0.1
W10B	Zápalenica Valley	Rudňany Fm	N-Gemericum	0.015	1.28	2.8
W10A	Zápalenica Valley	Rudňany Fm	N-Gemericum	0.013	1.72	0.1
W9A	Zápalenica Valley	Rudňany Fm	N-Gemericum	0.138	0.14	11.1
W9B	Zápalenica Valley	Rudňany Fm	N-Gemericum	0.013	0.78	0.2
S16	Dobšiná	Zlatnik Fm	N-Gemericum	0.096	1.11	8.7
S17	Dobšiná	Zlatník Fm	N-Gemericum	0.010	0.38	0.0
S9	Grajnar Quarry	Zlatník Fm	N-Gemericum	0.283	0.35	0.2
W8	Závistlivec	Zlatník Fm	N-Gemericum	0.006	0.19	0.1
W7	Závistlivec	Zlatník Fm	N-Gemericum	0.006	0.34	0.0
W6	Závadka	Zlatník Fm	N-Gemericum	0.006	0.19	0.0
W5	Závadka	Zlatník Fm	N-Gemericum	0.006	0.30	0.0
W4	Závadka	Zlatník Fm	N-Gemericum	0.010	0.24	0.1
S11	Margecany	Hámor Fm	N-Gemericum	0.007	0.50	0.0
S12	Margecany	Hámor Fm	N-Gemericum	0.017	0.12	0.1
S18 A	Dobšiná	Hámor Fm	N-Gemericum	0.009	0.79	0.1
S18 B	Dobšiná	Hámor Fm	N-Gemericum	0.017	1.07	0.0
BRU1-159	Brusník well	Turiec Fm	Brusník Anticline	0.041	0.48	11.6
BRU1-447	Brusník well	Turiec Fm	Brusník Anticline	0.015	0.25	0.0
BRU1-467	Brusník well	Turiec Fm	Brusník Anticline	0.009	0.44	0.1
BRU1-507	Brusník well	Turiec Fm	Brusník Anticline	0.055	0.32	0.0
BRU1-534	Brusník well	Turiec Fm	Brusník Anticline	0.038	0.18	0.2
BRU1-538	Brusník well	Turiec Fm	Brusník Anticline	0.058	0.36	0.1
BRU1-576	Brusník well	Turiec Fm	Brusník Anticline	0.172	0.35	5.8
U1	Lázbérc Lake	Tapolcsány Fm	Uppony	0.013	0.087	0.5
U6	Csernely Creek	Tapolcsány Fm	Uppony	0.030	0.453	0.2
U7	Csernely Creek	Tapolcsány Fm	Uppony	0.018	0.363	0.1
R1	Lower Michael Gallery B	Tapolcsány Fm	Uppony	0.021	0.520	0.0
R2	Lower Michael Gallery A	Tapolcsány Fm	Uppony	0.128	1.292	2.1
R3	Heinrich Gallery	Tapolcsány Fm	Uppony	3.188	7.892	0.5
R9	Franz Josel Gallery	Tapolcsány Fm	Uppony	0.017	0.233	0.0
R4	Franz Josel Gallery	Tapolcsány Fm	Uppony	0.027	0.285	0.1
R7	Dt-8 well	Tapolcsány Fm	Uppony	3.635	3.099	1.5
U2	Lázbérc Lake	Lázbérc Fm	Uppony	0.009	0.108	18.8
U3	Lázbérc Lake	Lázbérc Fm	Uppony	0.019	0.728	0.0
U4	Lázbérc Lake	Lázbérc Fm	Uppony	0.016	0.137	89.1

Table 1: *Continued.*

Sample	Locality	Formation	Tectonic Unit	S	TOC	C
R14	Sz-22 well	Szendrő Fm	Szendrő	0.007	0.712	1.6
R5	Sz-22 well	Szendrő Fm	Szendrő	1.150	0.494	11.1
R16	Sz-22 well	Szendrő Fm	Szendrő	0.008	0.725	0.0
R6	Sz-22 well	Szendrő Fm	Szendrő	0.033	0.596	7.9
R21	Sz-22	Szendrő Fm	Szendrő	0.012	0.620	6.5
U10	S Szendrő	Szendrő Fm	Szendrő	0.011	0.221	0.2
U12	Meszes	Szendrő Fm	Szendrő	0.008	0.643	0.1
U13	S Rakacaszend	Szendrő Fm	Szendrő	0.012	0.768	0.1
U14	S Rakacaszend	Szendrő Fm	Szendrő	0.011	0.539	0.5
U16	SW Rakaca	Szendrő Fm	Szendrő	0.010	0.462	0.0
U11	Szendrő	Median Slate	Szendrő	0.009	0.090	0.0
U15	SE Rakacaszend	Median Slate	Szendrő	0.010	0.462	0.0
U8	E Mártuskö	Mályinkai Fm	Bükk	0.019	0.264	0.2
U9	Mártoskö	Mályinkai Fm	Bükk	0.015	0.120	63.8
U17	NE Nagyvisnyo	Mályinkai Fm	Bükk	0.014	0.634	6.1
U18	Tótfalú-völgy	Szilvásvárad FFF.F Fm	Bükk	0.021	0.514	0.0
U19	Tótfalú-völgy	Szilvásvárad	Bükk	0.012	0.522	0.0
U20	Tótfalú-völgy	Szilvásvárad	Bükk	0.008	0.306	0.2
Szab 9-303	Szabadbattyán 9 well	Szabadbattyán Fm	Transdanubian Range	0.712	0.519	23.6
Szab 9-304	Szabadbattyán 9 well	Szabadbattyán Fm	Transdanubian Range	0.644	0.317	47.4
Szab 9-310	Szabadbattyán 9 well	Szabadbattyán Fm	Transdanubian Range	1.116	0.528	57.8
Szab 10-335	Szabadbattyán 10 well	Szabadbattyán Fm	Transdanubian Range	1.550	1.143	3.9
Szab 10-370	Szabadbattyán 10 well	Szabadbattyán Fm	Transdanubian Range	0.444	1.125	1.6
Szab 10-380	Szabadbattyán 10 well	Szabadbattyán Fm	Transdanubian Range	0.173	0.994	1.1

Erlachgraben and Nötsch Formation (Late Visean–Early Westfalian) from the Austroalpine Carboniferous of Nötsch

The 400 to 600 m thick very low-grade metamorphic (Rantitsch 1995) Erlachgraben and Nötsch Formation comprises greyish to blackish slates, sandstones, and quartz rich conglomerates (Schönlaub 1985; Krainer 1993). The formations are separated by a breccia (Badstub Formation) with rounded metamorphic clasts and few limestone clasts (with conodonts of Late Visean–Early Serpukovian age) in a dense green matrix of tholeiitic basalts (Krainer & Mogessi 1991). The depositional environment is interpreted as a marine molasse type foredeep in front of the rising Variscan chain (Flügel 1977; Krainer 1993).

Auernig Group (Late Moscovian–Gzhelian) from the Southalpine Carnic Alps

The 600 to 800 m thick, very low-grade metamorphic (Rantitsch 1997) Auernig Group comprises quartz-rich conglomerates, cross-bedded sandstones, bioturbated, often fossiliferous siltstones, slates, and limestones. It forms a sequence of clastic-carbonatic transgressive and regressive cycles with individual thicknesses of 10 to 40 m. The sea-level lowstands are characterized by clastic sediments of deltaic beach and shoreface environments, whereas limestones were formed during the sea-level highstands (Schönlaub & Heinisch 1993; Krainer 1993; Schönlaub & Histon 2000). In the Carnic Alps, the climax of the Variscan collision occurred during Late Namurian to Late Westphalian (Early Bashkirian–Middle/Late Moscovian) times. The post-orogenic character of a marine to terrestrial molassse environment is impressively documented by angular unconformities between the Auernig Group and the pre-Variscan sedimentary sequence.

Hochwipfel Formation (Middle Visean–Namurian) from the Southalpine Carnic Alps

The more than 1000 m thick very low- to low-grade metamorphic (Rantitsch 1997) Hochwipfel Formation comprises an arenitic to pelitic turbiditic sequence with intercalations of several meter thick chaotic debris flows, olistoliths and limestone breccias. The depositional environment is given by a flysch basin at an active plate margin (Ebner et al. 1991; Schönlaub & Heinisch 1993; Schönlaub & Histon 2000). The flysch basin evolved after a tectonic reorganization of the depositional realm. This event is indicated by the collapse of carbonate platforms, by the formation of a subaerial paleokarst relief, and by the formation of intraplate alkali basalts.

Zollner Formation (Pragian–Tournaisian) from the Southalpine Carnic Alps

More than 100 m thick, very low-grade metamorphic (Rantitsch 1997), almost carbonate free black to greenish slates, siltstones, siliceous slates and bedded cherts have been deposited within a deep-water basinal environment (Schönlaub & Heinisch 1993; Schönlaub & Histon 2000).

Samples and analytical methods

The 260 samples of the present database are clastic sediments, which are black shales in the broadest sense. Most of the samples analysed are outcrop samples. The 91 sam-

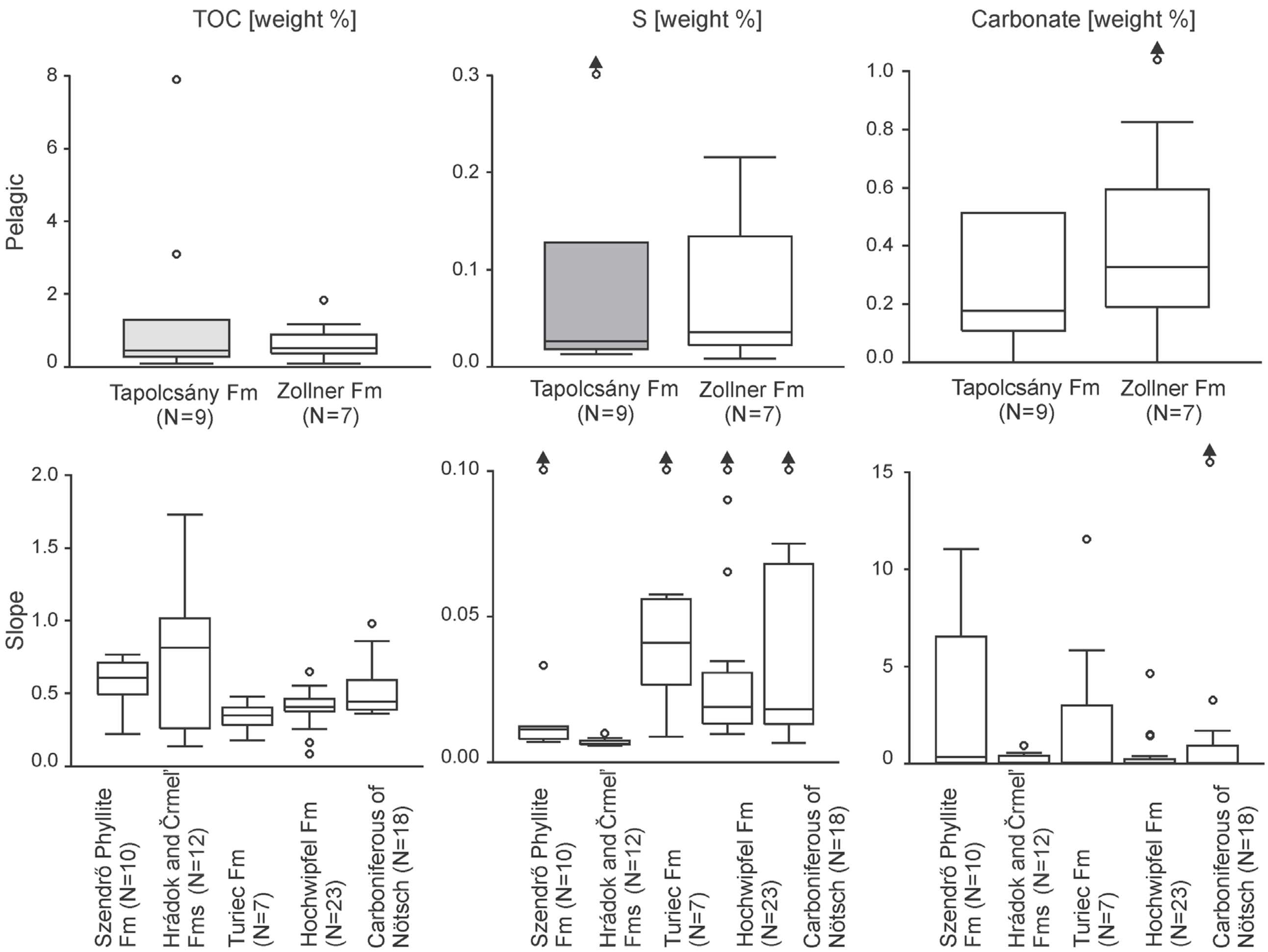

Fig. 4. Total organic carbon (TOC), sulphur (S) and carbonate content in Carboniferous pelagic and slope environments of the ALCAPA region. Statistically separated groups are indicated by a shading of the boxplots.

ples of this study (Table 1) complete the dataset of Russegger et al. (1997).

It is a fact that the original concentration of organic carbon and pyrite sulphur can be lowered due to oxidative loss during subaerial weathering (e.g. Littke et al. 1991). We have attempted to avoid this problem by considering only samples without evidence of oxidation. The total sulphur content is assumed to be pyritically bound sulphur as the organic sulphur content of the sediment would be insignificantly small (cf. Raiswell & Berner 1986). The carbon (organically and inorganically bound carbon) and total sulphur content (weight %) of the samples was estimated using a threefold measurement on a LECO CS-300 instrument calibrated with analytical standards. The uncertainty of the carbon analysis amounts to a maximum of 14 % for concentrations <0.05 % and to a maximum of 6 % for higher values. For the sulphur values the respective maximum uncertainties are 26 % for concentrations <0.06 % and 11 % for higher concentrations. From the measured organically (TOC) and inorganically bound carbon the bulk carbonate content ($CaCO_3$) was calculated from the stochiometry of $CaCO_3$ ($CaCO_3 = 8.33 \times (C_{bulk} - TOC)$.

Comparison of the analytical data is done by applying a one-way analysis of variance. This technique separates the total variance of the dataset into various components. Equality of mean and variance of these components are tested simultaneously by applying an F-Test. Variance analysis demonstrates a significant (at a significance level of 0.95) difference between the S-, TOC and carbonate-content of the elements in dependence of the sampled formation and in dependence of the depositional environment. Performing a Duncan Test the elements are separated into different groups of homogeneous elemental concentration (Figs. 4–7). Within these groups it is not possible to reject the hypothesis of equal mean and variance of TOC, S and carbonate content.

Results

Because the TOC-, S- and carbonate content of sediments is related to the prevailing depositional environment, all data are pooled in respect to the reconstructed environment. We distinguish a pelagic environment, a slope-related environment, a paralic environment, a continental environment

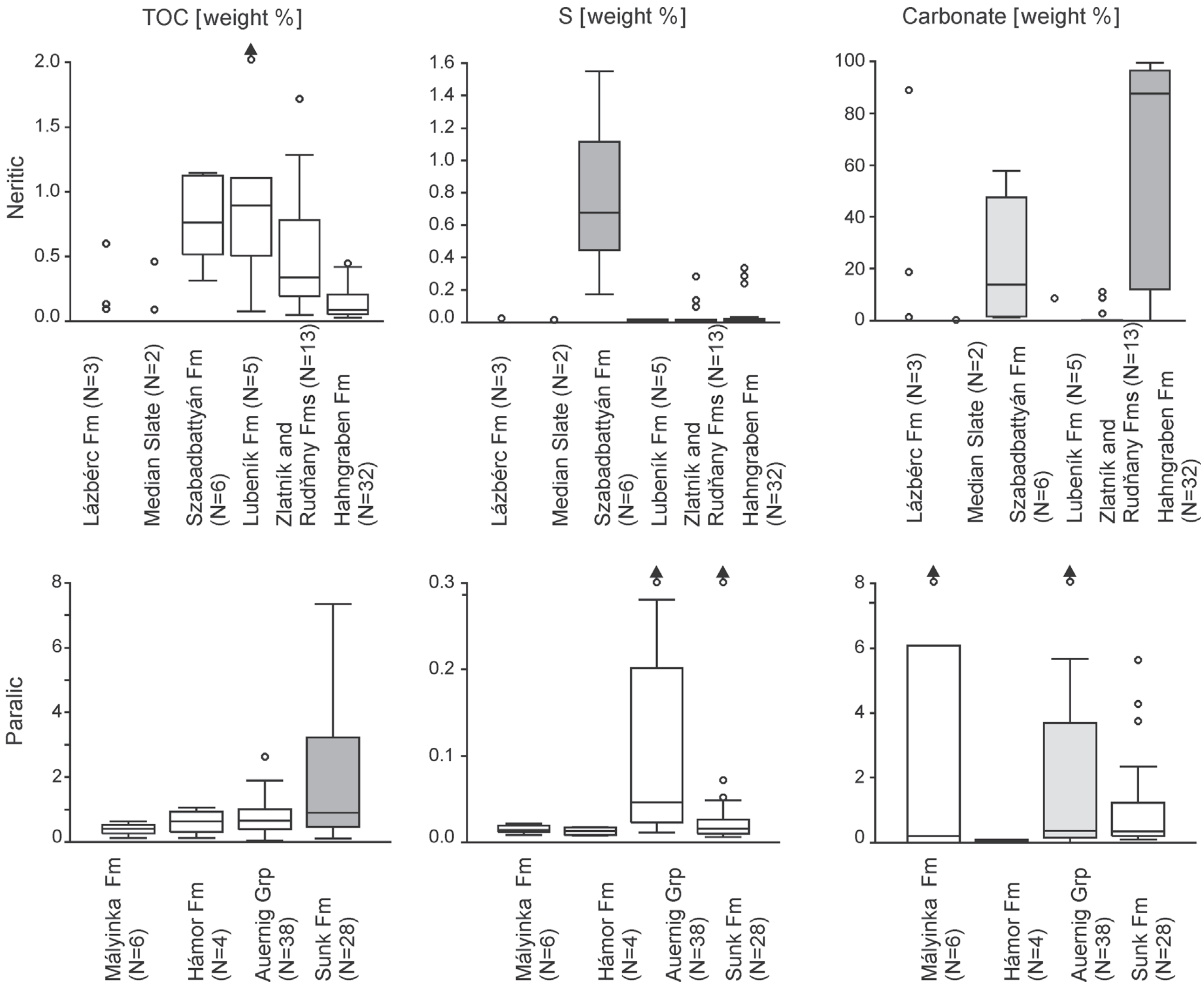

Fig. 5. Total organic carbon (TOC), sulphur (S) and carbonate content in Carboniferous platform and paralic environments of the ALCAPA region. Statistical separated groups are indicated by a shading of the boxplots.

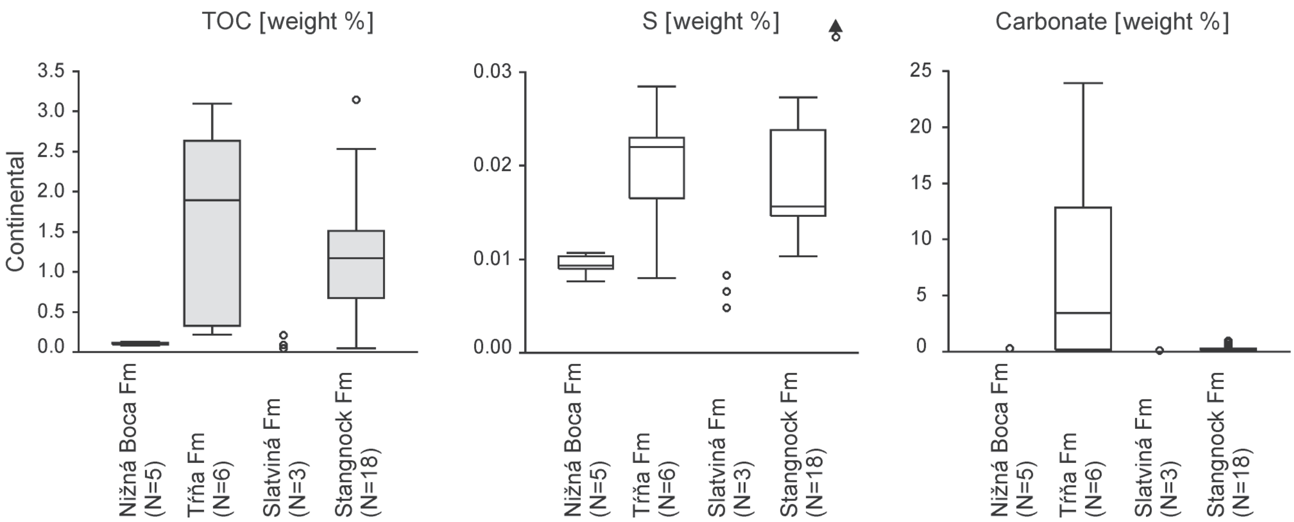

Fig. 6. Total organic carbon (TOC), sulphur (S) and carbonate content in Carboniferous continental environments of the ALCAPA region. Statistically separated groups are indicated by a shading of the boxplots.

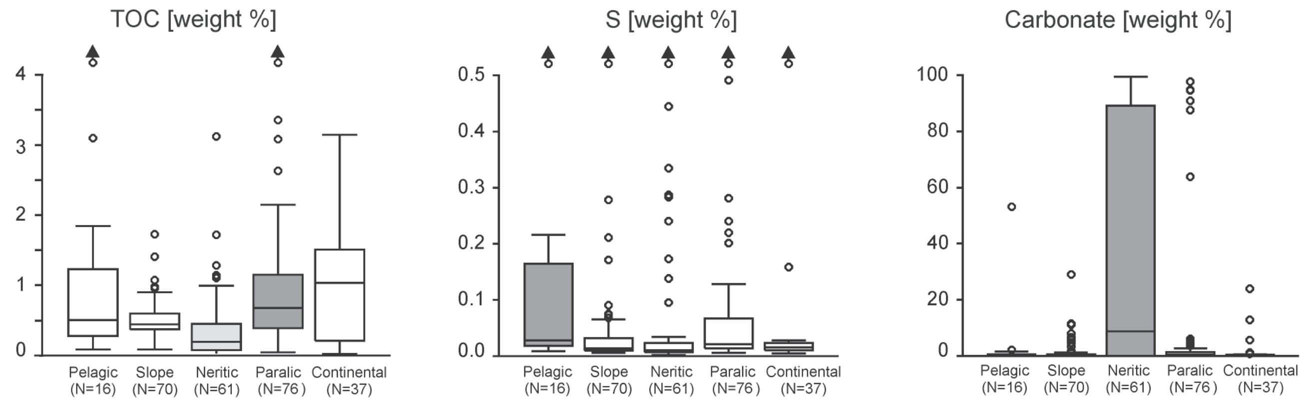

Fig. 7. Total organic carbon (TOC), sulphur (S) and carbonate content in the investigated samples. Statistical separated groups are indicated by a shading of the boxplots.

and an environment related to a carbonate platform. The basic statistics are presented in Table 1. In Figs. 4–6 the data distribution in a distinct depositional environment is presented by boxplots. Fig. 7 shows the data distribution of the measured parameters if the tectonic setting and the stratigraphic age are neglected.

Discussion

Comparing the parameters in respect to the sampled formations, the Tapolcsány Formation and the Szabadbattyán Formation show significantly higher S-contents than all other formations. The high TOC-content in the Sunk Formation separates this sample group from all other formations. The Tŕňa, Tapolcsány and Stangnock Formations have intermediate S contents. This group has similarities to the group of high S-values as well as to the group of low S-values. Three groups can be separated if the carbonate content is evaluated. Samples from the Hahngraben Formation form the group with the highest carbonate content, whereas the Lázbérc Formation together with the Szabadbattyán Formation and the Auernig Group form a group, which shows similarities to the Hahngraben Formation as well as to a group consisting of the remaining formations.

If the parameters are compared in respect to their depositional environment, the S-content discriminates the pelagic environment, the TOC-content the paralic and the platform environment and the carbonate content the platform environment (Fig. 7).

TOC/S plots are used in Fig. 8 to investigate the relationship between reactive organic matter and sedimentary pyrite (Berner 1984). In these plots a line with a gradient of 2.8 determines the correlation between TOC and S in a marine environment (Berner & Raiswell 1984; Leventhal 1983). If outliers are neglected, a predominantly marine environment is reflected by the TOC/S relationship observed in the pelagic and paralic formations. A spread of the data points along the TOC axis indicates a freshwater environment. This is observed in samples coming from a slope, platform and continental environment. An euxinic environment can be inferred if the correlation line between TOC and S has a positive intercept on the S axis (Leventhal 1983). Such a relationship can be seen in samples of the Szabadbattyán Formation and in some isolated samples of the other formations.

Therefore, the relationship between TOC and S in samples coming from pelagic, paralic and continental environments is in accordance with the paleogeographical interpretations. Samples from a slope and platform environment are characterized by S-contents which are too low for their respective environment. However, if the corresponding TOC/S ratio is compared to the worldwide dataset of Berner & Raiswell (1983) this discrepancy diminishes. This is due to the fact that during Carboniferous times a global shift from marine to continental environments resulted in strongly elevated TOC/S ratios. However, this global trend does not explain the observed ratio in the local marine environment. An explanation for the low S-content may be given by a limited pyrite formation due to an increased supply on terrestrially derived pre-oxidized organic debris (see also Russegger et al. 1997).

Variable TOC- and carbonate contents can be explained by the dominant sedimentary process (Ricken 1983). If the composition of sediments is divided into carbonatic, siliciclastic and organic fractions, a simple crossplot of the TOC against the carbonate content can be interpreted in terms of the dominating depositional process. A carbonatic controlled deposition (TOC and carbonate-content are negative correlated) can be explained by a variability in the bioproductivity, a deposition controlled by a siliciclastic deposition (TOC and carbonate-content are positive correlated) is indicative for variations in the input of clastic debris, and an organically controlled deposition (TOC and carbonate-content are unrelated) can be explained by variations in the bioproductivity, in the preservation conditions of the organic matter or by a varying nutrient supply.

An organically controlled deposition is seen in the pelagic environment (Fig. 9). All other environments show a composite relationship. In the slope environment, a combination of an organically controlled with a carbonatic controlled deposition is obvious for the Szendrő Phyllite Formation and the samples from the Carboniferous of Nötsch. All other formations of this setting are explained by an organically controlled deposition. The same model

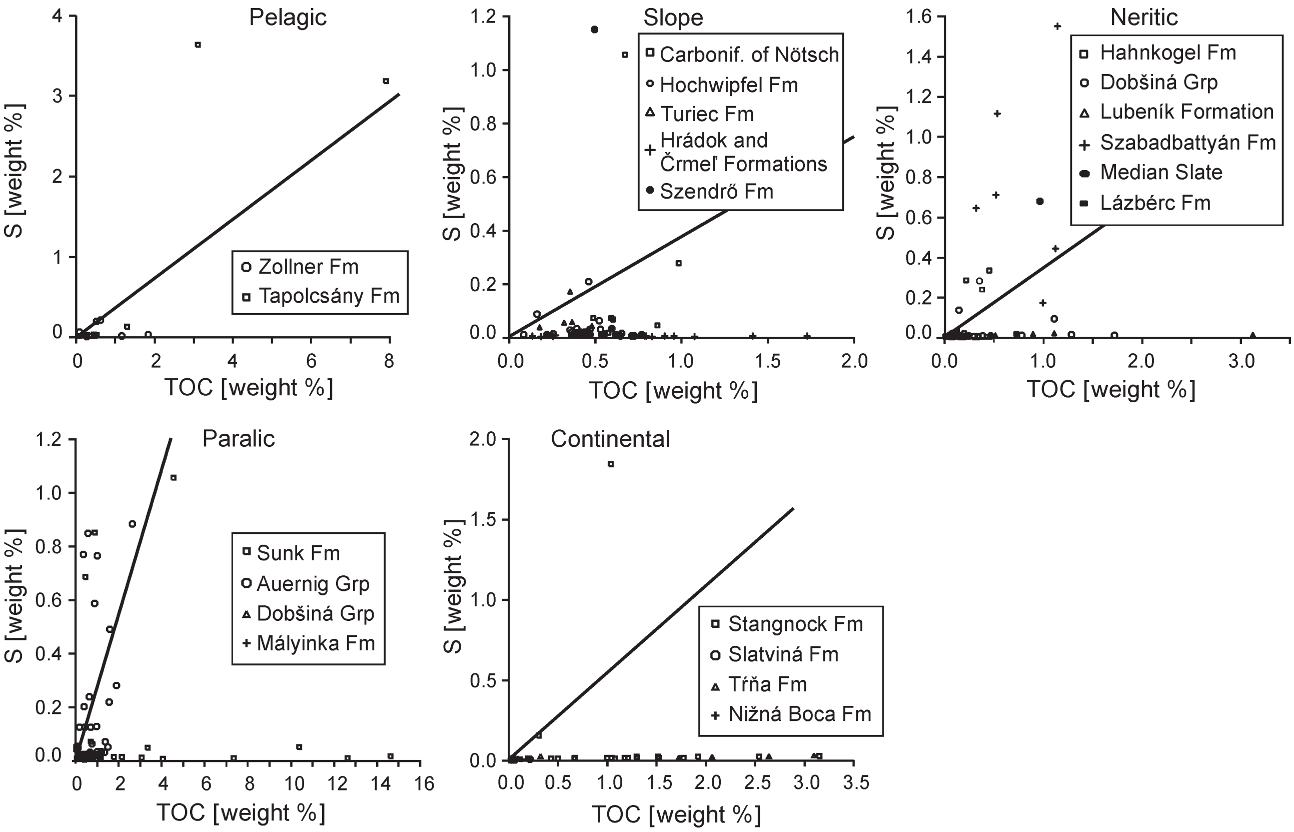

Fig. 8. TOC/S relationship in the investigated samples.

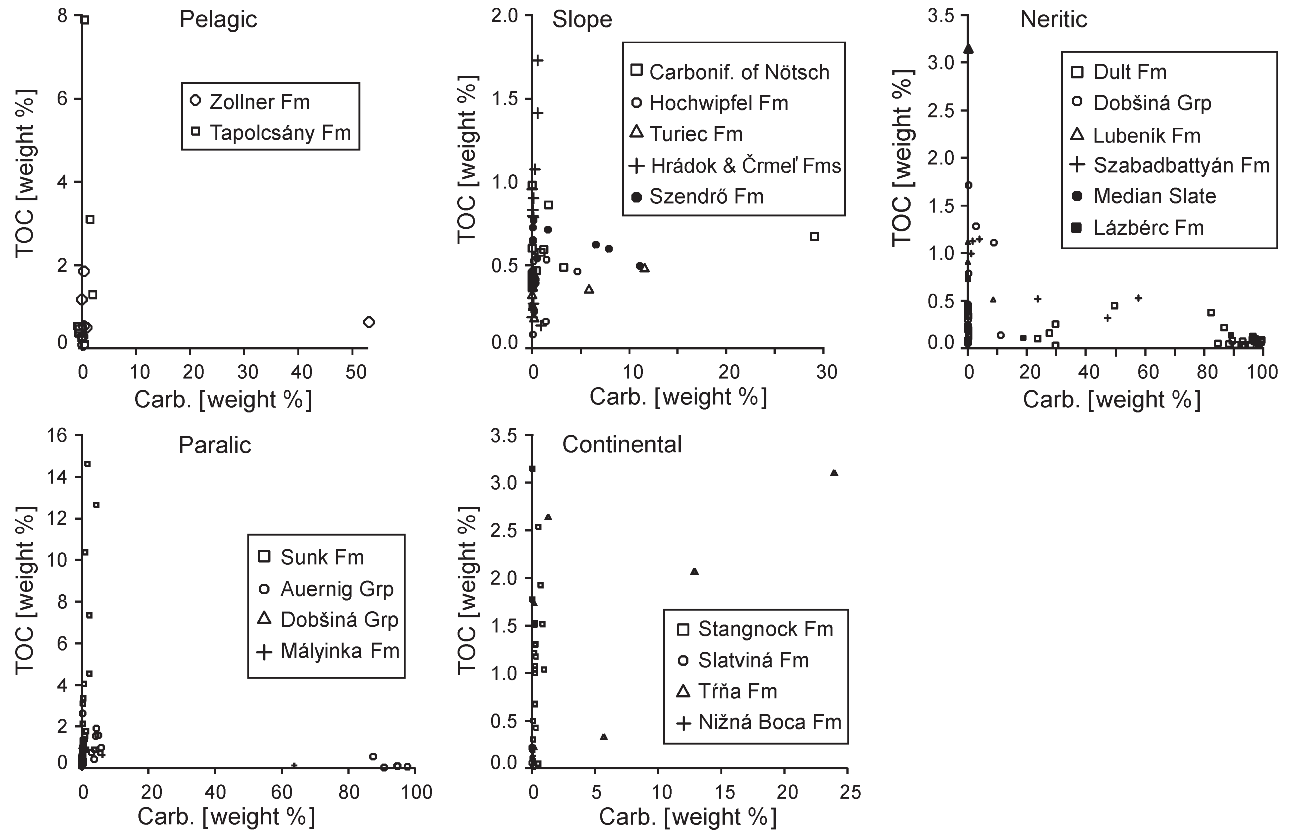

Fig. 9. TOC versus carbonate content in the investigated samples.

can be applied for the Hahngraben, Szabadbattyán and Lázbérc Formations in the platform environment and the Auernig Formation in the paralic environment. In contrast, in the continental environment the combination of a clastic controlled with an organically controlled deposition in the Tŕňa Formation is opposed to all other formations of this setting.

Conclusions

Carboniferous clastic sediments from different tectonic units of the Alpine-Carpathian-Pannonian realm were characterized by the total organic carbon content (TOC), the sulphur (S) content and the carbonate content. The obtained data were interpreted in respect to their reconstructed depositional environment.

The TOC/S ratio in pelagic and continental environments is in accordance with the ratios observed in several studies. High TOC/S ratios in slope and platform related environments are explained by a limited pyrite formation due to an increased supply of terrestrially derived pre-oxidized organic debris. A high S-content in the Szabadbattyán Formation suggests a euxinic environment in an intra-platform basin. This is a distinctive feature of all other formations of the same depositional environment.

The dominating depositional processes can be characterized by plotting the TOC against the carbonate-content. Apart from the pelagic environment, sedimentary processes in the distinct basins result in composite TOC/carbonate relationships, which are indicative for a combination of an organically controlled with a carbonatic controlled deposition. The Tŕňa Formation does not fit into this model. To explain the observed dilution trend in this formation a significant influence of the detrital input has to be assumed.

The combined use of TOC, S- and carbonate-content can give valuable information for a reconstruction of the former depositional environment. These data can also be used as a lithostratigraphic correlation tool.

The presented data base consists of 260 samples from all Carboniferous sedimentary sequences in the Alpine-Carpathian-Pannonian realm. In some formations the small number of samples prevents a statistically significant correlation. Nevertheless, the data of this study demonstrates that the analysed geochemical data can be interpreted in terms of the sedimentary environment. Therefore, the database can be used for further research in the reconstruction of the Carboniferous paleogeography in this area.

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