

A contribution to petrology of dark grey to black interbeds within Upper Permian and Triassic carbonate rocks in the area between Ljubljana and Bloke, Central Slovenia

Prispevek k petrologiji temno sivih do črnih plasti v zgornjepermskih in triasnih karbonatnih kamninah na območju med Ljubljano in Blokami

Stevo DOZET¹, Tjaša KANDUČ² & Miloš MARKIČ¹

¹Geological Survey of Slovenia, Dimičeva ulica 14, Ljubljana, SI-1000, Slovenia; e-mail: stevo.dozet@gmail.com; milos.markic@geo-zs.si

²Jožef Stefan Institute, Jamova ulica 36, Ljubljana, SI-1000, Slovenia; e-mail: tjasa.kanduc@gmail.com

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Abstract

This paper presents results of macroscopic, microscopic, chemical, and isotopic investigations of 12 samples of dark grey to black coloured interbeds occurring within Upper Permian and Triassic lime-, dolo- and marlstones in an area of Outer Dinarides between Ljubljana and Bloke in Central Slovenia. An additional sample is anthracite of the Carnian age from the Orle locality. Concentration of C_{org} in four samples is below 1 %, and in seven samples it varies between 1 and 2.3 %. Only in one sample, in the black Carnian limestone of the Lesno Brdo area, it is somewhat higher than 5 %. The highest C_{org} content, 30.61 %, was analysed in the Orle anthracite.

Chemical analysis of major elements (as oxides) showed that four samples are clearly siliciclastic mudrocks, with 65–80 % SiO₂ + Al₂O₃. Three samples are typical calcite rich – dolomite poor rocks, with high loss on ignition (LOI about 40 %) derived from calcite decomposition. Four samples are calcite – dolomite characterized rocks with LOI of 34–43 %. One sample, from the Slugovo quarry, is composed of quartz, dolomite and calcite. The anthracite sample from Orle has inorganic matter composed almost exclusively of SiO₂ + Al₂O₃ (clays), and some iron and sulphur which form pyrite.

Isotopic composition of the calcite carbon ranges from $\delta^{13}\text{C}_{\text{CaCO}_3}$ -5.7 to 1.9 ‰, whereas isotopic composition of the organic carbon varies between $\delta^{13}\text{C}_{\text{org}}$ -34.7 and -21.6 ‰. The most negative $\delta^{13}\text{C}_{\text{org}}$ value of -34.7 ‰ was analysed in a sample, which is the most organic-rich limestone. Isotopic investigations of nitrogen, expressed by $\delta^{15}\text{N}$ values, also did not express notable differences in respect to lithology. They vary between 4.6 and 9.1 ‰.

Microscopy of polished surface samples showed clearly fine grained siliciclastic, carbonate and coal composition of the treated rocks.

Izvleček

V članku predstavljamo rezultate makroskopskih, mikroskopskih, kemičnih in izotopskih preiskav 12 vzorcev temno sivih do črnih plasti, ki nastopajo znotraj zgornjepermskih in triasnih apnencev, dolomitov in laporovcev na območju Zunanjih Dinaridov med Ljubljano in Blokami. Dodatni vzorec je vzorec antracita karnijske starosti z območja Orel pri Ljubljani. Koncentracija organskega ogljika (C_{org}) štirih vzorcev je nižja kot 1 %, v sedmih vzorcih pa se spreminja med 1 in 2,3 %. Samo v enem vzorcu, z Lesnega Brda, je nekoliko višja kot 5 %. Največja vsebnost C_{org}, 30,61 %, je bila analizirana v vzorcu antracita z Orel.

Kemična analiza glavnih prvin je pokazala, da so štirje vzorci glinavci s 65–80 % SiO₂ + Al₂O₃. Trije vzorci so izrazito kalcitni s podrejenim deležem dolomita. Vsi ti trije izkazujejo visoko žaroizgubo (LOI), okoli 40 %. Štirje vzorci so kalcitno dolomitni z žaroizgubo 34–43 %. Vzorec iz kamnoloma Slugovo vsebuje kremen, dolomit in kalcit, en vzorec pa je antracit z Orel, katerega anorganska snov je sestavljena praktično v celoti iz SiO₂ + Al₂O₃ (gline) in nekaj železa ter žvepla, ki tvorita pirit.

Izotopska sestava kalcitnega ogljika se giblje v okviru vrednosti $\delta^{13}\text{C}_{\text{CaCO}_3}$ med -5,7 in 1,9 ‰, izotopska sestava organskega ogljika $\delta^{13}\text{C}_{\text{org}}$ pa med -34,7 in -21,6 ‰. Najbolj negativna vrednost $\delta^{13}\text{C}_{\text{org}}$, -34,7 ‰, je bila ugotovljena za vzorec, ki je najbolj z organsko snovjo bogat apnenec. Tudi izotopske preiskave dušika niso pokazale povezav z litološkimi razlikami. $\delta^{15}\text{N}$ se spreminja med 4,6 in 9,1 ‰.

Mikroskopska preiskava poliranih obruskov je jasno pokazala siliciklastično, karbonatno in premoško (antracitno) sestavo obravnavanih vzorcev.

Introduction

The aim of this study was to investigate basic petrologic, mainly microscopic and chemical characteristics of dark-coloured interbeds within Upper Permian and Triassic rocks in the territory south of Ljubljana, towards Bloke. More precisely, the investigated area extends between Ljubljana in the north, Postojna in the west, Velike Bloke in the south and Ribnica in the east (Fig. 1). From the geographical point of view, this area belongs to the Notranjska and Dolenjska karst area (MELIK, 1959). Tectonically, it is a part of the Notranjska-Dolenjska Mesozoic Blocks (BUSER, 1974) and geotectonically, a part of the External Dinarides (PREMRU, 2005; PLACER 2008; and references therein).

The Dolenjska and Notranjska area was firstly mapped by LIPOLD (1858). Results of this mapping that LIPOLD realized together with STACHE, were two manuscript map sheets on the scale of 1 : 75,000, namely the Višnja Gora–Cerknica and the Laze–Čabar sheets. Fifty years later, KOSSMAT (1910) wrote an Explanatory guide to the Geological map of the area between Škofja Loka and Idrija. On the Basic Geological Map of Yugoslavia 1 : 100,000, our study area extends on the map sheets Ribnica (BUSER, 1969, 1974), Kranj (GRAD & FERJANČIČ, 1974, 1976), Postojna (PLENIČAR et al., 1967, 1970) and Ljubljana (PREMRU, 1983 a,b).

As known from the Basic Geological Map of Yugoslavia 1 : 100,000, and the monograph *Geology of Slovenia* (Eds.: PLENIČAR et al., 2009) the area of External Dinarides south of Ljubljana is built up mostly of Mesozoic carbonates, underlain by Permian and Carboniferous rocks. Occurrences of Tertiary rocks are “fragmental” and will not be discussed in this paper. Within Mesozoic rocks, our study is mostly restricted to the Triassic carbonates. We include only one locality from the Upper Permian rocks. The term “Triassic carbonates” refers mostly to limestones and dolostones which are more or less bedded and massive, respectively. In general, Triassic carbonates are prevalently grey in colour. Limestones and dolostones sporadically contain thinly bedded bed-sets of either carbonate or non-carbonate (Si-Al) mudrocks, which are quite often dark grey to black in colour. As already mentioned, exactly these dark interbeds, at some localities having appearance of coaly rocks and even true coals, were target lithologic varieties of our investigations.

Concerning coals, the most known locality in the study area is that at the Orle–Klen, where an anthracite-rank coal (Rm%: 4.5) (HAMRLA, 1987) occurs in three lenticular beds (up to 0.5, 0.5 and 1.0 m thick) within Carnian (Upper Triassic) organic-rich limestone beds (SEDLAR et al. (1948). Between 1878 and 1948, this coal was mined underground in small quantities (below 1500 tons/a) (ČEŠMIGA, 1959). Some other coal layers, that are currently considered to occur mostly in the Carnian beds, but are of lower extent than those at the Orle–Klen locality, were mentioned in the works of KOSSMAT (1902), KRAMER (1905), ŠPOLJARIČ

(1917), and PETRASCHECK (1926, 1926/29, 1927), and finally summarized to a great part by RAKOVEC (1955) in the book *History of Ljubljana*. In this book, RAKOVEC (1955) described coal occurrences in the borderland of the Ljubljana Moor and wider surroundings. He worked out occurrences of coal and anthracite, respectively, in Podlipska dolina, Drenov Grič, Lesno Brdo area, Klen (at Orle), Orle, eastern borderland of the Ljubljana Moor, Lipalnica south of Horjul, Vnanje gorice, and near Dule. ŽLEBNIK & GRAD (1953) mapped »Wengen and Raibl beds« between Drenov Grič, St. Jošt and Butajново. PLENIČAR et al. (1970) quoted coal lenses at Dule near Škofljica, Grič at Ligojna and Lipalnica south of Horjul. BUSER (1974) described Carnian beds with coal at Orle. DOZET (1979, 2002) studied lito- and biostratigraphy of the Carnian beds south of Ljubljana and described a paralic shallow-water coal-bearing formation termed as the Grosuplje–Orle Formation. Within this formation, bituminous coal and anthracite, respectively, is interpreted to occur within limestones of the lower part of the Julian stratigraphic sequence. DOLENEC & JELEN (1987) studied isotopic composition of carbon and oxygen of the Carnian beds in the Lesno Brdo quarry, and three years later JELEN (1990) published his study on litostratigraphy, bivalves and their paleobiological significance in the Carnian carbonate-clastic beds as exposed in two Lesno Brdo quarries. At the same locality, OBLAK (2001) studied Carnian Foraminifera. In 1990, a short contribution on fossil lamellibranch fauna from the Carnian beds at Orle was published by JURKOVŠEK & JELEN (1990).

Although coal resources in the Triassic beds, and also in the Pre-Triassic as well as in younger Mesozoic beds, are presently recognised as out of any economic value in Slovenia, dark varieties of Mesozoic rocks did invoke some attention as potential source rocks for hydrocarbon generation. In the area of External Dinarides in Slovenia, these rocks were for the last time under more detailed investigations in the 1980s. A published work about the oil and gas potential of carbonates of External Dinarides in Slovenia, based on almost 200 samples, is that of OGORELEC et al. (1996). Maturity of organic matter versus clay mineralogy of Carboniferous to Tertiary sediments was regionally studied on nearly 1000 samples by RAINER et al. (2002).

An overview study of isotopic composition of O and C of Mesozoic carbonates on almost 300 samples was carried out by OGORELEC et al. (1999). Isotopic composition of different geological materials and media, and geochemical processes leading to their characteristic isotopic composition is described in PEZDIČ (1999). Basic research work in Slovenia referring to C and O isotopic composition at the transition from Permian to Triassic strata was made and published by DOLENEC & OGORELEC (2001), DOLENEC & RAMOVŠ (1998), and DOLENEC et al. (1999 a,b, 2000, 2003, 2004, 2006).

Methods

Our study is based on regional geological mapping (1 : 10,000 and 1 : 25,000) of the area south of Ljubljana towards Bloke, and field sampling of dark coloured (organic-rich) rock varieties, either siliciclastics or carbonates. By the field outlook, the samples resembled to different organic matter rich rocks, as coaly, sapropelic, oil and/or gas sourcing, and oil shale rocks, respectively. All sites of sampling are shown on the map in Fig. 1 and were photographed (Figs. 2a-k). Litho-stratigraphic column of the rocks investigated and positions of samples 1 (bottom) to 13 (top) are shown in Fig. 3. The column was made by compilation of regional geological data from the map sheets Ribnica (BUSER, 1969, 1974), Kranj (GRAD & FERJANČIČ, 1974, 1976), Postojna (PLENIČAR et al., 1967, 1970), and Ljubljana (PREMRU, 1983 a,b) of the Basic Geological Map of Yugoslavia 1 : 100,000, and by regional geological mapping of the first author of this paper in recent years.

A representative fragment of each sample was photographed to show dark colour of the samples and their structure (Fig. 4). Colour was defined using the Rock Colour Chart (RCCC, 1970).

In addition to the field/stratigraphic/tectonic positioning of the samples, further aim of this study was to analyse these samples more in detail, using microscopic and bulk chemical analyses.

For microscopic investigation, polished blocks with reflective surfaces, as in ore and/or coal micro-petrography, were prepared – since more coaly materials were expected at the beginning of the investigation. Polished blocks were inspected under normal white reflected polarized light.

Preparation of samples for chemical analysis was done at the Geological Survey of Slovenia according to well established procedure as practiced by the survey's geochemical group. Samples were dried and pulverized, 10 grams in weight, and sent to the ACME (Canada) laboratory (www.acmelab.com – Acme Labs Schedule of Services & Fees 2009-2010). They were analysed on major “rock-forming” elements (as oxides) by the method of inductively coupled plasma (ICP) – emission spectrometry (ACME Group 4A). Total carbon and sulphur, graphite carbon and organic carbon were analysed by Leco (combustion infrared detection technique) (ACME Group 2A). Results of major elements analysis, together with loss on ignition (LOI) at 1000 °C, and forms of carbon are given in Tab. 1.

The isotopic composition of carbon and nitrogen was determined using a Europa 20-20 continuous flow IRMS ANCA-SL preparation module. 20 mg of homogenized sample was weighed in a tin capsule for nitrogen and 1 mg for carbon analysis. Samples for carbon analysis were pre-treated with 3 molar HCl to remove carbonates. The isotopic composition of nitrogen and carbon was determined after combustion of the capsules in a hot furnace (temperature 1000 °C). Generated products were reduced in a Cu tube (600 °C), where excess O₂ was absorbed. H₂O was trapped

on a drying column composed of MgClO₄. Gases were separated on a chromatographic column and ionized. NBS 22 (oil) and IAEA N-1 (ammonium sulfate) reference materials were used to relate the analytical results to the VPDB – Vienna Pee Dee Belemnite (karbonat fosilne školjke *Belemnitela americana*), and AIR standards as follows:

$$\delta^{13}\text{C}_{\text{sample}} (\delta^{15}\text{N}_{\text{sample}}) = ((R_{\text{sample}} - R_{\text{RM}}) / R_{\text{RM}})$$

Where:

R_{sample} - ratio $^{13}\text{C}/^{12}\text{C}$ in sample ($^{15}\text{N}/^{14}\text{N}$ for $\delta^{15}\text{N}$ in sample)

R_{RM} - ratio $^{13}\text{C}/^{12}\text{C}$ in reference material, ratio $^{15}\text{N}/^{14}\text{N}$ for $\delta^{15}\text{N}$ in reference material

$\delta^{13}\text{C}_{\text{CaCO}_3}$ in organic rich carbonate rocks (except anthracite sample) could only be measured in samples where beam area was above detection limit. 10 mg of sample was first flushed with He and then transformed to CO₂ by H₃PO₄ acid treatment. CO-1 and NBS 19 were used as reference materials. The carbon isotope composition of carbonate ($\delta^{13}\text{C}_{\text{CaCO}_3}$) was measured with a Europa Scientific 20-20 continuous flow IRMS ANCA - TG preparation module.

Stable isotope results are expressed in the conventional delta (δ) notation, defined as per mil (‰) deviation from the reference standard VPDB. Precision of working standards was $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{15}\text{N}$, respectively.

Description of sampling localities and investigated samples

On the basis of data from the already cited geological map sheets of the Basic Geological Map of Yugoslavia (PLENIČAR et al., 1967, 1970; BUSER, 1969, 1974; GRAD & FERJANČIČ, 1974, 1976; PREMRU, 1983 a,b), and self observations, we submit the following description of the sampling localities that cover the study area in Fig. 1.

Gorenji Lazi quarry (sample 1)

The Gorenji Lazi quarry is situated about one kilometre to the NW of Žlebič (Fig. 1). The quarried rocks (Fig. 2a,b) are the Upper Permian carbonates (Fig. 3) of the Žažar (Bellerophon) beds (RAMOVŠ, 1978) (or the Žažar Formation). The Upper Permian carbonates in the Gorenji Lazi quarry consist of dark dolomites, limestones, oolitic limestones and marls. From the Gorenji Lazi quarry, sample 1 was taken from a greyish black (N2) dolostone (Figs. 3, 4).

Črni potok (sample 2)

Črni potok locality (Fig. 1) (S of Velika Slevica) refers to a 600 m high hillock at Jazbine, which is built up of Scythian, Anisian and Cordevolian beds. For our study, especially interesting were the Scythian beds (Fig. 3) that are composed of rosy and yellowish grey, sandy (micaceous), platy and thin-bedded dolomite succession with some interbeds of a dark platy limestone. In the upper-

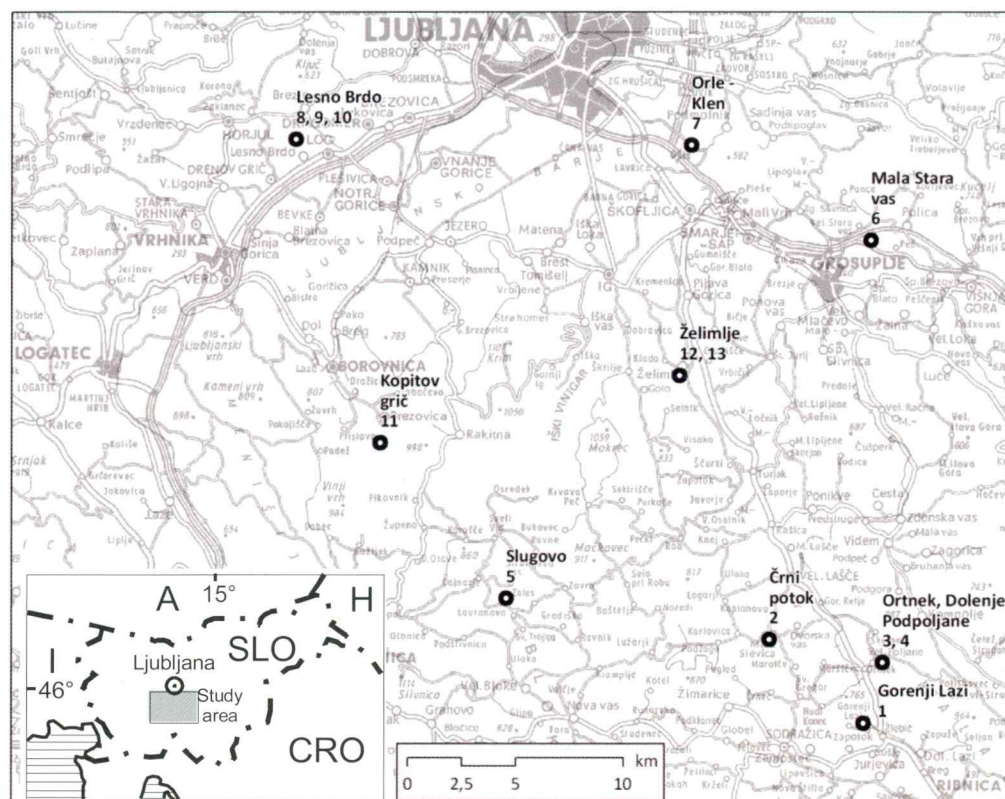


Fig. 1.
Map of sampling sites
Sl. 1.
Karta odvzema vzorcev

most part of the Scythian beds occurs 3.5 to 4.5 m thick bedset of dark grey to black (coaly like) carbonate rocks (mainly dolostone). The uppermost Scythian sedimentary succession is overlain by about 60 m thick sequence of pale yellowish grey bedded and massive Anisian dolomite, covered by thick-bedded medium light grey biotransparitic and biolithitic limestones of the Cordevolian age. Sample 2 was taken from greyish black Scythian dolostone (Figs. 3, 4).

Podpoljane quarry (sample 3)

The Dolenje Podpoljane quarry is situated at the road Velike Lašče – Ortnek (Fig. 1) along which variegated Lower Triassic (Scythian) clastic sediments and dolostones are exposed. Sample 3 was taken from the greyish black dolostone (Figs. 3, 4). Scythian beds in the Podpoljane quarry (Fig. 2c) are tectonically highly deformed. They form a syncline dipping approximately to the north. Ten metres thick synclinal core is built of black platy carbonate sediments (limestone, dolostone, marlstone) intercalated by up to 20 cm thick seams of dark grey to black (coal-like) mudstone (Fig. 2c). This dark grey to black organic matter enriched sequence, underlain by bedded and platy yellowish grey to grey sandy dolostone with a distinctive parallelepiped cleavage (Fig. 3) belongs most probably to the Brinje (Cencenighe) member of the Višnja Gora Formation of the Uppermost Scythian age (DOZET, 2000).

Ortnek (sample 4)

At Ortnek, at the cross-road Velike Lašče – Žlebič and Ortnek – Velike Poljane (Fig. 1), exposed are Anisian and overlying Ladinian rocks (Fig. 2d,

3). Thirty metres thick Anisian lithological interval is composed of light massive dolostone. It is concordantly overlain by the Ladinian carbonate sequence that may be separated in two parts. The lower part is composed of greyish black limestones alternating with dark olive grey marlstones (Fassanian), whereas the upper part is composed of rosy and reddish brown bedded intrasparitic limestones with red marlstones, claystones and black limestones (Langobardian). In the described sequence, Ladinian conodonts have been determined. Within the Anisian dolomite succession, a 7.5 m thick horizon of black marlstone and coaly claystone containing several intercalations of black dolomite, dolomitic breccia and up to 25 cm thick seams and bodies of hard coal occurs.

Slugovo quarry (sample 5)

The Slugovo quarry is situated in the Cerkljenščica valley N of Bloke (Fig. 1). Ladinian dark coloured bedded limestone with dark, organic matter enriched interbeds of platy micritic limestone (mudstone), marlstone and claystone is exposed in this quarry (Fig. 2e). Sample 4 (Figs. 3, 4) was taken from the micritic limestone. In a broader frame, these rocks belong to the lower part of the so called Slugovo Formation (RAMOVŠ, 1994/95; DOZET & BUSER, 2009). The upper unit of the Slugovo Formation is built of medium-grey, grey and medium dark grey, sometimes banded biomicritic, micritic and intramicritic limestone. The uppermost part of the upper unit consists of platy and bedded, dark micritic limestones and interbeds of reddish marlstones and shaly claystones. According to RAMOVŠ (1995), conodonts indicate the Upper Fassanian age of the investigated rocks.

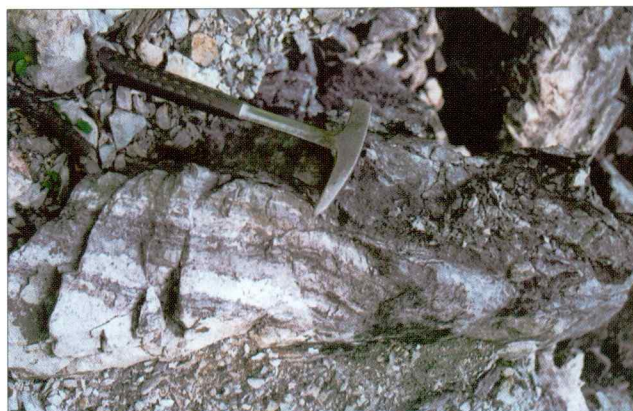
Fig. 2. Photographs of sample sites – for sample position and age see also Fig. 3, and for composition see Tab 1 (all photographs from the years 2005 to 2010):

Sl. 2. Fotografije mest odvzema vzorcev – za položaj vzorcev in starost glej tudi sliko 3, za sestavo pa tabelo 1:



a) Site of **sample 1**: Sample 1 was taken from a lense-like bed, 0.5–1.0 m thick, of greyish-black carbonate mudstone (Tab. 1) within carbonate Upper Permian beds in the Gorenji Lazi quarry at Ortnek.

a) Mesto odvzema **vzorca 1**: vzorec 1 je bil vzet iz 0,5–1,0 m debele lečaste plasti sivo-črnega karbonatnega muljevca (tab. 1) znotraj karbonatnih zgornjepermskih plasti v kamnolomu Gorenji Lazi pri Ortneku.



b) Upper Permian light stromatolitic bedded dolomite above the greyish-black (sample 1) carbonate mudstone (Gorenji Lazi quarry).

b) Zgornjepermski svetli stromatolitični plastnati dolomit nad sivo-črnimi karbonatnimi muljerci (vzorec 1).



c) Site of **sample 3**: Several metres thick horizon of platy black limestone with thin black (coaly-like) mudstone layers is lying between two lighter bed-sets of dolostone. Sample 3 is from black mudstone. Age of the whole sequence is Upper Scythian. Locality is the Podpoljane quarry at Velike Lašče.

c) Mesto odvzema **vzorca 3**: Nekaj metrov debelo zaporedje plastnatega in ploščatega črnega apnenca, ki se menjava s plastmi črnega muljevca, leži med dvema paketoma plastnatega dolomita. Vzorec 3 je vzet iz črnega muljevca. Starost plasti v celoti je zgornjeskitijska. Lokacija je kamnolom Podpoljane pri Velikih Laščah.



d) Site of **sample 4**: On the upper right of the photo is black bedded limestone (strongly weathered at the surface), from which sample 4 was taken. Lighter rock below the black limestone and on the left side of the photo is light-grey massive Anisian dolostone. Locality is Ortnek.

d) Mesto odvzema **vzorca 4**: Na desni strani fotografije je črn plastnat apnenec (na površini močno preperel), iz katerega je bil vzet tudi vzorec 4. Pod njim in na levi strani fotografije je viden svetlo-siv anizijski dolomit. Lokalnost je odcep od Ortneka proti Velikim Poljanam pri Ortneku.

Mala Stara vas (sample 6)

At this locality at Grosuplje (Figs. 1, 2f, 3) were observed alternating black to grey and light strata of limestones of the Carnian age. The black lithological varieties, from which sample 6 was taken (Fig. 4), were found to be prevalingly non-carbonate. Due to tectonic effects, the rock is highly crushed at this locality.

Orle–Klen (sample 7)

The Orle–Klen locality is situated about ten kilometres SE of Ljubljana (Figs. 1, 2g). It is a part of the Grosuplje–Orle Formation, a variegated succession of paralic and shallow marine sedimentary rocks between the Cordevolian *Di-*

plopura limestone or/and dolomites and the Main Dolomite Formation. The Grosuplje–Orle Formation is therefore of the Julian–Tuvanian age and is composed of colourful succession of limestones and marlstones interbedded by conglomerates, breccias, sandstones, shales and tuffs (Fig. 3). A particularity of this rock succession is coal of the anthracite rank (Rm%: 4.5 – by HAMRLA, 1987) that lies in the lower part of the Grosuplje–Orle Formation, i.e. in the Julian beds. Coaly matter, black shale and black limestone strata are visible in Fig 2g. As described in the older documentation, coal occurs in the form of up to 1.5 m thick seams as well as in plates and lenses. The thickness of the coal is variable in horizontal and vertical direction. Due to intensive tectonics, the coal thick-

Fig. 2. Photographs of sample sites – for sample position and age see also Fig. 3, and for composition see Tab 1 (all photographs from the years 2005 to 2010):

Sl. 2. Fotografije mest odvzema vzorcev – za položaj vzorcev in starost glej tudi sliko 3, za sestavo pa tabelo 1:



e) Site of **sample 5**: This photo shows bedded Ladinian limestone. Very thin beds of dark marlstone and black shale occur as inter-layers at the bottom of the shown sequence. Sample 5 was taken from black shale. Locality is the Slugovo quarry in the Cerknishica valley N of Bloke.

e) Mesto odvzema **vzorca 5**: Slika prikazuje plastnat ladinijski apnenec v kamnolomu Slugovo v dolini Cerknishice severno od Blok. Zelo tanke med-plasti (lezike) laporja in črnega glinavca nastopajo zlasti v spodnjem delu fotografirane sekvence. Vzorec 5 je bil vzet iz črnega glinavca.



f) Site of **sample 6**: Alternation of black and light strata of the Carnian age termed as the Grosuplje-Orle Beds. Sample 6 is from Si-rich black strata. Locality is Mala Stara vas at Grosuplje.

f) Mesto odvzema **vzorca 6**: Menjavanje črnih in svetlih karnijskih plasti, imenovanih Grosupeljsko-orelske plasti. Vzorec 6 je bil vzet iz Si-bogatih temnih plasti. Lokalnost je Mala Stara vas pri Grosupljem na Dolenjskem.

ness can locally enlarge up to 4 m. Coal seams pass laterally and vertically in coaly shales and claystones. At the Klen locality near Orle, three anthracite seams (50, 50 and 120 centimetres thick) were mined in the past (until 1948). Entrance into the mine is still visible (Fig. 2h). Sample 7 – anthracite (Fig. 4) – was taken from a waste dump site close to the mine.

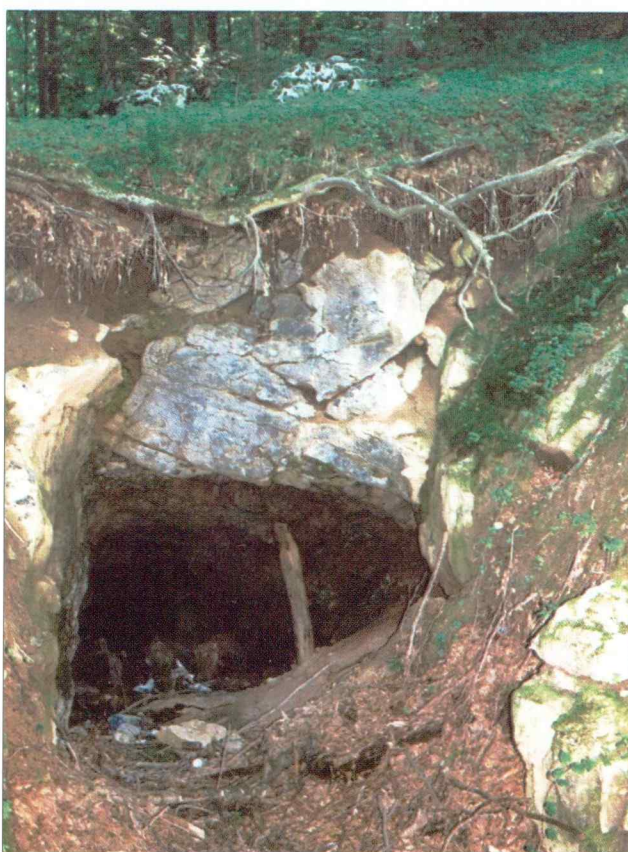
Lesno Brdo (samples 8, 9, and 10)

In the Lesno Brdo area, which is situated about 10 km SE from Ljubljana (Fig.1) and N of Drenov Grič, three quarries of limestone are known for



g) Site of **sample 7**: Sample 7 is anthracite which occurs in black strata like visible at the right of the photo. The black strata are composed of black shale, black limestone, and of thin beds (< 1 m) and lenses of anthracite of a limited spatial distribution. Anthracite was mined before 1948 in the Orle-Klen mine in the close vicinity. The black formation is underlain by typical platy violet-red jasper-quartz-carbonate sandstone on the left side of the photo. Whole sequence is of the Carnian (Julian-Tuvalian) age with typical macrofauna of this stage.

g) Mesto odvzema **vzorca 7**: Vzorec 7 je antracit, ki se nahaja v črnih plasteh, kot jih vidimo na desni strani fotografije. Te črne plasti sestavljajo muljevci, plasti črnega apnenca in leče ter plasti (< 1 m) antracita, ki so ga odkopavali pred letom 1948 v bližnjem rudniku Orle-Klen. Pod »črnimi plastmi« ležijo značilne plasti vijolično-rdečega jaspisno-kremenovo-karbonatnega peščenjaka (na levi strani fotografije). Plasti so v celoti karnijske (julske-tuvalske) starosti z značilno karnijsko makrofavno.



h) Entrance into the abandoned coal (anthracite) mine Orle-Klen. Dark limestone in the roof of the mine entrance is Carnian limestone, whereas lighter rock at the left and right of the photo is Cordevolian dolostone.

h) Vhod v opuščeni rudnik antracita Orle-Klen. Temen apnenec v stropu rova je karnijski apnenec, svetlejša kamnina na levi in desni strani slike pa je kordevolski dolomit.



i) Site of **samples 8, 9 and 10**: Dark bedded limestone with interbeds of black marlstone, limestone (samples 8 and 9) and claystone (sample 10). All three samples are taken from the lowermost three interbeds. Locality is the Lesno Brdo quarry.

i) Mesto odvzema **vzorcev 8, 9 in 10**: Temni plastnati apnenec z vmesnimi tankimi plastmi črnega laporja, apnenca (vzorca 8 in 9) in glinavca (vzorec 10). Vsi trije vzorci so odvzeti iz spodnjega dela prikazanega zaporedja plasti.



j) Site of **sample 11**: Geological hammer marks a bed-set of black marl and shale with a leaf and splitter disintegration pattern. Black bed-set lies within medium dark grey bedded fine-sparry dolostone of the Upper Triassic age. Sample 11 is taken from shale indicated by a hammer. Locality is Strmec at Borovnica.

j) Mesto odvzema **vzorca 11**: Geološko kladivo označuje plasti črnega (do sivega) laporja in glinavca z listasto in iverasto krojtvijo, ki ležijo med plastmi srednje-sivega plastnatega drobnosparitnega dolomita zgornjetriasne starosti. Vzorec 11 je iz glinavca. Lokalnost je Strmec pri Borovnici.

centuries by good quality building and statuary natural stone (VESEL et al., 1992; MIRTIC et al., 1999). The three quarries extend approximately in the W–E direction. The western one is opened in the Cordevolian limestone of a rosy colour, micritic, and with lenses and nests of red, pur-



k) “Main dolomite” (“Hauptdolomit”) i.e. Upper Triassic (Norian and Rhaetian) light dolostone in the Želimplje quarry. It contains very rare and very thin black to dark grey beds or laminas of bituminous carbonate or siliciclastic mudstones. **Samples 12 and 13** were taken from such thin lithologies – sample 12 being a siliciclastic mudstone whereas sample 13 a carbonate mudstone

k) Norijsko-retijski »glavni dolomit« v kamnolomu Želimplje. Ta dolomit lahko vsebuje zelo tanke plasti temnega karbonatnega ali pa siliciklastičnega muljevca z vonjem po bitumnu. Iz takih zelo tankih plasti sta bila odvzeta **vzorca 12** (siliciklastični muljevec) in **13** (karbonatni muljevec).

ple and greenish claystone (paleo-carstification). Laterally out of the quarry, and vertically downwards, this limestone transits to a light grey Cordevolian sparitic dolostone and limestone with a typical alga *Diplopora annulata* Schafhäütl. The two quarries to the east are opened in a prevalently dark grey to black micritic limestone beds (Figs. 2i, 3) from which samples 8 and 9 were picked out. In a jargon, these two quarries, which are not actively exploited at the present, were called “the black quarries”. Dark limestone was defined to be of the Julian (middle Carnian) age. However, the basement of this black limestone succession, which lies discordantly upon the Cordevolian dolomite, is composed of yellowish grey, somewhere poorly oolitic claystone passing locally into the iron-rich oolitic bauxite or a transgressive limestone conglomerate with a red clayey and limonitic groundmass. Upwards follows a clastic rock unit, which is about 15 m thick. It is composed of dark marlstone, mudstone and claystone (sample 10) with several seams of anthracite. Between 1900 and 1905, three of four known anthracite seams have been ascertained there with exploration trenches and a shaft. Individual seams were from 1.0 to 1.5 m thick. Between 1901 and 1902, the anthracite was excavated but very soon later the exploitation was stopped. Namely, due to numerous faults and displacements along the fault-surfaces, the coal seams disappeared already at short distances. A great problem was also underground-water. The anthracite-bearing unit is overlain by about 20 m thick sequence of a dark thick-bedded limestone, intercalated by shaly marlstone and claystone.

Borovnica, Kopitov grič, Strmec (sample 11)

Kopitov grič (Fig. 1) is a well known locality by occurrences of Carnian bauxite being formed as the consequence of chemical weathering of aerally exposed carbonate rocks of either Cordevolian

lian or Ladinian and Anisian carbonates (RAMOVŠ, 1953; BUSER, 1965, 1976; DOZET, 1975, 1978, 1979, 2004; CELARC, 2008). It is also known by occurrence of oolitic iron ore. Carnian strata above bauxite horizon are mainly clastites and limestones. Carnian beds pass gradually into the Norian-Rhetian dolostone (Main dolomite Formation). Light and dark, platy and bedded, fine-laminated and fine-stromatolitic dolostones with dark, bituminous marlstone and shale (Fig. 2j) form the »transitional beds« between the »true« Carnian and »true« Norian-Rhetian carbonates (Fig. 3). Sample 11 (Fig. 4) was chosen from a shale. Owing to an intensive weathering, the dark marlstone and shale became yellowish grey. Within marlstone, there occur sporadic inter-beds and lenses of hard coal and coaly shale, and marlstone.

Želimplje quarry (samples 12 and 13)

The Želimplje quarry (Figs. 1, 2k) is opened in a very typical light and bedded Main Dolomite Formation (»Hauptdolomit«) of the Norian age

(Fig. 3). This dolostone is micritic and fine-stromatolitic, respectively. What is interesting for this paper is that it contains about 25 cm thick and 7 m long lens-like seam of a very dark grey marlstone/claystone having an appearance of coaly shale. Samples 12 and 13 (Fig. 4) were analysed from the mentioned black to dark grey lens-like seam.

Results of chemical and microscopic analyses and discussion

Geologic position of investigated samples is given in Fig. 3. Chemical analysis of major elements (as oxides), is given in Tab. 1. As visible from Fig. 3, only one sample is Permian, whereas all others are Triassic.

Colour of samples varies from black (N1) to medium dark grey (N4) (Fig. 4). Structure of samples is massive to laminar. All samples are well lithified.

Chemical analysis shows that the samples are composed predominantly of either $\text{SiO}_2 + \text{Al}_2\text{O}_3$ or

STAROST AGE		GEOLOŠKI STOLPEC GEOLOGIC COLUMN	VZOREC SAMPLE	LOKACIJA LOCALITY	LITOLOGIJA LITHOLOGY	
P E R M I A N T R I A S S I C	Z G O R N J I U P P E R S P O D N J I S L O W E R M I D D L E			Kamnolom Želimplje Želimplje quarry	Glavni dolomit Main Dolomite ("Hauptdolomit")	
			13			
			12			
				11	Kopitov grič (Borovnica)	Temnosiv dolomit, laporovec Dark grey dolostone, marlstone
				10	Lesno Brdo	Temni, plastnati apnenci in ploščasti laporovci
				9	Lesno Brdo	Dark bedded limestones and plated marlstones
				8	Lesno Brdo	
				7	Orle - Klen	Temni apnenci - Dark limestones
				6	Mala Stara vas (Grosuplje)	Temni apnenci - Dark limestones
				5	a) Kamnolom Slugovo Slugovo quarry	Temni apneneci in laporovci Dark limestones and marlstones
		4	b) Ortnek	Svetel in temen dolomit, laporovec Light and dark dolostone, marlstone		
		3	Kamnolom Podpoljane Podpoljane quarry	Temen apnenec, dolomit, laporovec, Dark limestone, dolostone, marlstone		
		2	Črni potok (Mala Slevica)	Rumenkastosiv peščen dolomit Yellowish grey sandy dolostone		
	P E R M I A N U P P E R	150-350 m		1	Kamnolom Gorenji Lazi Gorenji Lazi quarry	Temni dolomiti, apnenci, oolitni apnenci in laporovci Dark dolostones, limestones, oolitic limestones es and marlstones

Fig. 3. Compiled litho-stratigraphic column of the studied rock-frame. Signed are positions of studied samples.

Sl. 3. Litostratigrafski stolpec obravnavanih kamnin z označenimi mesti odvzetih vzorcev.

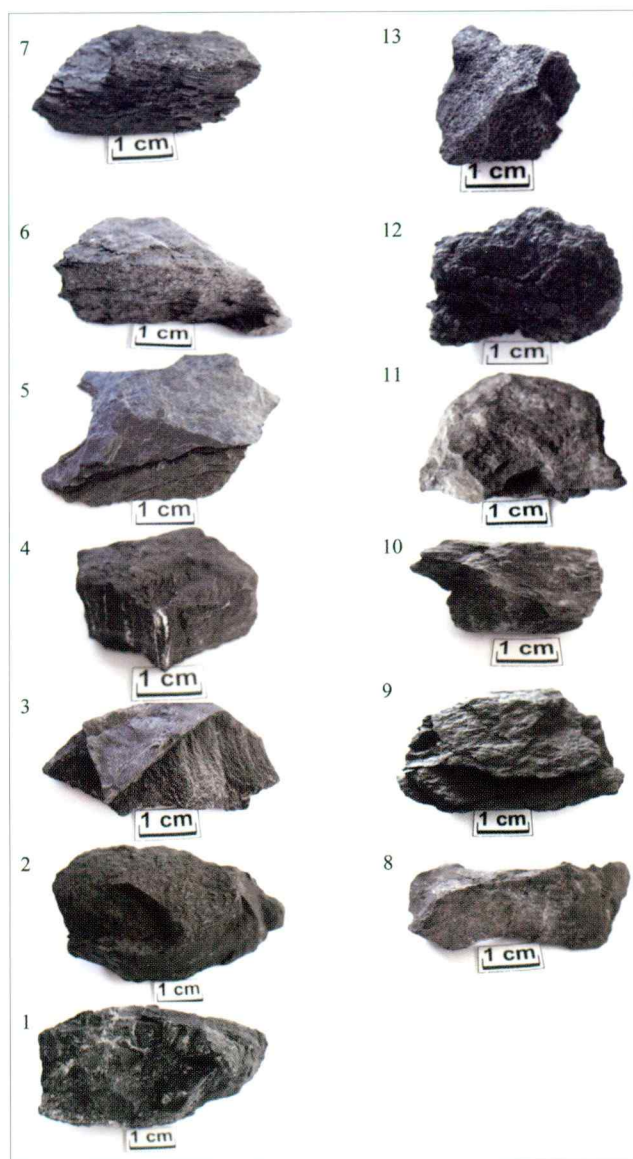


Fig. 4. Photographs of 1-13 samples – note their dark colour (N1 - N4) and structure from massive to laminated.

Sl. 4. Fotografije vzorcev 1-13. Značilna je njihova temna barva (N1-N4) ter tekstura, ki se spreminja od masivne do laminirane.

CaO + MgO components. $\text{SiO}_2 + \text{Al}_2\text{O}_3$ versus CaO + MgO relation for all samples numbered 1–13 is plotted in Graph 1. Prevalingly $\text{SiO}_2 + \text{Al}_2\text{O}_3$ samples are termed mudrocks (mudstones if massive and shales if laminated), whereas prevalingly CaO + MgO are termed carbonate mudrocks, if strongly reacting with a diluted HCl, they are called limestones.

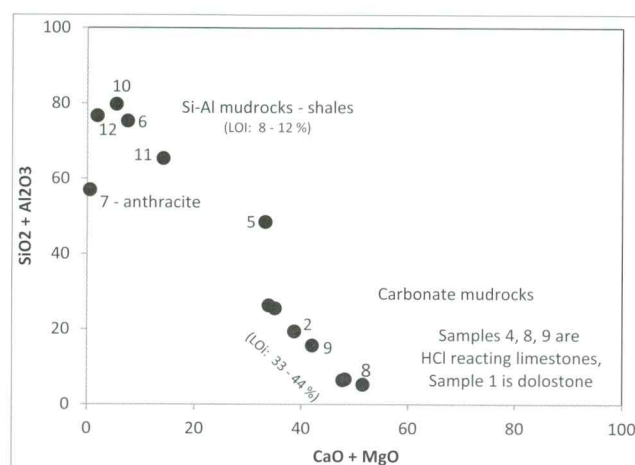
Table 1.

Bulk chemical and isotopic composition of investigated samples 1-13. For location of samples see Figs. 1, 2 and 3. Chemical analyses were done at the ACME Laboratory (Canada), isotopic analyses were done at the Jožef Stefan Institute.

Tabela 1.

Kemična in izotopska sestava preiskanih vzorcev 1-13. Za mesta odvzemov vzorcev glej slike 1, 2 in 3. Kemične analize so bile narejene v laboratoriju ACME (Kanada), izotopske pa na Inštitutu Jožef Stefan.

Age	Samples		Colour	HCl react.	Major Element Analysis (as major oxides) and Loss on Ignition (LOI)													TOT/S	CaO + MgO	SiO ₂ +Al ₂ O ₃	C _{org}	δ ¹³ C _{org}	δ ¹³ C _{CaCO₃}	δ ¹⁵ N
	Fld. No.	No.			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃	LOI	TOT/C							
					%	%	%	%	%	%	%	%	%	%	%	%	%							
Upper Triassic	204	13	N3		19.17	7.11	2.79	13.01	20.97	0.08	2.53	0.2	0.03	0.04	<0.002	33.8	9.9	0.51	33.98	26.28	1.9	-24.6	1.6	6
	205	12	N1		53.13	23.51	2.96	1.54	0.34	0.17	7.76	0.52	0.08	<0.01	0	9.8	2.35	0.98	1.88	76.64	2.3	-24.5	n.a.	9.1
	210	11	N4		53.01	12.39	2.47	11.26	2.9	0.23	5.15	0.25	0.02	<0.01	<0.002	12.1	1.22	<0.02	14.16	65.4	0.24	-21.6	n.a.	n.a.
	201	10	N2		57.8	21.9	1.1	0.54	4.84	0.48	1.82	0.63	0.03	0.01	0	10.7	2.18	0.12	5.38	79.72	1.06	-24.5	-5.7	5.1
	202	9	N2	Yes	11.77	3.92	1.07	0.77	41.31	0.13	0.7	0.13	0.25	0.06	0	39.8	14.3	0.23	42.08	15.69	5.36	-34.7	-2.2	7.7
	203	8	N2	Yes	3.6	1.66	1.61	0.92	50.7	0.06	0.35	0.06	<0.01	0.02	<0.002	40.9	12.2	0.75	51.59	5.26	1.54	-24.8	-0.2	6.2
	211	7	N1		37.1	19.91	2.83	0.38	0.14	0.2	0.42	0.77	<0.01	<0.01	0.01	38.1	30.6	1.39	0.52	57.01	30.61	-23.5	n.a.	6.9
mid. T	213	6	N4		60.71	14.6	2.36	0.51	6.99	0.48	3.86	1.93	0.02	0.01	0.01	8.2	1.8	0.6	7.5	75.31	0.4	-24	0.2	4.6
	206	5	N1		47.36	1.14	0.36	25.0	8.31	0.17	0.33	0.03	<0.01	<0.01	<0.002	16.9	3.42	<0.02	33.35	48.5	0.35	-22	-0.1	n.a.
	212	4	N1	Yes	4.04	2.39	1.65	16.56	31.22	0.03	0.4	0.08	0.01	0.06	<0.002	43.2	13	0.52	47.78	6.43	1.92	-30.7	1.4	6.8
low. T	208	3	N2		18.32	7.19	2.29	14.91	20.21	0.11	2.44	0.24	0.06	0.04	0	33.9	8.94	0.62	35.12	25.51	0.73	-27.6	0.3	6
	207	2	N2		12.62	6.77	1.63	14.75	24	0.05	1.13	0.22	0.05	0.05	0	38.4	11	0.12	38.75	19.39	1.84	-29.9	1.9	n.a.
up	209	1	N2		5.28	1.41	0.58	18.8	29.5	0.03	0.38	0.04	<0.01	0.02	<0.002	43.4	12.6	0.36	48.27	6.69	1.15	-26.5	0.7	n.a.



Graph 1. CaO + MgO versus SiO₂ + Al₂O₃ ratio
Graf 1. Razmerje CaO + MgO proti SiO₂ + Al₂O₃

Clearly limestones are samples number 4, 8 and 9, intensively reacting with 1:10 diluted HCl acid (Tab. 1, Graph 1). These samples are characterized by highly predominant CaO content and high loss on ignition (LOI) – between 40 and 43 %. Their CaO + MgO content is 42–52 %. In the Upper Triassic samples 8 and 9, MgO content is below 1 %, whereas MgO content is relatively much higher in the Middle Triassic sample 4 in which MgO : CaO ratio is close to 1 : 2. All three samples are black to greyish-black (Fig. 4). Sample 9 is outstanding by its C_{org} content which amounts to over 5 %. Microphotographs of samples 4 and 9 are shown in Figs. 5a and 5b. Sample 4 in Fig. 5a shows granular structure with more or less grown-together carbonate grains (bright grey colour), which still show euhedral forms up to 10–20 µm in size. Fossils were not found in this sample. Black colour (C_{org} ca. 2 %) and pyrite (Fig. 5a – right side) clearly indicate anoxic environment of formation of this black limestone. Black fields of approximately the same size as individual carbonate grains, or somewhat smaller, are pores. They seem to be more or less empty and quite well connected. Porosity, considerably effective, can be estimated to about 30 %. This characteristic can classify this limestone as a good reservoir rock. On the other hand, it might also be a source rock for oil and/or gas generation.

Sample 9 (Fig. 5b) can be classified as a micritic limestone with broken fragments of molluscs. As already mentioned, it contains more than 5 % C_{org}. Organic matter is finely dispersed within dark micritic matrix. In addition, fragments of blown-in coal (vitrinite) particles can be found (see highly magnified insert picture in Fig. 5b), but they are very rare (below 1 %). Such rocks might be source rocks for oil and/or gas generation at sometime in the geological past after their deposition.

Also carbonates are samples number 1, 2, 3, and 13, with MgO + CaO varying between 34 and 49 %, CaO and MgO both taking considerable shares. CaO content varies between 20 and 30 % and MgO content between 13 and 19 %. Due to carbonate composition, also these samples exhibit high LOI – between 34 and 43 %. Sample 13 (Fig. 5c) contains fragmental fusinite.

On the contrary to the above described limestones, clearly mudrocks are samples number 6, 10, 11, 12 (all Upper Triassic) (Tab. 1, Graph 1). All these samples contain 65–80 % SiO₂ + Al₂O₃. SiO₂ : Al₂O₃ ratio varies between 2.3 and 4.3 : 1. They are predominantly composed of quartz and clay minerals. Among clay minerals, remarkable MgO and K₂O contents may indicate small occurrences of chlorite and illite, or, feldspars. They are very poor in organic matter, except for sample 12, which is black (N1) and contains 2.3 % C_{org} which is almost equal to C_{tot}. Other samples contain less than 1 % C_{org}. Samples 10 and 12 are shown in microphotographs in Figs. 5d and 5e.

Sample 5 – Anisian dolomite (silicified) – is the most Mg characterized sample (Graph 1). Its chemical composition (considerable shares of SiO₂, and MgO, very subordinate CaO and negligible Al₂O₃) indicates presence of quartz, dolomite and subordinately calcite.

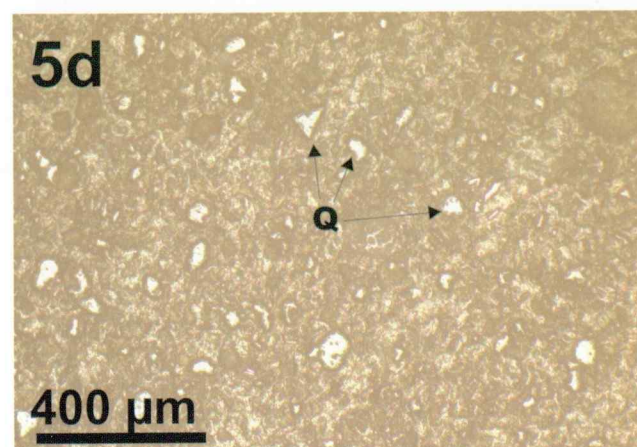
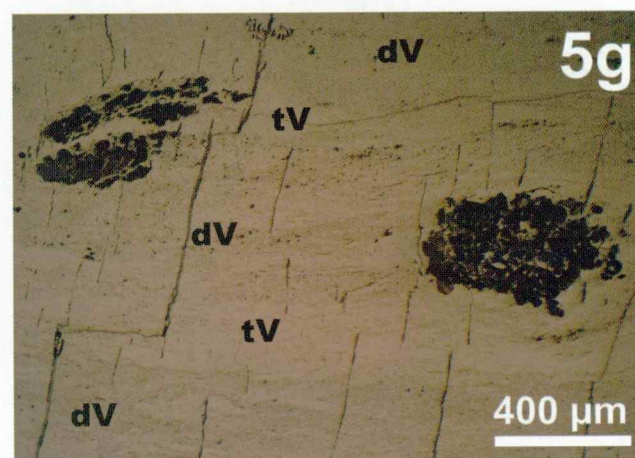
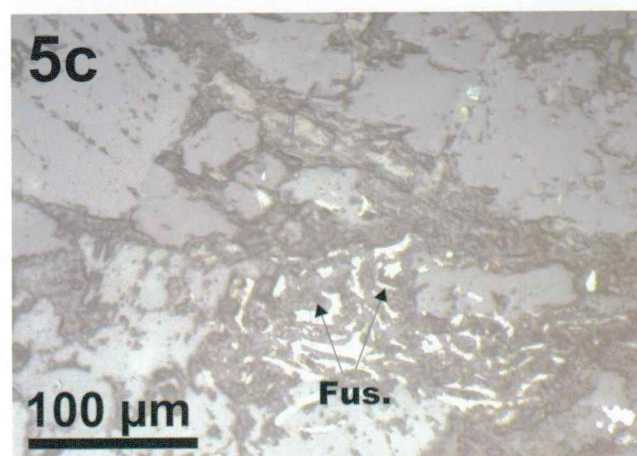
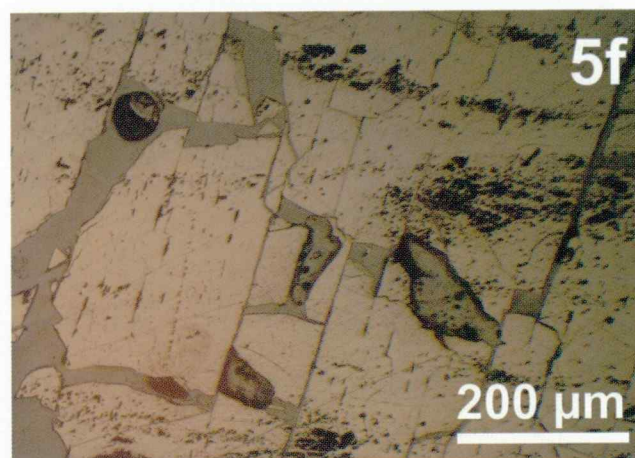
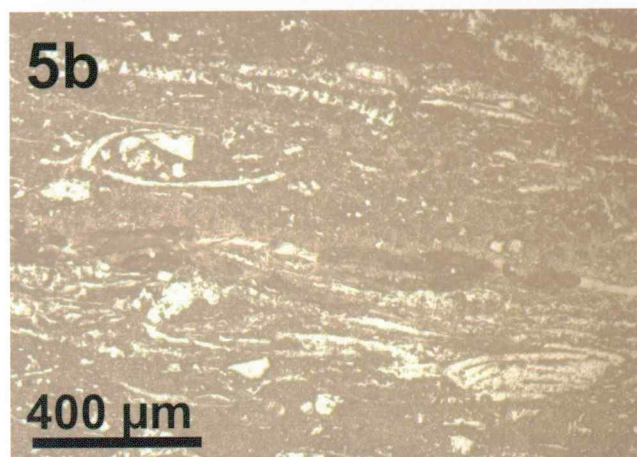
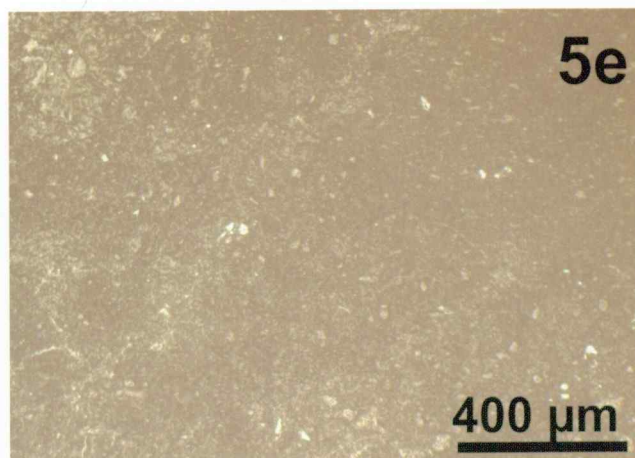
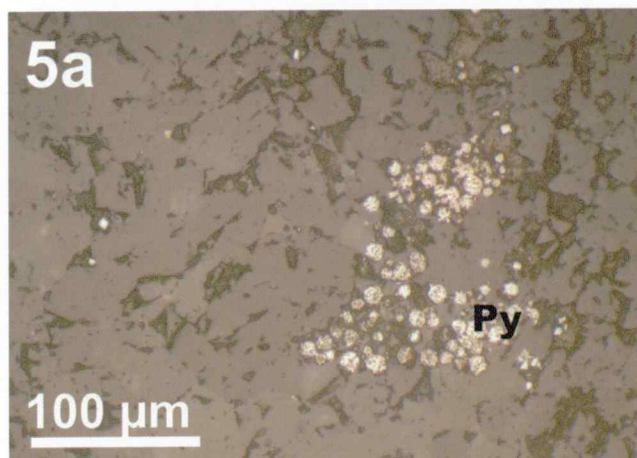
Sample 7 is anthracite from Orle. This anthracite occurs in the Carnian limestone. It was sampled on the waste dump because there was no possibility to gain fresh samples from the interior of the abandoned mine. As visible from Figs. 5f and g, this anthracite is composed of detro- and telovitrinite. Typical are dark oval structured “bodies” filled with clay (note almost exclusive SiO₂ + Al₂O₃ composition of the inorganic matter for this sample in Graph 1).

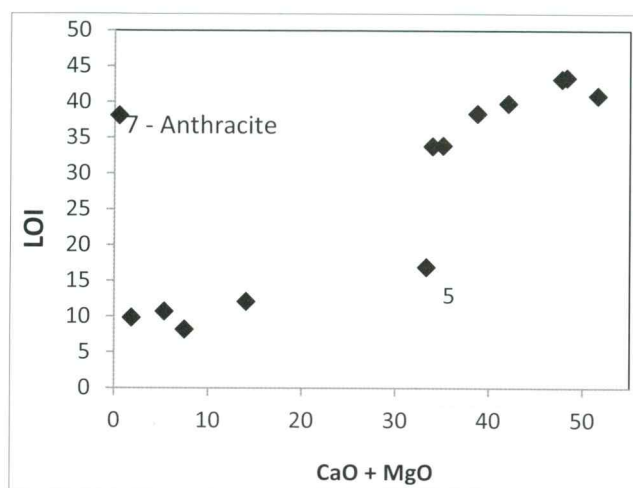
Fig. 5. Microphotographs of selected samples prepared as polished blocks – all in normal white polarized light in air (For sample numbers and chemical composition see Graphs 1–6).

- Sample 4: Limestone (calcite) with framboidal pyrite (Py).
- Sample 9: Micritic limestone with broken shells of molluscs.
- Sample 13: Carbonate rock with fragmental fusinite (Fus).
- Sample 10: Si-Al mudstone with relatively big quartz (Q) grains
- Sample 12: Si-Al mudstone
- Sample 7: Anthracite from Orle
- Sample 7: Anthracite from Orle – telovitrinite (tV) and detrovitrinite (dV)

Sl. 5. Mikrofotografije izbranih vzorcev, pripravljenih kot poliranih obruskov – slikano v normalni beli polarizirani svetlobi v zraku.

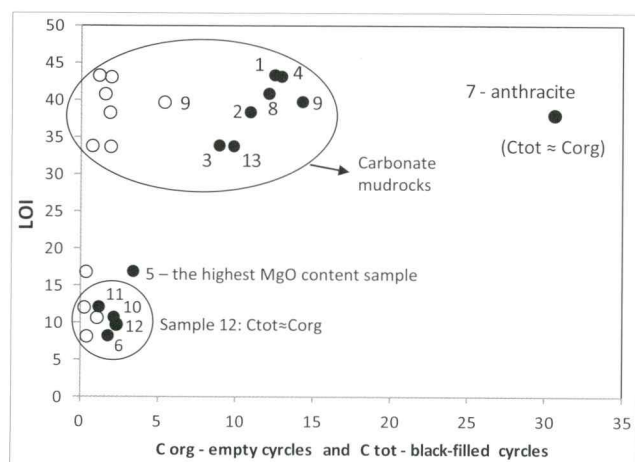
- Vzorec 4: apnenec s feamboidalnim piritom (Py).
- Vzorec 9: mikritni apnenec z zlomljenimi lupinami moluskov
- Vzorec 13: karbonatna kamnina z odlomki fuzinita (Fus.)
- Vzorec 10: Si-Al glinavec z razmeroma velikimi zrnici kremena (Q)
- Vzorec 12: Si-Al glinavec
- Vzorec 7: antracit z Orel
- Vzorec 7: antracit z Orel – telovitrinit (tV) in detrovitrinit (dV)





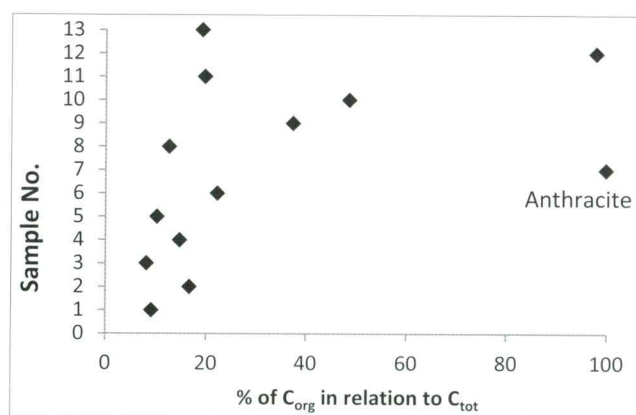
Graph 2. Loss on ignition (LOI) as a function of CaO + Mg content

Graf 2. Žaroizguba kot funkcija vsebnosti CaO + Mg



Graph 3. C_{org} and C_{tot} contents, and loss on ignition (LOI)

Graf 3. Vsebnosti organskega (C_{org}) in skupnega (C_{tot}) ogljika ter žaroizguba (LOI).



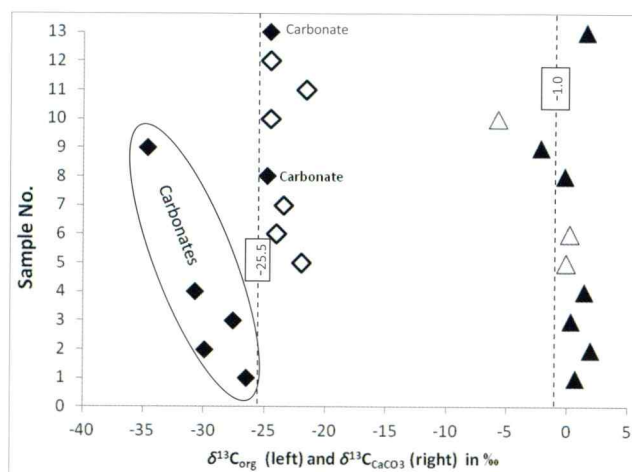
Graph 4. Percent of C_{org} in relation to C_{tot} for samples 1-13

Graf 4. Delež (%) vsebnosti C_{org} v celotnem ogljiku (C_{tot})

Because both relatively significant organic matter and carbonate matter were expected to be present in the samples, C_{tot} and C_{org} were analysed. In most samples, LOI was found to be primarily dependant on carbonates (Graph 2). Relation between forms of carbon (C_{org} and C_{tot}) and LOI is shown in Graph 3. Percent of C_{org} in relation to C_{tot} is shown in Graph 4. In general (nine of thirteen

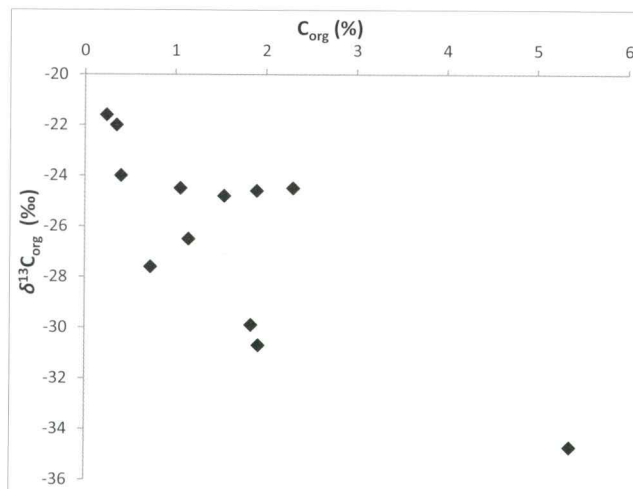
samples), it is below 20–25 %. In two samples, it is around 40 %, and in two samples (7 and 12) it is 98 and 100 %, respectively.

C_{org} varies in all samples from 0.25 to 2.30 %. Only in sample 9 (Carnian limestone), it is 5.36 %, and in the anthracite sample 7, it is 30.61 % (Tab.1, Graph 3). Carnian limestone is regionally well known by its black colour. Due to Alpine tectonics, it is thoroughly folded and fissured, the fissures being filled with calcite. It contains black laminated interbeds and locally hosts even thin beds and lenses of coaly matter. The Orle anthracite (sample 7) (see also introduction) occurs in such beds. Similar occurrences of bituminous



Graph 5. Isotopic composition of organic and of calcite carbon expressed by $\delta^{13}C_{org}$ and $\delta^{13}C_{CaCO_3}$ values.

Graf 5. Izotopska sestava organskega in kalcitnega ogljika, izražena z vrednostmi $\delta^{13}C_{org}$ in $\delta^{13}C_{CaCO_3}$.



Graph 6. Relation between C_{org} content and $\delta^{13}C_{org}$ value (marked are three outstanding samples).

Graf 6. Relacija med vsebnostjo C_{org} in $\delta^{13}C_{org}$ vrednostjo (označeni so trije izstopajoči vzorci).

coal to anthracite are also known at some other localities (Ligojna, Drenov Grič). Further-on, also from previous investigations, Carnian limestone is well known by its outstanding C_{org} content. Namely, OGORELEC et al. (1996), in their regional study about the Permian and Mesozoic carbonate rocks of W Slovenia as potential source rocks for hydrocarbon generation, clearly show the highest C_{org}

content in the Carnian limestone beds. According to their data (OGORELEC et al., 1996 – their Fig. 2), C_{org} content in the Carnian limestone considerably exceeds 2 % and is markedly the highest in comparison to all other Permian, Mesozoic and even Paleocene (Liburnian) formations, where it does not exceed 1%.

In organic matter of the investigated samples, $\delta^{13}C_{org}$ varies between -34.7 and -21.6 ‰ (Graph 5). In most carbonate mudrock samples, except for samples 8 and 13, $\delta^{13}C_{org}$ is below -25.5 ‰. In more Si-Al mudrocks and the anthracite sample, $\delta^{13}C_{org}$ is somewhat above -25.5 ‰. Maybe, this slight partition could be attributed to different diagenetic effects of organic matter in different geochemical media, namely carbonate (alkaline) and silico-aluminous (acid), respectively. Alkaline environment is well known to be an enhancer of biochemical transformation of organic matter (e.g. TAYLOR et al., 1998). Another reason could be different types of original organic matter. The most negative $\delta^{13}C_{org}$ value of -34.7 ‰ was analysed in sample 9, which is the most organic-rich limestone sample. Depletion in $^{13}C_{org}$ (decreasing in $\delta^{13}C_{org}$ values to more negative values) correlates quite remarkable with increasing C_{org} content (Graph 6).

$\delta^{13}C_{org}$ values for our carbonate samples, which are mostly below -25.5 ‰, are comparable to those in DOLENEC & OGORELEC (2001).

Isotopic composition of the calcite carbon ranges from $\delta^{13}C_{CaCO_3}$ -5.7 to 1.9 ‰, but mostly between -1.0 and 1.9 ‰ (Graph 5). There is almost no dependence in isotopic composition of calcite carbon referring to lithology and bulk chemical composition of the investigated samples. In comparison to results of isotopic composition of calcite carbon in Mesozoic carbonate rocks published by OGORELEC et al. (1999), our samples correspond to their organic-rich limestones, dedolomites and diagenetically altered dolomites, respectively.

Isotopic investigations of nitrogen, expressed by $\delta^{15}N$ values, also do not express distinctive differences in respect to lithology. They vary between 4.6 and 9.1 ‰. Both extreme values refer to Si-Al rich rock samples 6 and 12 (Tab. 1). The whole range of isotopic composition of nitrogen is comparable to soil material investigated in the watershed of the Idrijca River (KANDUČ et al., 2008).

Conclusions

This study was performed as a preliminary study to investigate some varieties of so called black mudrocks occurring as more or less thick bed-sets within Upper Permian and Triassic carbonate rocks in the area between Ljubljana and Bloke, recently geologically mapped by the first author. For this purpose, 13 samples of dark grey to black interbeds within mainly carbonate rocks were collected. For all sites of sampling, detailed textual and photographic descriptions with representative citations of previous researchers

are given in this paper. The samples were investigated chemically, microscopically and by isotopic composition of carbon and nitrogen. At the first glimpse, on the field, the samples resembled to coaly materials, but in fact, only one sample was really coaly – the Orle anthracite – in fact authracitic minerite. All other 12 samples were clearly grouped into Si-Al mudrocks with 65–80 % $SiO_2 + Al_2O_3$ and into carbonate mudrocks with less than 25 % $SiO_2 + Al_2O_3$, more than 35 % $CaO + MgO$ and ca. 35–45 % loss on ignition (at 1000 °C) derived from decomposition of carbonates. C_{org} of four samples (mostly siliciclastic mudrocks) was below 1 %. It was somewhat higher in carbonate mudrocks, up to 2.3 %, and the highest in sample 9 (HCl reacting limestone) which contained 5.36 % C_{org} . According to the SCHLUMBERGER Oil Field Glossary, rocks with 1 to 4 % C_{org} can be termed as fair to good oil/gas source rocks, and those with more than 4 % as very good source rocks. It can be concluded that carbonate mudrocks are better source rocks than Si-Al mudrocks.

Detailed field observations at localities of sampling, broader regional geological information and results of microscopic and chemical analyses indicate in general that the Upper Permian as well as Triassic organic matter enriched carbonate and noncarbonate (siliciclastic) sediments accumulated in relation to transgressive-regressive cycles in restricted shallow lagoonal environments (with more or less intensive water and organic matter influxes from the hinterland terrains).

Isotopic composition of organic carbon slightly differs between Si-Al mudrocks and carbonate mudrocks. In first case, $\delta^{13}C_{org}$ is somewhat above -25.5 ‰, and in the second case somewhat below -25.5 ‰. The whole range of $\delta^{13}C_{org}$ values for all samples varies from -34.7 to -21.6 ‰. The reason could be isotopic differentiation due to different diagenetic effects in organic matter in different original litho-geochemical environments – either Si-Al (relatively acid) or carbonate (relatively alkaline).

Isotopic composition of calcite carbon varies between $\delta^{13}C_{CaCO_3}$ -5.7 and 1.9 ‰. The results did not show dependence on lithological and/or chemical composition of the investigated samples, but are well comparable to organic-rich limestones, dedolomites and diagenetically altered dolomites as thoroughly defined by OGORELEC et al. (1999). Isotopic investigations of nitrogen also did not show distinctive differences in respect to lithology. $\delta^{15}N$ values varied between 4.6 and 9.1 ‰. Both extreme values were analysed in Si-Al mudrocks.

This study showed some approaches and contributions to previous investigations, especially those of oil and gas potential of carbonate rocks having been carried out by OGORELEC et al. (1996) and RAINER et al., (2002), as well as to previous isotopic studies of Mesozoic carbonate rocks by OGORELEC et al. (1999).

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