6. HRVATSKI GEOLOŠKI KONGRES
s međunarodnim sudjelovanjem

6TH CROATIAN GEOLOGICAL CONGRESS
with international participation

09.–12. 10. 2019.
Zagreb

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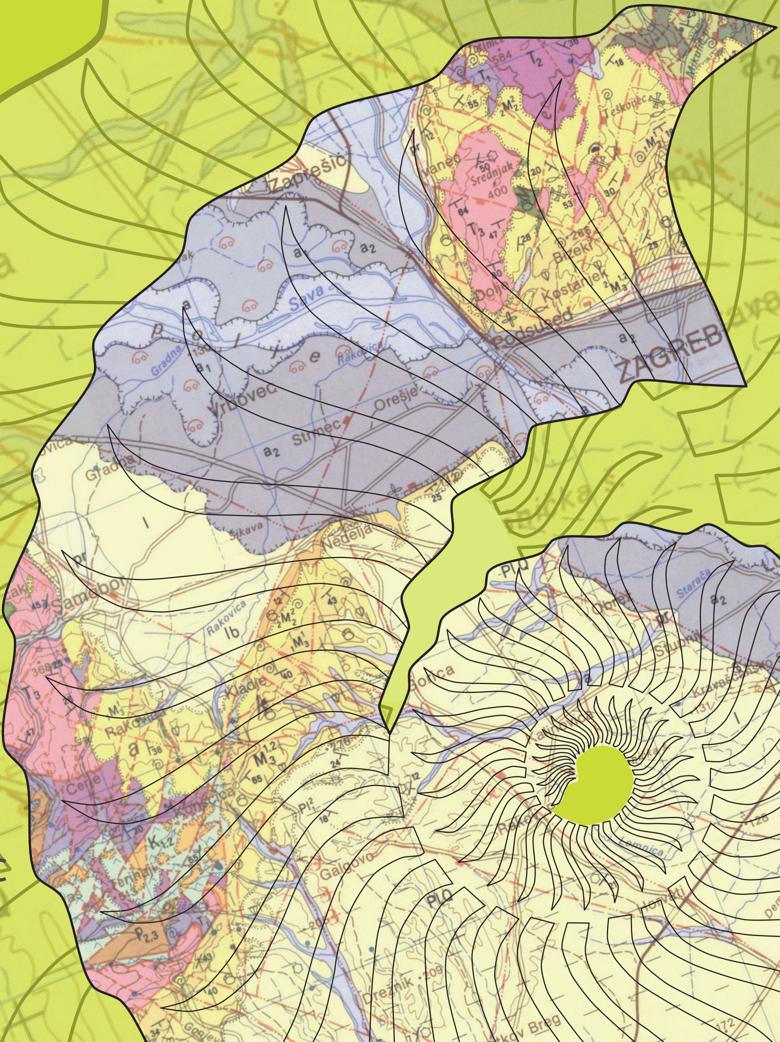

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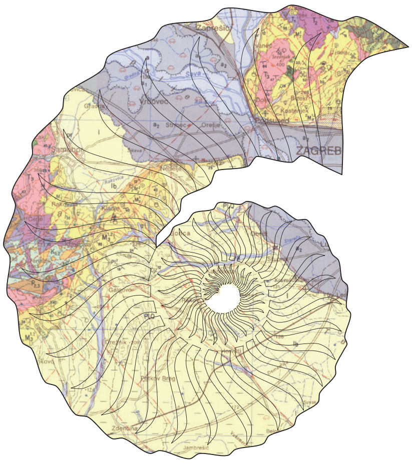

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EXCURSION 2 • Hrvatsko Zagorje

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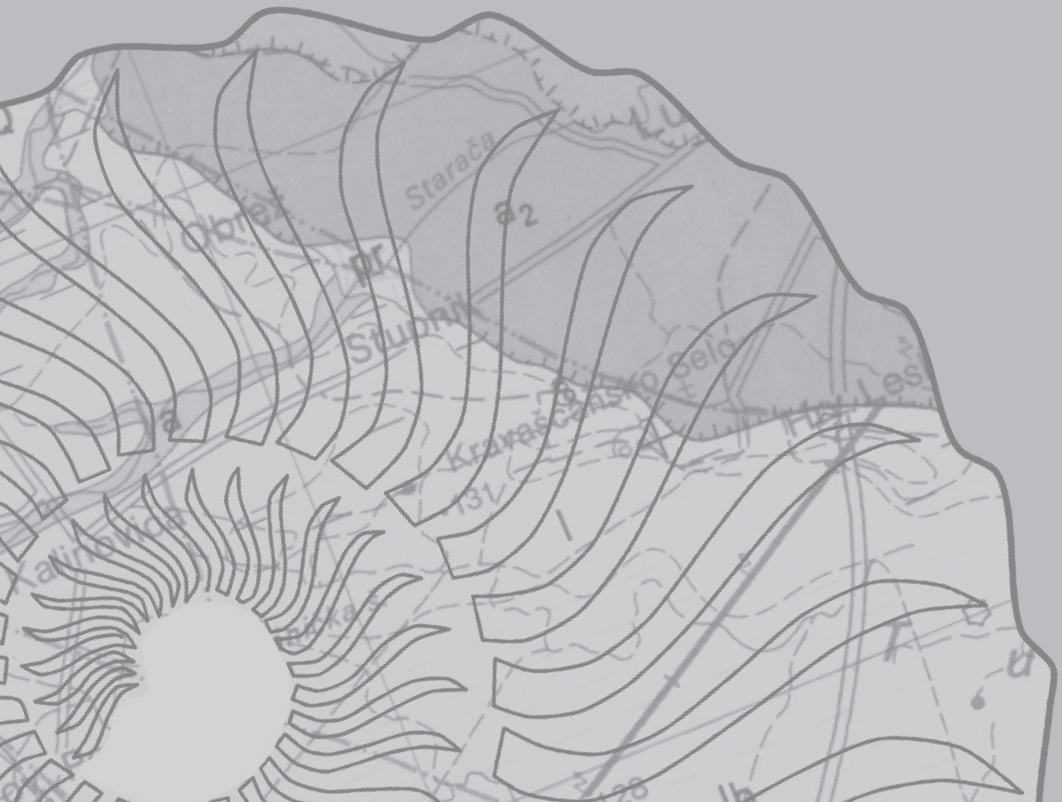
EXCURSION 1
Banovina



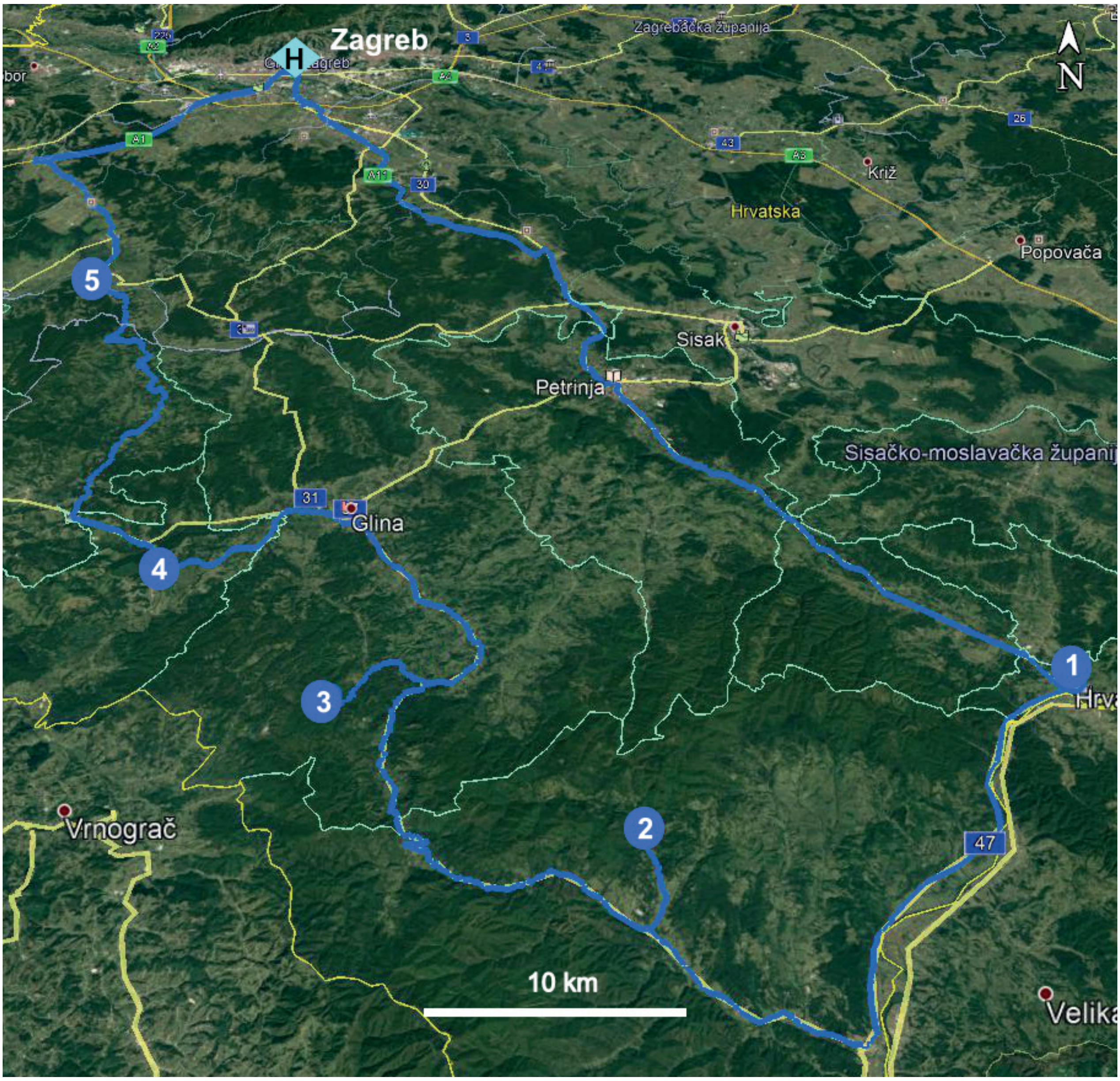


Fig. A. Excursion route with stops: H – Hotel International, Zagreb; 1 – Hrvatska Kostajnica; 2 – Gornja Stupnica; 3 – Slatina; 4 – Topusko (lunch); 5 – Lasinja (Google Earth, modified).

Geology of Banovina

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INTRODUCTION

Geographically, Banovina belongs to the southern part of central Croatia, and extends over an area between the Glina River in the west, the lower part of the Kupa River in the north, the Sava River in the northeast, to the Una River in the southeast, and the state border with Bosnia and Herzegovina in the west. The Banovina area and excursion route with stops are shown in Fig. A.

The geological structure of the Banovina area is extremely complex containing most stratigraphic units from the Lower Devonian to the Quaternary (Fig. B). It covers parts of three very important, genetically distinct tectonic units: (a) the External Dinarides in the western-southwestern part of Banovina, (b) the south-western margin of the Pannonian Basin in the NE, and (c) the Internal Dinarides in the central part representing the "suture zone" between the other two aforementioned tectonic units. These units cover a wide area of southern Europe, and in Banovina they occur in their closest proximity which makes this area very difficult to interpret from the point of its geological development. The most comprehensive and detailed description of the geology of the Banovina area was given by ŠIKIĆ (2014a, b) through the Bosanski Novi Sheet of the Basic Geological Map of Croatia (Fig. B). Extensive research in the Banovina area was also undertaken by MAJER (1993), especially concerning the ophiolites. A large part of the introduction of this guide refers to these aforementioned publications.

The oldest lithologic units which are part of the Sana-Una Palaeozoic belt, can be observed in the southern

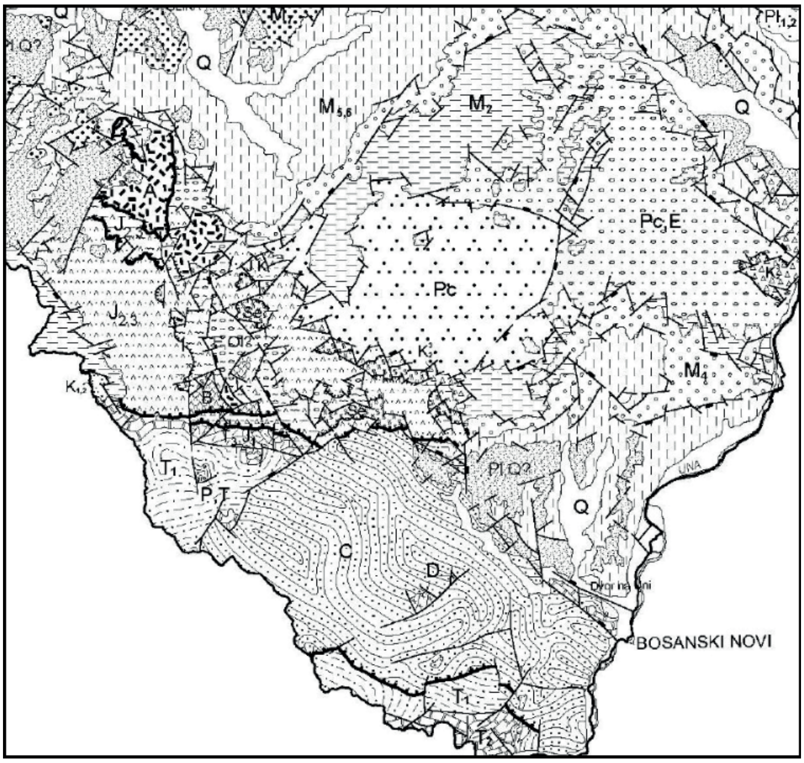

Fig. B. Modified geological map of the Banovina area (ŠIKIĆ, 2014b). Legend: D – Devonian (carbonates and clastics); C – Carboniferous (clastics and subordinate carbonates); P, T – Permian–Triassic (clastics, gypsum); T_1 – Lower Triassic (clastics and carbonates); T_2 – Middle Triassic (carbonates, clastics, cherts, pyroclastics); $T_3^{2,3}$ – Norian–Rhaetian (carbonates); $J_{2,3}$ – Middle–Upper Jurassic (metamorphites and magmatic-sedimentary complex – ophiolites); Se – Serpentinites and serpentinised peridotites; A – Amphibolites and amphibole schists; B – Basaltic magmatites; J, K – Tithonian–Barremian (clastics, limestones, cherts, magmatites); K_1 – Hautervian–Lower Albian (clastics, limestones, cherts); $K_{1,2}$ – Albian–Cenomanian (flysch); K_2^3 – Upper 'Sennonian' (Scaglia, flysch, volcanics, pyroclastics); Pc – Palaeocene (flysch and carbonates); Pc, E – Upper Palaeocene–Lower Eocene (coarse grained clastics); E, Ol? – Middle Eocene–Oligocene? (clastics, coal); M_2 – Ottnangian (clastics, coal, pyroclastics); M_4 – Badenian (carbonates, clastics, pyroclastics); $M_{5,6}$ – Sarmatian–Pannonian (carbonates and clastics); M_7 – 'Pontian' (clastics); $Pl_{1,2}$ – Dacian–Romanian (clastics); Pl, Q? – Romanian–Lower Pleistocene (clastics); Q – Quaternary (loess, talus, alluvium).

and southwestern parts of Banovina (Fig. B) where they form Trgovska Gora Mt. These units are composed of Lower Devonian, Carboniferous and Permian–Triassic deposits. Their occurrence can be traced from Karlovac to Banja Luka. The Lower Devonian units are very rare and consist of interchangeable deposits of shales, silts, and sandstones with limestone interlayers (ŠIKIĆ, 2014a). Their age is based on conodont fossils (ĐURĐANOVIĆ, 1966, 1968, 1973). Carboniferous deposits cover larger areas, extending almost all over Trgovska Gora Mt. They are mostly represented by shales, siltites and sandstones, with minor occurrences of carbonate deposits (ŠIKIĆ, 2014a). An Early Carboniferous age of these deposits was determined on the basis of conodont fossils discovered within dark gray, clayey limestones (ĐURĐANOVIĆ, 1973). The Middle Carboniferous was documented by foraminifera from dolomitized, sandy limestones (ŠIKIĆ, 2014a), and the Late Carboniferous on the basis of plant remains (STUR, 1868) and corals within limestones rich in crinoids and brachiopods (KOSTIĆ PODGORSKA, 1956). The Upper Carboniferous rocks are also interesting as metalliferous deposits. The Fe, Pb and Cu ore deposits, and barite, the genesis of which is linked to the Upper Palaeozoic submarine magmatism (ŠIKIĆ, 2014a), are frequently found within the Carboniferous deposits of Trgovska Gora. Permian deposits in Banovina have not been proven with certainty, but there are rare occurrences in the area of Trgovska Gora Mt., which consist of coloured sandstones and siltites, quartz conglomerates, shales, poriferous limestones and gypsum. These are assumed to be of Permian–Triassic age (ŠIKIĆ, 2014a).

The oldest Mesozoic rocks are of Triassic age and occur within the Trgovska Gora Mt., where the Lower Triassic is mostly marked by clastic deposits due to material transported from the continent. Marls, shales, siltites and sandstones are the most representative, with rare occurrences of limestones and dolomites (ŠIKIĆ, 2014a). The transition to the Anisian (Middle Triassic) is marked by a reduced terrestrial influence, which led to deposition of thicker carbonate deposits (dolomites and dolomitized limestones). An Anisian age has been confirmed by the discovery of microfossils (ŠIKIĆ, 2014a). Ladinian is represented by deposits of clastic and carbonate origin, respectively dolomitized limestones, marls, shales and sandstones, and pyroclastites, indicating volcanic activity. The age of the deposits was confirmed from numerous bivalve fossils (ŠIKIĆ, 2014a). The youngest Triassic deposits (Norian, Rhaetian), represented mostly by dark to light gray well-layered dolomites, are located almost exclusively on the northernmost parts of Trgovska Gora Mt., forming a narrow belt, which borders the ophiolite mélange of Jurassic age (Fig. B). These Palaeozoic and Triassic units represent the marginal parts of the former Gondwana continent and basement of the Mesozoic carbonate platform.

The Jurassic period in the Banovina area is mainly linked to the formation of the ophiolite belt complex, which represents a separate tectonic unit belonging to the Inner Dinarides. Composed of sedimentary, metamorphic and magmatic rocks it is most visible in the central part of Banovina. Towards the northwest, this belt is gradually covered by Cenozoic deposits with rare occurrence of ophiolites in the Kupa River area. To the southeast, this belt is also covered by younger deposits, but outcrops again near the Town of Hrvatska Kostajnica, from where it can be traced in a southeastern direction through Bosnia and Herzegovina. Formation of the ophiolite complex is thought to be related to the initial stages of ocean opening, in other words, to extension of the continental crust and the injection of hot mantle into the existing surface deposits with occasional submarine magma effusions. Later compressional tectonics caused the disintegration of the ophiolite complex and the mixing of different lithological units leading to formation of the ophiolite mélange (MAJER, 1993). Lower Jurassic deposits occur as larger or smaller olistolites within the ophiolite mélange and are mainly of carbonate composition. Their age was determined from various fossil remains, among which ammonites, gastropods, crinoids, brachiopods, echinoderms and sponges are the most common (ŠIKIĆ, 2014b). All magmatic and metamorphic rocks with associated sediments are of Middle to Late Jurassic age (ŠIKIĆ, 2014a). Sedimentary rocks of Middle to Upper Jurassic are represented mainly by sandstones, shales and cherts, and to a lesser extent by marls and carbonates (ŠIKIĆ, 2014a). Within the sandstones, tuff particles can be observed. Additionally, interlayering and merging of sandstones with tuffs and lavas is common, suggesting volcanic activity. Limestones occur only as thinner layers, lenses, inserts and even as enclaves within the volcanics. Numerous fossil remains of pelagic organisms indicate a Middle Jurassic or younger age. Metamorphic rocks are important members of the ophiolite complex and are composed of parametamorphites and orthometamorphites of low to medium metamorphic grade. The largest masses of metamorphic rocks are observed in the northwestern part of the ophiolite belt between the Maja and Buzeta Rivers. The most prevalent parametamorphite rocks are metasandstones, metapelites, slates, phyllites and various types of mica shists, formed from clayey pelites and greywackes with a relatively high aluminum content, typical for deposits from the marginal parts of the continent (MAJER, 1993). A major proportion of the orthometamorphites are amphibolites, with minor occurences of amphibolitites and greenschists. These rocks were formed from basaltic magmatic rocks, most probably basalt, diabase and a gabbro protolith (MAJER, 1993). Using the dating method, absolute ages of about 170 million years have been obtained for the metamorphic rocks, confirming their Middle Jurassic age (MAJER, 1993). As a member of the magmatic rocks, ultramafic bodies of peridotite have great importance. These rocks can be best traced in the central part of the ophiolite belt (Fig. B). The ascent of these bodies to the surface was closely related to the formation of the metamorphic rocks and they are thus considered to be of Middle Jurassic age (MAJER, 1993). Smaller microgabbro and diabase lenses also appear frequently within the serpentinite. The most significant occurrences of effusive rocks are related to spilites and diabase, and to a lesser extent to keratophyres and pyroclastics. Most spilites occur as pillow lavas, suggesting submarine activity.

The absolute age obtained for the diabase samples by Rb–Sr dating is approximately 160 million years (MAJER, 1985). Cretaceous deposits are significantly less well represented than Jurassic ones. The oldest Cretaceous deposits are located at the northern edge of Trgovska Gora Mt., along the Žirovnica River from Žirovac to Komora village. These rocks, composed of shales and marly shales with limestones and chert layers (ŠIKIĆ, 2014a) were probably emplaced beneath the Jurassic ophiolite mélange together with the Triassic deposits (ŠIKIĆ, 2014b). The fossiliferous limestones, which include crinoids, echinoderms, algae, and benthic foraminifera, indicate a Hauterivian–Early Albian age (OLUIĆ, 1979). Clastic to carbonate sedimentation with flysch-turbidite characteristics continued into the Late Cretaceous. The lithology is dominated by marls and shales. An Albian–Early Cenomanian age was determinated on the basis of pelagic fossils within the marls and micrites. 'Lower Senonian' deposits containing useful planktonic foraminifera, are of similar character and consist predominantly of clastic to carbonate deposits, but with frequent occurrence of spilites, spilite-keratophyres and keratophyres, as well as pyroclastics, which can occur separately in thinner layers or lenses, or directly in contact with volcanic rocks. These deposits are located in the broader area around the Town of Hrvatska Kostajnica. 'Upper Senonian' deposits occur within a relatively narrow belt extending from the central part of Banovina to the southeast (Fig. B). Within the younger part of the 'Upper Senonian' deposits, it is important to mention the presence of Scaglia limestones which contain tuffite layers, indicating volcanic activity (BABIĆ & ZUPANIČ, 1976). A gradual transition to clayey limestones, calcareous marls and marls indicates a change to the younger Maastrichtian deposits which continuously progress into flysch deposits with variously interchangeable layers of clayey marls, limestone shales, silty sandstones, sandstones and silty limestones.

Palaeogene, Neogene and Quaternary deposits belong to a separate tectonic unit, namely the Cretaceous–'Tertiary' zone of the Inner Dinarides. This tectonic unit is situated in the northern and northeastern part, occupying more than half of the Banovina area (ŠIKIĆ, 2014a). The most important Palaeogene deposits are Palaeocene flysch deposits, which today occupy the western part of Zrinska Gora Mt. (Fig. B), and the biogenic and bioclastic limestones, which occur superficially in the eastern part of Banovina, near Velešnja village. The age of the flysch deposits has been mainly derived from planktonic foraminifera and calcareous nannoplankton records, while the Palaeocene limestones are dated according to observations from the abundant remains of corals, hydrozoa, bryozoa, crinoids, sea urchins, snails and bivalves (ŠIKIĆ, 2014a). Assumed Eocene and Oligocene deposits are closely related to the ophiolite melange and occur exclusively as transgressive deposits within the ophiolite belt. These are mostly clastics represented by breccias and conglomerates, consisting of metamorphic and magmatic rock fragments from the basal ophiolite members, with minor amounts of Cretaceous and Palaeocene rounded limestone fragments (ŠIKIĆ, 2014a). Clastic deposits gradually pass into finer-grained clastics and coals, sometimes evaporites, indicating a freshwater or lacustrine environment. Their age was documented by freshwater fossils (TIETZE, 1872). Apart from within the ophiolite belt, Oligocene deposits have not been found in other areas in Banovina, suggesting an emersion phase and explaining why Neogene deposits, starting from the Ottnangian, transgressively overlie older, commonly Palaeocene deposits (PAVELIĆ & KOVAČIĆ, 2018). The emersion phase was followed by flooding with deposition mainly in lacustrine environments. Various bounded and unbounded clasts, carbonates, coals, pyroclastics and clays can be observed within the Ottnangian units, occupying the northern and southern margins of Zrinska Gora Mt. Short-term emersion resulted in the absence of Carpathian sediments, leading to the deposition of Badenian sediments transgressively on Ottnangian and Palaeogene units. In the base of the Badenian, mainly mixed carbonate and clastic material can be observed, with rare pyroclastics. Younger alluvial deposits gradually pass into deposits with an increasing carbonate component. Development of reefs, represented by red algal (*Lithothamnium*) bioherms, biocalcrudites and biocalcarenites, was significant (ŠIKIĆ, 2014a). Sarmatian deposits continuously overlie the Badenian with very similar lithologies. In coastal areas, large-grained clasts were deposited, and in distal regions, mostly fine-grained marls and limestones. Similar conditions continued during the Pannonian, but in less energetic environments, with the deposition of limestones with smaller quantities of clay (*croatica* beds) in the lower Pannonian, followed by younger marly *banatica* beds (ŠIKIĆ, 2014a). Upper Pannonian ('Pontian'), mostly marl deposits, can only be observed in the northern part of Banovina, in the Glina basin (Fig. B). Upper Pannonian deposits have been dated from mollusc remains, especially the bivalves *Paradacna abichi* and *Congeria rhomboidea*. Pliocene deposits consist mainly of large to fine-grained clastics, as observed in the northeastern part of Banovina. Older Pliocene deposits can be correlated with the *Viviparus* (formerly *Paludina*) beds of the Sava Depression. During the Pleistocene, clastic sedimentation continued, and due to the pronounced orogenic uplift, river and stream valleys were created in higher terrains where sedimentation continued through the Quaternary (ŠIKIĆ, 2014a).

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Landslide “Kubarnovo Brdo – Stari Put” in Hrvatska Kostajnica

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INTRODUCTION

The landslide “Kubarnovo brdo – Stari put” in the town of Hrvatska Kostajnica (Fig. 1.1 a) was activated on March 13th 2018. It occurred within the landslide prone areas on the slopes close to the Una River. There is still no systematic collection of landslide data or a landslide database/inventory for this area, only several geotechnical reports/data regarding mitigation of some locations, most of which belong to the private sector (PODOLSZKI et al., 2019).

The “Kubarnovo brdo – Stari put” landslide is located in the area of the Town of Hrvatska Kostajnica, north of the Una River and west of the Kostajničica stream, on the south-eastern slopes of Kubarnovo brdo Hill (Fig. 1.1 b – yellow mark).

Basic geological data and a description of the deposits from this area are given in the Basic Geological Map of SFRY 1:100 000, Sheet Kostajnica (JOVANOVIĆ & MAGAŠ, 1986a) and Geology of Kostajnica Sheet (JOVANOVIĆ & MAGAŠ, 1986b) (Fig. 1.2).

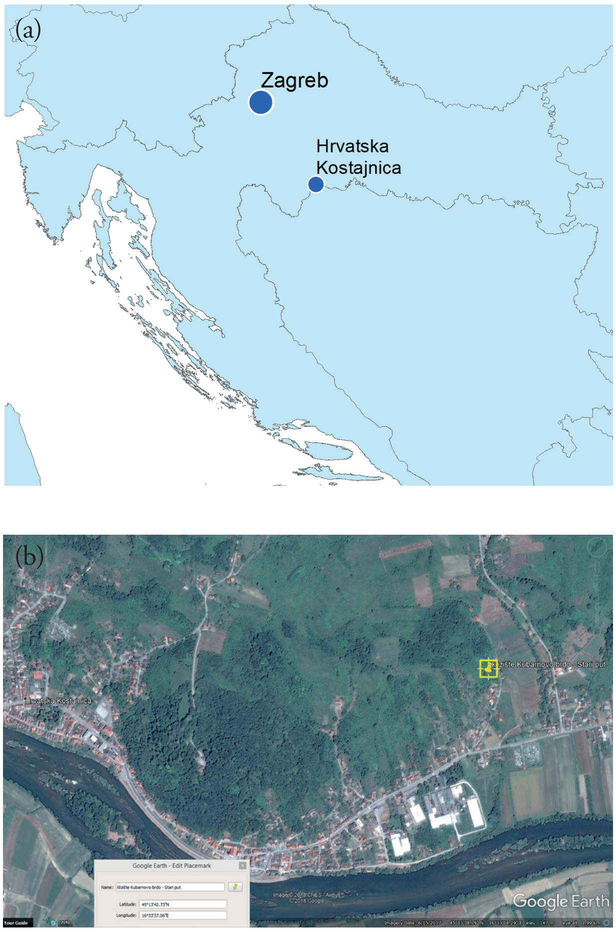

Fig. 1.1. a) Location of the Town of Hrvatska Kostajnica on the map of Croatia, b) Google Earth satellite image showing location of the “Kubarnovo brdo – Stari put” landslide (yellow mark) in Hrvatska Kostajnica.

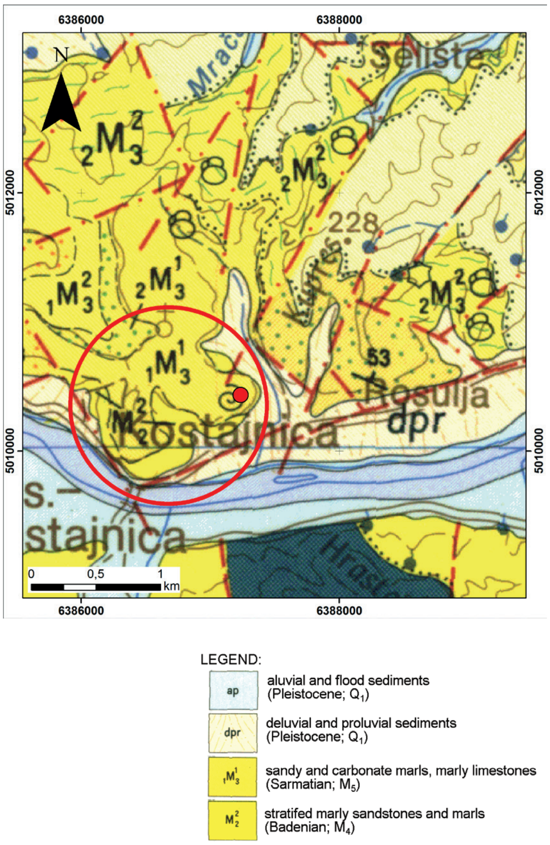

Fig. 1.2. Detail from the Basic Geological Map of SFRY 1:100 000, Kostajnica Sheet (JOVANOVIĆ & MAGAŠ, 1986a) showing wider area of Hrvatska Kostajnica. The red circle on the map represents the area of Kubarnovo brdo Hill, and the red dot represents the location of the “Kubarnovo brdo – Stari put” landslide. A description of the mapped units (units in a red circle) on the landslide area is visible in the Legend.

DESCRIPTION

Kubarnovo brdo Hill is composed of bedrock, deluvial deposits and the soil layer (PODOLSZKI et al., 2018a). The thickness of the soil layer varies but is generally thinner than 0.5 m. At the main scarp area the soil layer thickness is between 0.3 and 0.7 m. Below the soil layer is a layer of deluvial sediments represented by clays and clayish marls up to 3m thick (estimated). These sediments are weathered and the weathered zone, composed of sand, silt and clay, can reach depths of <5 m (estimated). The bedrock is represented by clayish marls, silty marls, layers of sandstones and weathered clayey limestones. The Landslide has affected all these zones, soil layer, weathered zone and bedrock zone, with a wide range of present deposits (PODOLSZKI et al., 2018a): from coherent soils (clays, silts) through hard soil/soft rock (weathered marls) to rocks (marls, silts, sandstones, clayish limestones).

INTERPRETATION

The landslide area is relatively large, approximately 300 x 300 m, with clearly visible landslide contours (in 2018) and the main scarp <30 m high and around 285 m long (Fig. 1.3). The "Kubarnovo brdo – Stari put" landslide in Hrvatska Kostajnica destroyed or heavily damaged around 10 houses, but without casulaties though this was a mere coincidence (PODOLSZKI et al., 2018a, 2018b).

The Una River is situated 500 m south from the landslide area and the Kostajničica stream lies 100 m to the east. In March 2018 the Una River flooded and during the period of landslide activation (March 13th 2018) active flood mitigation measures were in place for the Town of Hrvatska Kostajnica. The Una River overflowed the river banks and flooded the agricultural area in the wider area of the landslide.

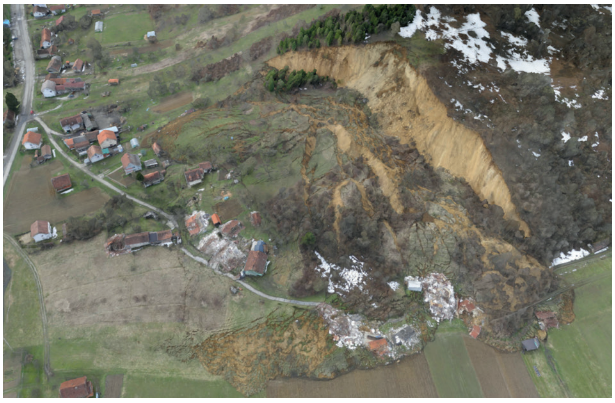

Fig. 1.3. 3D model of the landslide "Kubarnovo brdo – Stari put", based on aerial photos (drone data) showing clear landslide features (Croatian Geological Survey, March 14th 2018) (PODOLSZKI et al., 2018a).

The activation of the landslide was probably caused by a temperature change from below to above zero and the sudden snowmelt of an 80 cm thick snow cover. As the water level of the Una River was already high, the drainage of the additional water was slowed down or inhibited. This increased the pore pressure in the soil and eventually led to exceedance of the soil shear strength resulting in landslide occurrence.

A history of movements can be seen in the wider area (Fig. 1.4). An "older landslide" (Fig. 1.4 – yellow dashed

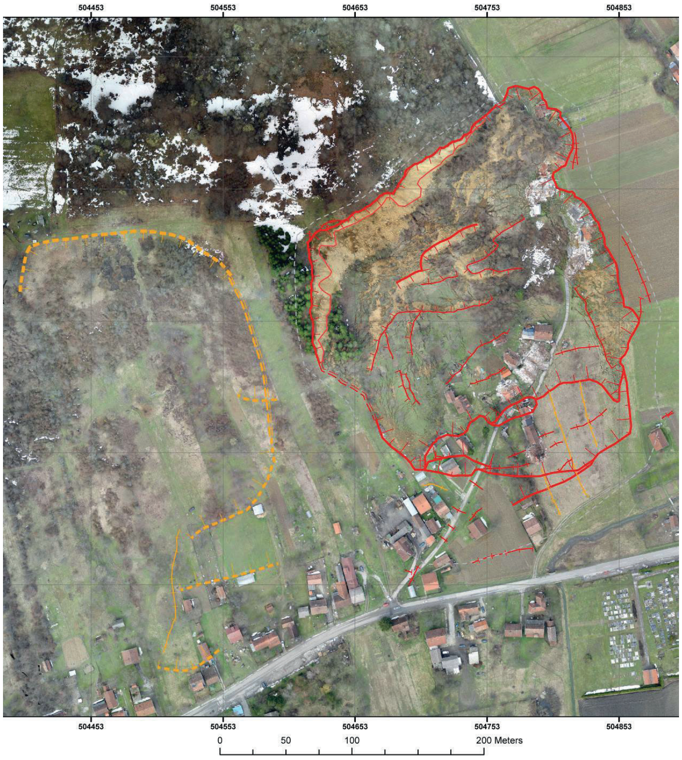

Fig. 1.4. Elements of an "old landslide" (yellow dashed line) and the "new landslide" (red lines) defined by engineering geological mapping of the terrain and analysis based on drone data (Croatian Geological Survey, March 14th 2018) (PODOLSZKI et al., 2018a).

lines) with an unknown time of activation can be recognized on the surface of the terrain west of the "newly" formed landslide (Fig. 1.4 – red lines). Between the "old landslide" and the "new landslide" is a populated area. Based on engineering geological mapping and aerial photos (drone data) it can be assumed that this area could be endangered in the future.

In the future it is expected that this landslide will spread in every direction until the colluvium reaches stability. These processes are expected to be long-lasting. It will take years until the movements in this area will cease.

As a basic preventive measure for the reduction and avoidance of landslide damage it would be desirable to create an inventory of landslides for the area of Hrvatska Kostajnica and a landslide susceptibility map of the wider area. These landslide data sets, in combination with clearly defined legislative terms and means of construction, can provide the possibility of optimizing economic resources and increasing the safety of both citizens and property.

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Stop 2 Stupnica (Mt. Zrinska Gora)

Late Cretaceous to Palaeogene Deep Water Sedimentation

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INTRODUCTION

The valley of Stupnica creek in the southern part of Mt. Zrinska gora exposes a Late Cretaceous to Palaeocene deep water sedimentary succession consisting of pelagic limestones which transition into clastic deposits characterized by their progressively increasing grain size and siliciclastic component. It represents the lower part of the dominantly Palaeocene and Eocene siliciclastic basin deposits which cover most of Mt. Zrinska Gora (ŠIKIĆ, 2014). The sediments can be best observed in an abandoned roadside quarry north of the village of Gornja Stupnica, as well as in the Stupnica creek bed and along adjacent tributaries (Fig. 2a). The succession has been reconstructed based on detailed outcrop sampling and new biostratigraphic data (Fig. 2b). Stratigraphic relationships within the succession, as well as those with neighboring units, are difficult to observe in the field due to the lack of continuous outcrops and a considerable tectonic overprint. Older deposits are poorly exposed in several smaller outcrops and consist of deep-water marls, shales, sandstones and pelagic limestones which have been mapped as uppermost Jurassic to lower Cretaceous in age and occur in tectonic contact with the Jurassic ophiolitic mélange (ŠIKIĆ, 2014).

DESCRIPTION

The lower part of the Late Cretaceous to Palaeocene succession near Gornja Stupnica is characterized by gray micritic "scaglia" type limestones which have been dated as middle Campanian based on planktonic foraminifera (BABIĆ & ZUPANIČ, 1976). The total thickness of the micritic limestones is approximately 70 m, while individual bed thicknesses range from 5–45 cm. At their top the limestones become slightly marly and the pelagic succession is interrupted by a conspicuous, approximately 2 m thick interval consisting of coarse grained calcarenites alternating with fine grained calcareous sandstones to siltstones. The calcarenites are well sorted grainstones consisting almost entirely of bioclasts. These are dominated by echinoderms, corallinaceans, benthic foraminifera, and bryozoans (Fig. 2c). Echinoderm fragments and spines originate from echinoids and crinoids. Fragmented and rounded coralline red algae thalli belong mostly to the Melobesioideae subfamily. These sometimes contain rounded borings probably of the *Entobia* ichnogenus. Lamellar-perforate large benthic foraminifera include the orbitoid foraminifera Lepidorbitoidinae and Clypeorbinae. Bryozoans are represented by fragments of erect rigid Cyclostomatid colonies. Additionally, rare fragments of bivalve shells (including rudists), clasts of pelagic mud, and planktonic foraminifera encased and filled with pelagic mud are also present. Angular siliciclastic grains occur in minute amounts scattered among the carbonate grains. Intercalated with the coarse grained calcarenites are fine grained calcareous sandstones which can be classified as wackestones containing abundant planktonic foraminifera along with fine siliciclastic detritus and rare fragments of echinoderms, red algae and benthic foraminifera. These grade into siltstones dominated by siliciclastic detritus with abundant mica, which are commonly bioturbated.

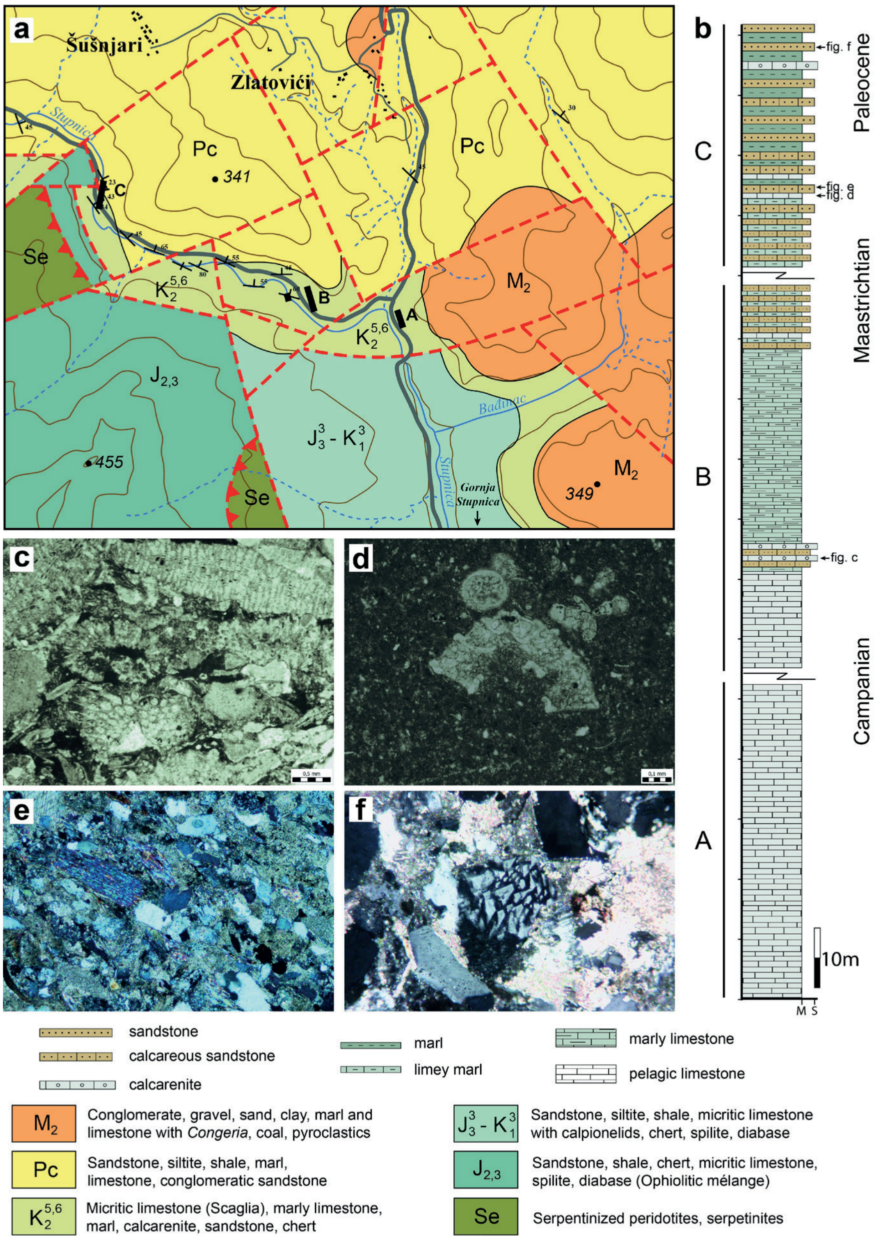

Fig. 2. a) Geological map of the Stupnica creek and surrounding area situated north of the village Gornja Stupnica (modified after ŠIKIĆ, 2014); b) Simplified sedimentary log of the Late Cretaceous to Palaeocene deep water succession reconstructed from several outcrops marked A–C on the map; c) Thin section of a calcarenite depicting echinoderms, benthic foraminifera, and bryozoans; d) Maastrichtian planktonic foraminifera (Globotruncanita conica) from a thin pelagic limestone bed intercalated with marls and turbiditic sandstones; e) A thin section of a sandstone from the Maastrichtian part of the succession dominated by quartz and lithics, particularly grains of low grade metamorphic lithologies; f) A lithic grain with granophyric texture from a Palaeocene sandstone.

Above the interval with coarse grained calcarenites the succession again becomes fine grained, consisting of laminated and somewhat fissile marly limestones which continue uninterrupted for another 30 m. Further above, the succession changes into an alternation of marls and turbiditic sandstones of mixed calcareous-siliciclastic composition, along with occasional thin pelagic limestone beds. Pelagic foraminifera from the upper segment of the laminated marly limestone interval and from the thin pelagic limestone beds indicate a Maastrichtian age (Fig. 2d). Nannoplankton data indicates that the sequence of alternating marls and sandstones continues into the Palaeocene. Upsection this part of the succession is characterized by a general increase in the siliciclastic component and grain size, and a slight thickening of both sandstone and marl beds. Turbidite sequences consist of predominantly thin sandstone beds (3–10 cm) without clear sedimentary structures topped by slightly thicker marl intervals. Occasional thicker sandstone beds (10–23 cm) display Tb-e and Tc-e sequences. Rare coarse grained calcarenite beds (cca 40 cm thick) with complete Ta-e sequences occur in the upper part of the succession exposed in the Stupnica creek bed.

Sandstones from the Maastrichtian part of the succession are fine to medium grained and dominated by quartz and lithic components. Quartz occurs as both monocrystalline and polycrystalline grains which are largely angular to subangular. Lithics are highly dominated by grains of low grade metamorphic lithologies (Fig. 2e). These range from very low ranking slate and metasiltstones with small amounts of sericite, low ranking phyllites and quartz-sericite aggregates with well-developed cleavage, to schistose muscovite, chlorite, quartz-muscovite and muscovite-chlorite grains. Sedimentary pelitic and siltstone lithics are also very common. Mafic volcanic lithics and chert rarely occur. Both plagioclase and alkali feldspars are present in modest amounts, commonly altered to sericite and in some cases replaced by calcite. Chlorite, muscovite and biotite flakes are highly abundant both in thin sections and the heavy mineral fractions. Carbonate grains include poorly discernible micritic and recrystallized grains, occasional fragments of red algae, echinoid spines and benthic and planktonic foraminifera. In the Palaeocene samples there is a slight increase in the feldspar component which occurs as lone grains or parts of quartz-feldspar rock fragments with or without mica of granitic or metamorphic origin. Chessboard albite and grains with granophyric texture are also observed (Fig. 2f). Low grade metamorphic and sedimentary lithics equivalent to those in Maastrichtian samples are common, and a slight increase in the proportion of schistose lithics is noticeable. Mafic volcanic lithics with intersertal texture occur regularly, while felsic volcanic lithics are also present in lower amounts. The Maastrichtian and Palaeocene sandstones share similar heavy mineral assemblages consisting of apatite, tourmaline, zircon, rutile, garnet and Cr-spinel.

INTERPRETATION

Collectively the Late Cretaceous to Eocene sedimentary units of Mt. Zrinska Gora record a foreland basin fill which progresses from initial pelagic deposition into flysch, and further transitions into molasse (JELASKA et al., 1969; BABIĆ & ZUPANIČ, 1976). Following a period of tectonic quiescence and the widespread deposition of pelagic limestones in the Campanian, the relatively rapid increase in siliciclastic influx recorded in the Maastrichtian probably reflects the advancement of thrusting related to continental collision along the margin of the Adria plate at the end of the Cretaceous and into the Palaeogene. Arenites within Maastrichtian and Palaeocene deposits at Stupnica record multiple ‘crystalline’ and ‘carbonate’ sources of material. Petrographic and geochemical data indicate a mixed felsic-ophiolitic provenance, probably reflecting the initial erosion of thrusted units of the Adria plate (LUŽAR-OBERITER et al., 2019). The material contained in the calcarenites can be linked to contemporaneous shallow marine carbonate environments that are known from the stratigraphic record of the Sava zone and neighbouring areas (BABIĆ et al., 1976; POLŠAK, 1979; USTASZEWSKI et al., 2009). These probably represent phases of marine transgression along emerging tectonic units uplifted within the collision zone. The increase in volcanic lithoclasts and plutonic/hypabyssal rock fragments, as well as higher-grade metamorphics, noticeable in the Palaeocene sandstones (and which become prominent in the Eocene deposits exposed further north on Mt. Zrinska Gora) was likely related to erosion of the magmatic arc that formed along the subduction zone of the Adria plate beneath Europe (PAMIĆ, 1993), as well as of metamorphic units exhumed in the accretionary wedge and/or possibly from the Tisza unit of the overriding plate.

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Stop 3 Slatina

Peridotites, Pyroxenites and Amphibolites from the Banovina Ophiolithic Mélange

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INTRODUCTION

Ophiolites are remnants of old oceanic lithosphere that have been tectonically emplaced into continental margins. Thus, they serve as witnesses of magmatic, tectonic and hydrothermal processes associated with the evolutionary history of ocean basins (DILEK & FURNES, 2014). A well preserved ophiolite sequence comprises from top to bottom: a) sedimentary cover (clastic, hemipelagic and pelagic sedimentary rocks), b) pillow lavas, c) sheeted dykes, d) isotropic to layered gabbro, e) cumulate ultramafic rocks and f) upper mantle peridotites. Worldwide, different types of ophiolites can be identified that have been affected by various geochemical processes that occur under different tectonic and magmatic regimes. In addition, the degree of preservation of the ophiolite sequence reflects different emplacement mechanisms (DILEK & FURNES, 2014). Ophiolites are broadly classified as subduction-related (suprasubduction type and volcanic arc type) and subduction-unrelated types (continental margin type, mid-ocean ridge type and plume type). Different types are distinguished from each other on the basis of mineralogical, petrological and geochemical criteria. The majority of the more extensive ophiolites were formed above a subduction zone, in a setting known as a suprasubduction zone (SSZ).

Tethyan ophiolites are remnants of marginal basins that evolved as a result of rifting of the northern edge of Gondwana, which began in the Permo–Triassic. They are characterized by an age progression from the Jurassic in the Alpine-Apennine and the Dinaride-Albanide-Hellenide mountain belts in the west, to Cretaceous in the Anatolide-Tauride, Zagros and Tibetan-Himalayan mountain belts in the east (DILEK et al., 2008). Their geochemical features also change from MORB-types in the Alps-Apennines to a suprasubduction type in Cyprus, Turkey and further east (DILEK et al., 2008). Middle Jurassic ophiolites of the Dinaride-Albanide-Hellenide mountain belt exhibit both mid-ocean-ridge basalt (MORB) and supra-subduction zone (SSZ) affinities (PAMIĆ et al., 2002), indicating a zone of transition. Tethyan ophiolites have special significance because many modern ideas and models of ophiolite genesis have been developed from detailed structural, mineralogical, petrological, geochemical, geochronological and tectonic studies of these ophiolites during the last 30 years (DILEK & FURNES, 2009 and references within).

DESCRIPTION

The ophiolite mélange of Banovina belongs to the Central Dinaridic Ophiolite Belt (CDOB) or Dinaridic ophiolite belt *sensu stricto* (DB) (Fig. 3.1). It runs NW-SE for ~700 km from the Southern Alps in Slovenia across Croatia, Bosnia and Herzegovina, Serbia, Montenegro to Mt. Šara in Kosovo. The Dinarides have been recognized as a part of the Alpine-Himalaya Tethyan orogenic belt (DILEK et al., 2008). The Dinaridic ophiolite belt, traditionally known as the Diabas-hornstein formation (DIMITRIJEVIĆ, 1982) is located NE of the Dinaridic carbonate platform exposed in the Central Bosnian Mts. and East Bosnian Durmitor units. It is bordered further to the NE by the ophiolites of the Vardar zone western belt and the Drina-Ivanjica unit. The DB extends up to the Metohija depression, where it continues as the Mirdita-Pindos ophiolite belt.

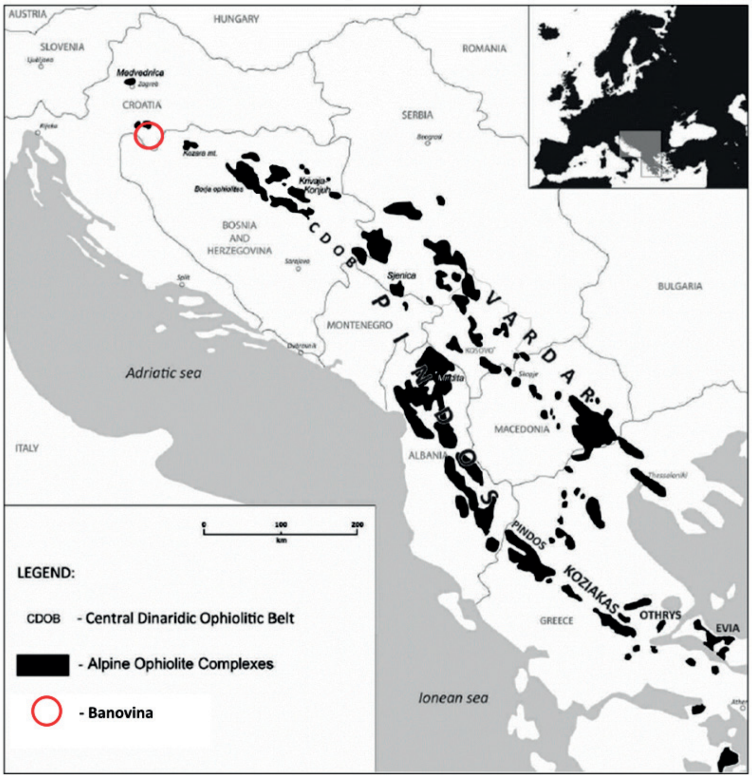

Fig. 3.1. Schematic position of the Central Dinaride Ophiolite Belt or lherzolite province (CDOB) and the Vardar Zone ophiolite belt or harzburgite province (VZOB); modified after ŠEGVIĆ et al. (2014).

The ophiolite complex of Banovina, together with Pokuplje, represents the northwestern end of the DB, terminating at the Kupa River, southwest of Zagreb (MAJER, 1993). It is bordered to the south-southwest by Upper Palaeozoic and Triassic formations, and to the east-northeast by Upper Cretaceous and Neogene deposits (MAJER, 1993). As a whole, the ophiolite complex represents a mélange composed of tectonically dismembered ophiolite bodies, along with slices and blocks of metamorphic and sedimentary rocks.

The peridotite bodies from the ophiolite outcrops are small, up to 3 km long, and according to MAJER (1975) 16 of the largest bodies crop out in the area between Gornji Klasnić and Stupnica in Mt. Zrinska Gora. MAJER (1975, 1993) studied this ophiolite complex and found the dominant ultramafics to be variably serpentinized lherzolites. They are locally associated with layers or dykes of pyroxenites, garnet pyroxenites and upper mantle amphibolites. Other rock types in this ophiolite suite include plagioclase wehrlite, amphibole gabbro, gabbroic pegmatite, hornblendite, noncumulate dolerite, diabase, plagiogranite, spilite and keratophyre. According to MAJER (1993) the lherzolites are characterized by porphyroclastic to mylonitic textures, and geochemical signatures (low MgO, high Al_2O_3 and CaO, with near chondritic Ca/Al values) which indicate a highly fertile nature with low degrees of partial melt extraction corresponding to subcontinental lithospheric mantle (SCLM). They contain olivine, orthopyroxene, clinopyroxene (Cr-diopside) and high-Al, low-Cr picotite and record the final subsolidus conditions of 900–1000 °C at a pressure of ca. 20 kb. Such P-T determinations do not agree with calculations made by ŠEGVIĆ (2010) for the lherzolite of the Krivaja-Konjuh ophiolite complex, which lies ca. 200 km away. Here, the final equilibration occurred at 550–682 °C and 10 kb. Plagioclase lherzolite is extremely rare in Banovina and was reported from only one locality (MAJER, 1993). These rocks exhibit cumulate textures and originated at lower pressures in the crust. Along with the cumulates, MAJER (1993) also described an amphibole-rich gabbro. Rare pyroxenites, locally associated with lherzolites, cover the compositional range from orthopyroxenites to clinopyroxenites and websterites. They have strong cataclastic textures and contain pyroxenes exhibiting extensive exsolution textures (MAJER, 1993). The occurrence of garnet pyroxenites is typical for the DB. At Banovina, they are characterized by garnet and clinopyroxene associated with pargasitic or kaersutitic amphibole and neoblastic, intermediate plagioclase. MAJER (1993) interpreted these garnet pyroxenites as having crystalized from a melt at high pressure in the upper mantle that were subsequently influenced by metasomatism. Amphibolites associated with the garnet pyroxenites contain amphibole, most probably Ti-hornblende, clinopyroxene, Ca-rich plagioclase, and in some cases green spinel-ceylonite have also been interpreted as high-pressure mantle cumulates (MAJER, 1975, 1993).

Noncumulate members of the Banovina and Pokuplje ophiolite complex include dolerites and diabases, characterized by neutral to acid plagioclase and amphibole, with rare augite, showing geochemical affinities of high-Al plagioclase tholeiites typical of back-arc basin tholeiites (MAJER, 1975, 1993).

Volcanic rocks occur as spilites and very rarely as keratophyres. Spilites are characterized by albite and Ti-augite, whereas amphibole was not observed. Spilites differ from diabase by their higher Na and Ti and lower Mg and Ca contents; geochemical characteristics similar to more evolved or E-MORB tholeiite. Therefore, it is clear that the spilites belong to a different group of rocks compared to the dolerites and diabases (MAJER, 1975, 1993).

Metamorphic rocks associated with the ophiolites of Banovina occur as slices and blocks (MAJER, 1993). Two different groups of metamorphic rocks are distinguishable: 1) paraschists and 2) metabasites. The paraschists comprise gneisses, mica schists, phyllites, calcsilicate schists, hornfels and rare skarns and marbles. There is a great mineralogical variability in the gneisses and mica schists with the most important index minerals being andalusite, sillimanite, cordierite, staurolite, garnet, biotite and zoned andesine plagioclase (MAJER, 1984). On the basis of mineral stabilities and index mineral isograds, MAJER (1984) calculated metamorphic P-T conditions for paraschists of T = 615 ± 30 °C and P = 4 ± 0.5 kb. Metabasites are represented by amphibolites, which have quite monotonous mineralogy of amphibole and plagioclase. Their protoliths have a tholeiitic affinity (i.e. within-plate basalts). Rarely, pyroxene occurs in the paragenesis, pointing to a higher metamorphic grade. On the other hand, zoisite and epidote formed by retrograde metamorphism (MAJER & LUGOVIĆ, 1985). According to these authors, the amphibolites formed at temperatures of 580–645 °C and pressures of 3.5–4.5 kb. Although the field area is covered and the primary contacts between individual parts of the ophiolite complex are obscured, MAJER (1984) concluded that the metabasites (amphibolite) form the upper part of a metamorphic series that is thicker and more frequently exposed than its lower part, which is represented by paraschists. The metamorphic rocks and associated ophiolitic bodies occur in nearly equal volumes. The gneisses, mica schists and amphibolites yield Middle Jurassic K–Ar ages of 163–168 ± 3 Ma (MAJER, 1993).

The most frequent sedimentary rocks in the mélange are fine-grained sandstones and shales of Middle to Late Jurassic age. They occur with subordinate radiolarian cherts and erratic blocks of limestone of different ages, pointing to pericontinental basin deposits (MAJER, 1993).

MAJER (1993) concluded that the Banovina ophiolite complex was formed and emplaced into a marginal pericontinental marine basin during the Middle Jurassic and was subsequently involved in a complex post-emplacement geotectonical history that was terminated in the Late Cretaceous by the formation of an ophiolitic mélange.

FIELD STOP, SLATINA QUARRY

The Slatina quarry lies some 20 km south of the town Glina, between Donji Klasnić and Brezovo polje, in Sisak-Moslavina county (Fig. A in Geology of Banovina). There, an area of about 14 000 m^2 was opened by mining activities. It is a huge outcrop of the Banovina ophiolitic mélange, which consists of serpentinised peridotites occurring in association with amphibolite lenses (Fig. 3.2) and metapyroxenite bands (Fig. 3.3).

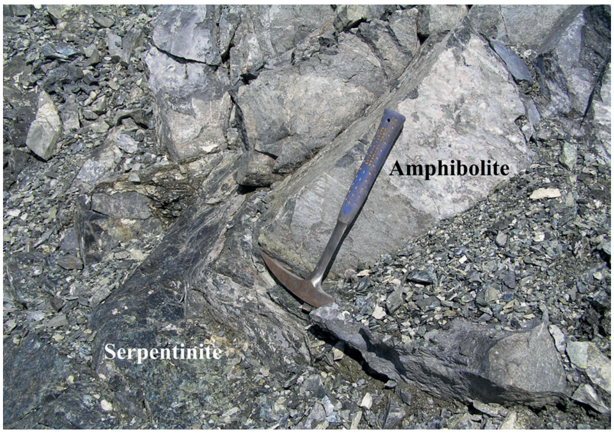

Fig. 3.2. Amphibolite lens in contact with serpentine. Open pit, Slatina mine.

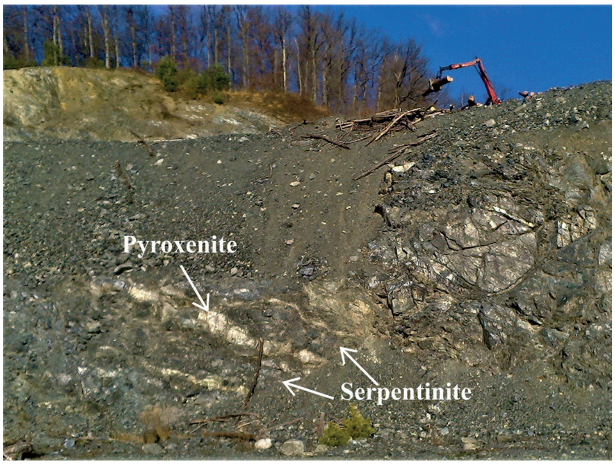

Fig. 3.3. Interchangeable bands of metapyroxenites and serpentinites. Open pit, Slatina mine.

Peridotite

Due to extensive serpentinization, the primary mineral assemblage of the Slatina peridotite is rarely preserved. Therefore, the majority of the studied samples were classified as serpentinite or spinel serpentinite. However, in a few samples, a mineral assemblage consisting of rare relicts of olivine, orthopyroxene, clinopyroxene and spinel showing porphyroclastic texture has been observed and determinated as altered spinel lherzolite. Locally spinel has a corona consisting of chlorite.

Pyroxenite

Pyroxenite layers, ranging in thickness from centimetres to half metres, occur within serpentinised peridotites. They are characterized by banded structures, in which thin layers of serpentine and green spinel (pleonaste) embracing Cr-rich spinel (Fig. 3.4) interchange with broader bands of fine-recrystallized pyroxenes in which a few large deformed pyroxene restites showing extensive exsolution of green spinels occur.

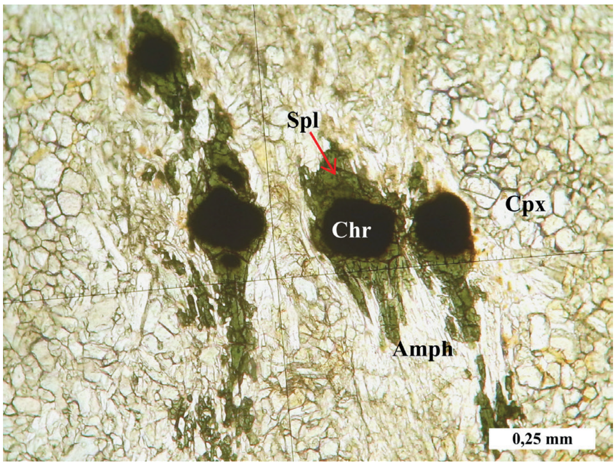

Fig. 3.4. Chromite (Chr) embraced by green pleonaste (Spl) and amphibole (Amph), surrounded by fine-grained clinopyroxenes (Cpx) of metapyroxenite.

Amphibolites

Different types of amphybolites have been found within peridotites. Fine-grained amphibolite is characterised by a fine banded structure and nematogranoblastic to porphyroblastic texture. The bands of hornblende (being significantly altered into actinolite) alternate with plagioclase bands. Plagioclase has been altered to a mixture of clay minerals and clinozoisite. Coarse-grained amphibolites have a homogenous structure and nematogranoblastic to porphyroblastic texture and consist of coarse-grained hornblende, fine-grained plagioclase, partly altered to clay minerals and prehnite, and rare garnet relicts, surrounded by kelyphite (Fig. 3.5).

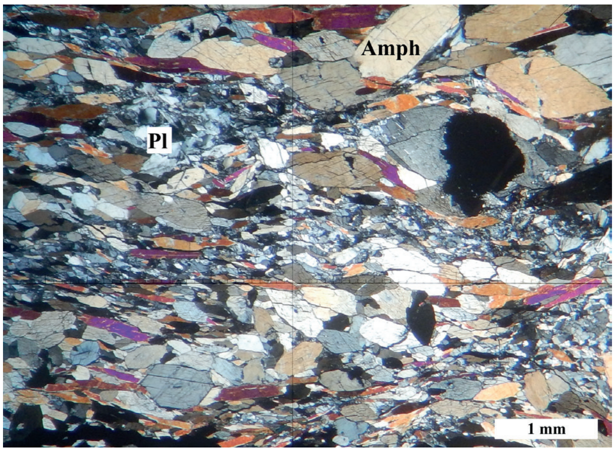

Fig. 3.5. Coarse-grained hornblende (Amph) alternating with fine-grained plagioclase (Pl) in amphibolite.

The occurrence of mafic layers in upper mantle peridotites is common. Usually they have been interpreted as tectonic-type mafic layers, composed of minerals being indigenous to the peridotite, and believed to form by solid differentiation of deforming peridotite and as magmatic-type mafic layers, composed of minerals which are often not stable constituents of the peridotite (DICKEY, 1970). Additional research needs to be done to decipher the genesis of the mafic layers in the peridotites of Slatina quarry.

EXPLOITATION OF CRUSHED STONE AGGREGATES IN THE SLATINA QUARRY

Exploitation of crushed stone aggregates in the Slatina quarry began in 1982 by Croatian Forests Ltd. who used this material for forest roads. The capacity of this exploitation amounted to 50 000 m^3 annually (ŠTAMBUK et al., 1999) and lasted until 2016. Afterwards, Turković Ltd. won the public tender in 2016 for the exploration and exploitation of mineral raw material in the Slatina quarry. Since then additional research has been undertaken, the raw mineral reserves have been recalculated leading to the expansion of the area of exploitation which presently has the form of an irregular polygon with a surface of 5.7 ha.

During this exploration, four boreholes were initially drilled with a total depth of 116.7 m, followed by an additional seven boreholes with a total depth of 218.5 m and four shallow pits with a total length of 15 m.

The quality of the crushed stone aggregates in this quarry is determined by seven partial laboratory analyses and four complete laboratory analyses (Table 3.1).

Based on the analysed physico-mechanical parameters of the examined core from the boreholes, it was found that the crushed stone aggregates according to the results of the medium values meet the criteria for the production of: a) crushed stone for construction of pavement subbase, b) crushed unseparated stone for the construction and maintenance of economic roads, c) aggregates for making asphalt mixtures of asphalt concrete on motorways and roads.

The calculation of the reserves is determined by the method of parallel sections in such a manner that nine longitudinal cross-sections are laid on the situational map. The main plateau, i.e. the lower limit represents the elevation of 265.0 m. The predicted angles of the final slope of the surface digs within the exploitation field at Slatina are between 50° and 60°. The overall reserves of the crushed stone aggregates from the exploration field amount to 1 510 747 m^3, of which approximately 31 % are off-balance-sheet reserves of 587 140 m^3. The planned exploitation of

Table 3.1. The main physical–mechanical parameters of the raw mineral resources.

Physical – mechanical parameters	Serpentinite	Amphibolite	Modified amphibolite
Uniaxial compressive strength in dry conditions (MPa)	197	139	224
Actual density (kg/m^3)	2 666	2 946	3 014
Total porosity (%)	1.45	0.72	0.19
Water absorption (%)	0.667	0.145	0.026
Ultrasonic pulse velocity (Longitudinal wave), m/s	4 859	5 369	6 301

crushed stone aggregates in this relationship is 50 000 m^3 per year, and with the coefficient of distraction Kr=1.45 for the loose material is 72 500 m^3 per year. In addition, given an average selling price of crushed stone aggregates of 21.00 kn/m^3, the total income on that basis is 1 522 500 kn per year.

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Stop 4 Topusko

Topusko Thermal Water Site

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INTRODUCTION

The existence of thermal water springs in Croatia can be traced via the incidence of toponyms *toplica/e* – meaning hot water spring/s, and *topličica* – meaning warm water spring (the diminutive refers to the lower water temperature). Some of the localities were utilized even in prehistoric times (ŠIMUNIĆ, 2008a). Before the Roman Empire, a number of Illyrian tribes populated areas of present day Croatia. One of the tribes inhabited its north-western part with many natural warm and hot springs (Fig. 4.1), and they became known as *Iassi* all around ancient Europe (SCHEJBAL, 2003). Their name derives from the Greek root *-ias/-iat* meaning cure, because they were medicine-men using the healing powers of hot water. The same root is present today in the form *iatros* – physician (e.g. paediatrician). This fact shows that thermal springs had a specific place in the cultural landscape of the area even in prehistoric times.

During the Roman Empire thermal springs were known as curative destinations, especially *Aquae Iassae* (Varaždinske toplice), *Aquae Balissae* (Daruvarske toplice), *Aquae Vivae* (Krapinske toplice), *Aquae Vitae* (unknown location) and *Ad fines* (Topusko) with many archaeological remains standing to this day (Fig. 4.2).

DESCRIPTION

The geological structure of the Topusko area includes, from older to younger, the following deposits: Cretaceous clastic and volcanic rocks, clastic and carbonate sediments of the Upper Miocene, and Plio-Quaternary and Holocene de-

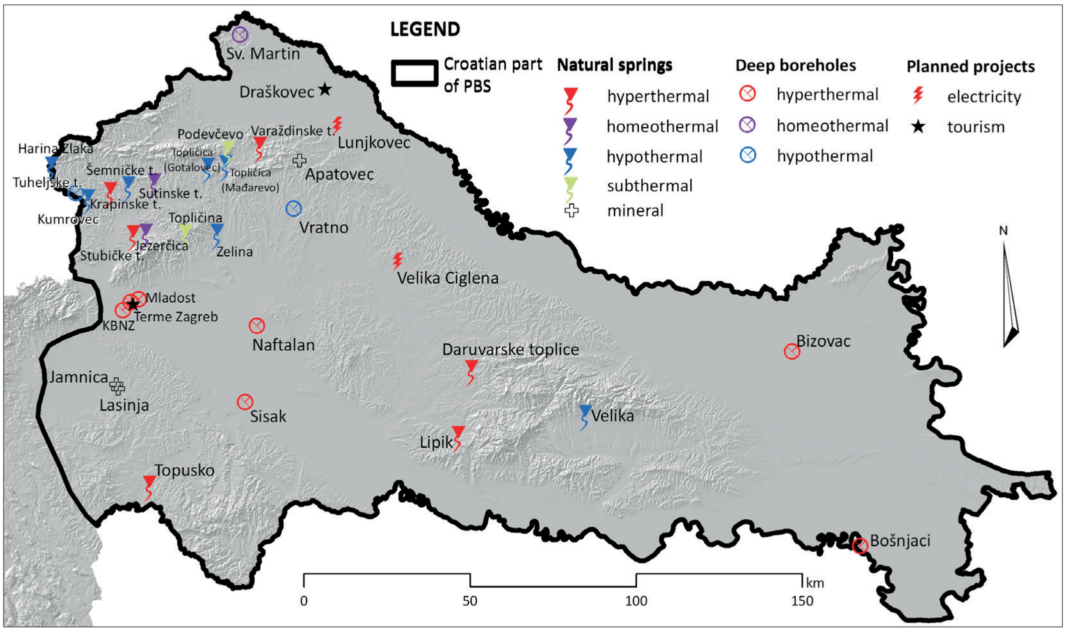

Fig. 4.1. Thermal water localities in the north-eastern Pannonian part of the Republic of Croatia (BOROVIĆ et al., 2016).

Fig. 4.2. Roman archaeological remains near the Glavno vrelo spring in Topusko (from ŠIMUNIĆ, 2008b).

posits (ŠIMUNIĆ, 2008b). The youngest sediments cover most of the surface, making it difficult to interpret deep geological structures (Fig. 4.3 a). However, due to exploratory drilling it is known that the discharge area of the thermal water is bounded by three faults, forming a block in the form of a three-sided prism, where the Triassic dolostones were uplifted (Fig. 4.3 b).

INTERPRETATION

Dolostones appear at depths of 67 m and below (URLI, 1978). They are not equally permeable throughout the borehole, and significantly higher permeability/thermal water inflow was identified by the flowmeter at two intervals between 67 and 81 m. Below those depths the dolostones are compact and the inflow is lower, which was also proven by electro-log: permeable intervals show apparent resistivity

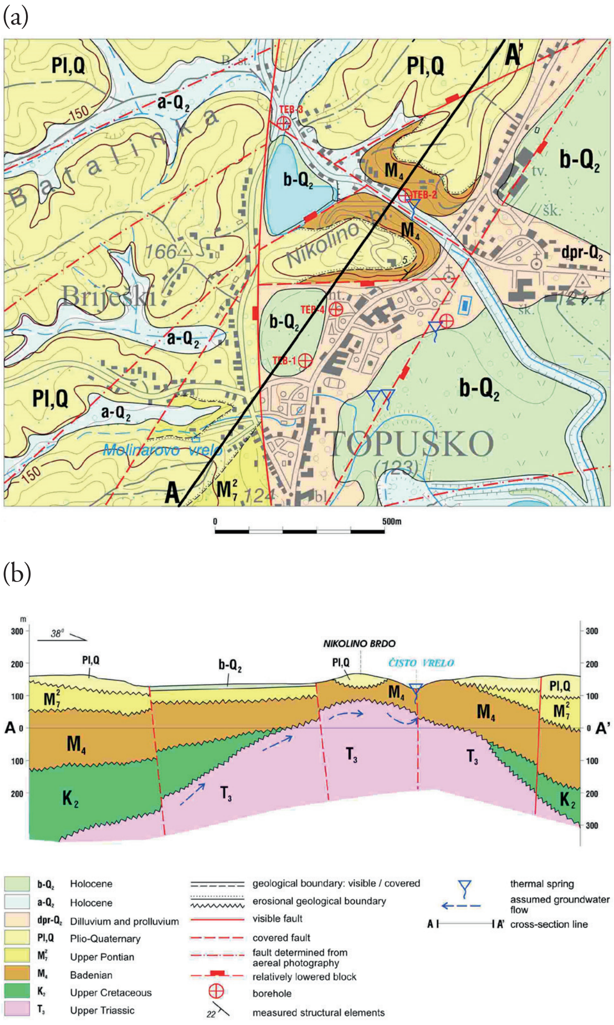

Fig. 4.3. The geological structure, natural thermal springs and boreholes in Topusko: (a) map view; (b) cross-section view (modified after ŠIMUNIĆ, 2008b).

of 400 Ωm, while deeper and impermeable parts shows ≥ 1500 Ωm.

From a hydrogeological point of view, the Triassic carbonates represent geothermal aquifers throughout the Republic of Croatia (ŠIMUNIĆ, 2008a). In Topusko, three natural thermal springs existed, with an estimated total yield of about 25 l/s, and temperatures ranging from 49 to 55 °C, making it the second warmest natural thermal water spring in Croatia, preceded only by Lipik (JAMIČIĆ & CRNKO, 2008) (location shown in Fig. 4.1). In the drilled wells temperatures reach up to 68 °C, but only in wells within the uplifted prismatic dolostone block mentioned above.

Chemical analyses of major ions in thermal water point to a Ca-HCO$_3$ hydrochemical facies (Fig. 4.4 a). An elevated concentration of SO$_4^{2-}$ also needs to be mentioned, but its origin has not yet been interpreted. It is known from drilling and well logging that water resides in the dolomite aquifer. However, ratios of equivalent concentrations of Ca^{2+} and Mg^{2+} cations, shown in comparison to the dissolution of calcite and dolomite, as indicated by STUMM & MORGAN (1996) (Fig. 4.4 b), do not explicitly point to that type of aquifer.

During the monitoring activities (ČUBRANIĆ, 1984a), tritium (^{3}H) activity and general radioactivity (RA) measurements were conducted at the same observation points, four times per year for ^{3}H and twice per year for RA. The presence of ^{3}H in the thermal water would indicate mixing with meteoric water (precipitation and/or groundwater from shallow aquifers). All of the samples were negative, which

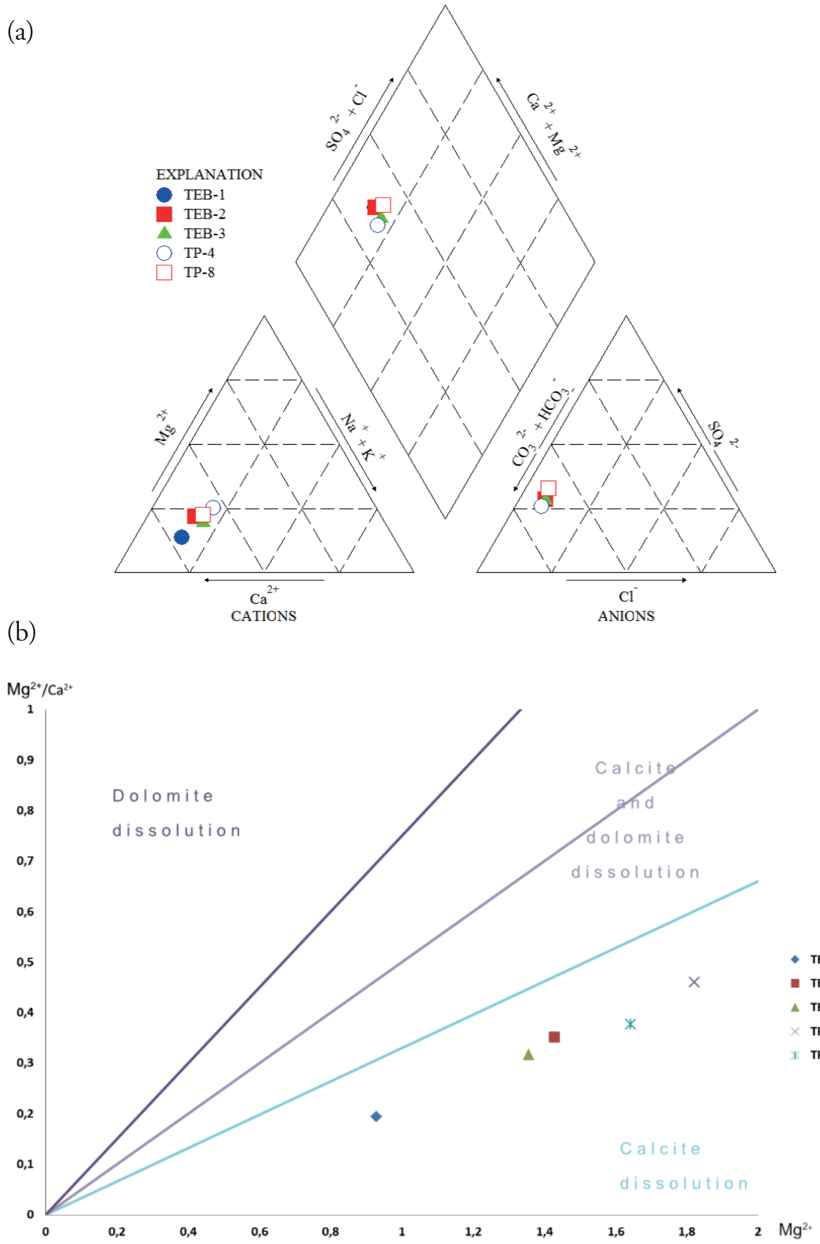

Fig. 4.4. (a) Piper diagram, and (b) equivalent Mg^{2+} and Ca^{2+} ratios of the waters from wells (TEB) and piezometers (TP) in Topusko (constructed from data reported in ČUBRANIĆ, 1984a).

lead to the conclusion that thermal water was not mixing with waters of < 40 years mean residence time (GEYH et al., 2000). However, in a subsequent study (BLINJA, 1986) the authors reported activity of 2.2 ± 1.6 tritium units in the water from a new well, TEB-4, and therefore concluded that the aquifer pressure decline, as a result of a few years of pumping, led to the mixing with relatively younger water from shallower aquifers.

The waters also exhibit radioactivity similar to many other Croatian spas, which was proven by the chemical analyses of water samples (ČUBRANIĆ, 1984a), as well as by natural RA logging in TEB-2 (URLI, 1978) and TEB-4 (BLINJA, 1986). HARAMUSTEK et al. (1952) considered that the major contribution to RA came from radium and radon. Radium (^{226}Ra) concentrations for thermal waters in Croatia were reported by MAROVIĆ et al. (1996) and BITUH et al. (2009), but the authors did not analyse water from the Topusko locality. However, the concentration of radon (^{222}Rn), a daughter-isotope of ^{226}Ra produced by its α-decay, was reported in RADOLIĆ et al. (2005), and the concentration in *spring water* (not specified from which well) was 34.02 ± 2.44 Bq/l, which is the second highest concentration in Croatia, preceded only by water from Stubičke toplice (location shown in Fig. 4.1). However, other reports (ČUBRANIĆ, 1984a; BLINJA, 1986) mention a much higher contribution to total RA produced by ^{40}K, ^{232}Th and ^{238}U, ranging from a minimum of 670 up to 1435 Bq/l in wells TEB-1–4, during the course of five sampling campaigns between 1978–1985. At this point it is worth noting that the regulation on water for human consumption (NN 125/17) allows the activity of up to 100 Bq/l for Rn in drinking water, indicating that the aforementioned levels are far below that threshold. Regulation on pool water quality (NN 88/14) does not consider RA at all, because mentioned levels of RA do not have any impact on the human body if not ingested.

THERMAL WATER UTILIZATION

From 1977 to 1985 seven exploratory boreholes (TP-1–7), four abstraction wells (TEB-1–4) and one deep exploration well (TP-8) were drilled in the Topusko area. Most of them are, unfortunately, no longer operating. From 1986 until the Croatian War of Independence (1991–1995) thermal water was utilized around the settlement – for therapy and recreation, public and residential buildings and factories, 70 l/s on average, while the capacity of TEB-1–3 was estimated to be 137 l/s (ČUBRANIĆ, 1984b). Water utilization was regulated by a good contract between the health and recreational tourism facilities, residential facilities and industrial facilities administrators (S. O. VRGINMOST, 1986). After the devastation during the war many systems were not revitalized, i.e. at the present time only a health tourism centre and hotel are being heated using thermal water (Fig. 4.5 a, b).

Fig. 4.5. Current utilization in (a) hotel Toplica and (b) Top Terme spa (from ŠIMUNIĆ, 2008b); and (c) inappropriate discharge from TEB-2 (from KUREVIJA et al., 2014).

This can be considered as a major loss because the resource is clearly being wasted, but also released into the environment without proper procedures (Fig. 4.5 c). According to Croatian legislation (NN 3/16) water can be released into natural recipients only after being cooled down to 30 °C. That is not the case in Topusko (e.g. Fig 4.5 c), where thermal water flows out through a damaged wellhead. However, such legislation is problematic in itself, since it treats all thermal waters equally: those from deep boreholes (which are not part of contemporary hydrological cycle), as well as those from hydrothermal systems, which would be discharging into the environment in any case: either through natural springs or the artificial objects (boreholes/wells). This problem and dilemma is present in many places in Croatia where thermal water is utilized by wells in the area of existing natural springs (PRANJIĆ, 2000; BOROVIĆ, 2015).

In the early stages of research it was considered that the water discharging at the Topusko springs was heated by a magmatic body, based on the existence of basalts in the surrounding area (e.g. Lasinja – next stop of this excursion) (GORJANOVIĆ-KRAMBERGER, 1905, 1917). However, magmatic bodies older than 1 Ma cannot represent a heat source for contemporary hydrothermal systems (CATHLES et al., 1997). Since those basalts are much older, there is no basis to postulate that they are the heat source in the area. For the time being, the most likely hypothesis is that the aquifer receives recharge west of the thrust fault front of the Petrova Gora Mt. where Triassic dolomites crop out. In accordance with the structure, the water descends below the thrust, warms up under the influence of the geothermal gradient and discharges into a highly permeable fault damage zone at the contact of the three faults in Topusko itself. Defining the recharge area is an important task, in order to protect it from destruction, because the outflow from the hydrothermal systems of this type depends on continuous recharge. If the recharge area is devastated (e.g. by quarries), the fragile equilibrium of the system may be irreversibly disturbed (BOROVIĆ et al., 2019). For this purpose, systematic research of the wider basin area was already proposed in the early stages of the investigation (e.g. DUMANČIĆ & PAVIN, 1986), but was not conducted until now.

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Stop 5 Lasinja Quarry

The Spilites of Lasinja Quarry

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INTRODUCTION

In the broader area of Lasinja, between the Kupa River in the north, Mt. Petrova Gora in the south, the Sjeničak settlement in the west and the Velika Trepča brook to the east, numerous magmatic bodies occur ranging in the size from one to a few hundred metres in diameter. According to MAJER (1978) they belong to the “Diabase-Spilite-Keratophyre associaton” which is part of the magmatic-sedimentary complex of the Mesozoic epoch in the Internal Dinarides and represents the north-western end of the Central Dinaride Ophiolite Belt (CDOB) or lherzolite province (Fig. 3.1 in Stop 3 Slatina).

The tectonic evolution of the Dinarides is very complex, especially due to the existence of two ophiolite belts: the Central Dinaride Ophiolite Belt (CDOB) or lherzolite province and the Vardar Zone Ophiolite Belt (VZOB) or harzburgite province. Both ophiolite belts are of Jurassic age and were obducted at the Jurassic–Cretaceous boundary. Different hypotheses have been proposed to explain such a geological situation: a) two ophiolite belts represent two separated oceanic basins, one of them located to the west and the other to the east of the Pelagonian microcontinent (ROBERTSON, 2002; DILEK et al., 2005; KARAMATA, 2006); b) separation of the two ophiolitic belts by continent-derived tectonic units is a result of Cretaceous to Cenozoic out-of-sequence thrusting and there was only one ocean and obduction of the Vardar ophiolites onto the Adriatic margin (western Vardar Ophiolitic Unit) and European margin (Eastern Vardar Ophiolitic Unit) during the Jurassic–Cretaceous boundary (SCHMID et al., 2008); c) two ophiolite belts originated from the same large Vardar ocean, but the narrow Pindos ocean, characterised by deep water sediments, did exist at the same time, separated from the Vardar ocean by the Pelagonian microcontinent (ARGNANI, 2018).

The magmatic bodies of spilites, keratophyres, diabases and dolerites, among which spilites predominate, are located in the Mesozoic sedimentary rocks. Due to intensive weathering, primary contacts are often hidden and it is not clear, whether the relationships observed are primary or whether the magmatic rocks represent allochtonous chaotic blocks which are embedded in a sedimentary matrix (MAJER, 1978). Mesozoic sedimentary rocks include sandstones, shales, marly limestones, cherts and rarely, conglomerates.

Previous geochemical investigations (LUGOVIĆ et al., 1991; MAJER, 1993) have shown that spilites gechemically corespond to more evolved or E-mid ocean ridge basalt (E-MORB) whereas diabases and dolerites have the characteristics of back arc basin tholeiite (BABT).

DESCRIPTION

The Lasinja quarry is located about 2 km SE of the Lasinja settlement, close to the road connecting Lasinja and Vrgin Most (Fig. A in Geology of Banovina). Spilites occur within sandstones in the form of a thick sill (100–120 m in thickness) stretching along the right side of the Kremešnica Creek (MAJER & TIŠLJAR, 1973). In the contact areas with spilites the sandstones are strongly cataclastically deformed pointing to the fact that they are older than spilites (MAJER & TIŠLJAR, 1973). Unfortunately, due to the intensive weathering of the spilites (Fig. 5.1) a closer view of the contacts between the sandstones and spilite mass is not possible. The sandstones are grey in colour, classified as subgreywackes and contain quartz, feldspar, muscovite and chert fragments in a matrix of quartz, sericite, clay minerals, goethite, pyrite and organic materials (MAJER & TIŠLJAR, 1973).

The spilites occur mainly as massive flows and pillow lavas (Fig. 5.2). Locally brecciated spilite structures have also been recorded (Fig. 5.3).

The modal composition of spilites is quite similar. The main minerals are clinopyroxene and plagioclase, occurring both as phenocrysts and as groundmass phases (Fig. 5.4). The interstices between plagioclase laths and clinopyroxene grains in the groundmass are locally filled with chlorite occuring as product of devitrification of basic glass. Ilmenite is an accessory mineral. Clinopyroxene is usually fresh, but due to the hydrothermal alterations and weathering, plagioclase, especially plagioclase phenocrysts, are altered to albite, epidote and chlorite, whereas ilmenite is partially replaced by titanite, magnetite and leucoxene.

The amygdules occuring in some spilites are filled with calcite and chlorite (Fig. 5.5).

The texture of spilites ranges from porphyritic, often glomeroporphyritic, ophitic to intersertal and ophitic.

Fig. 5.1. Intensive weathering of spilites in the Lasinja quarry.

Fig. 5.2. Pillow lavas of the Lasinja quarry.

Fig. 5.3. Brecciated spilite structure in the Lasinja quarry.

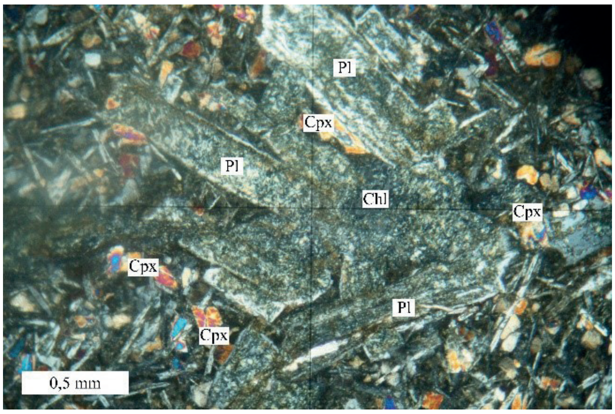

Fig. 5.4. The glomeroporpyric texture of spilite, with plagioclase (Pl) phenocrysts altered in chlorite (Chl) in the groundmass consisting of plagioclase (Pl) laths and clinopyroxene (Cpx) grains, ilmenite and devitrificated glass.

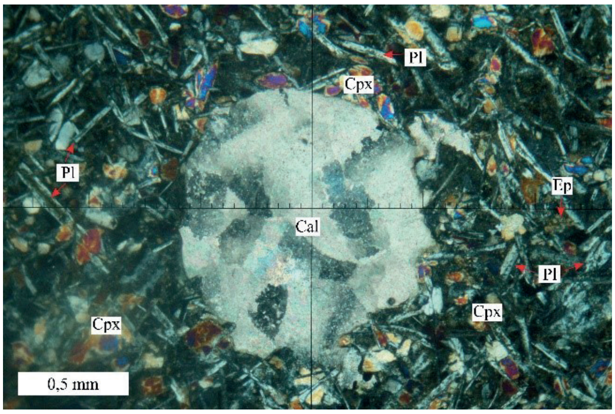

Fig. 5.5. Amygdule filled by calcite (Cal) in the spilite groundmass consisting of plagioclase (Pl) laths, clinopyroxene grains (Cpx) and black ilmenite grains.

INTERPRETATION

Detailed geochemical investigations of spilites from the Lasinja quarry, using major and trace elements, revealed that they are basaltic to basaltic andesite rocks, which were the products of subalkaline tholeiitic magmas. In many aspects they have geochemical characteristics typical of magmas being recently extruded at a mid-oceanic ridge (N-MORB), but the distribution of chondrite normalized concentrations of rare earth elements is not characterized by the lesser enrichment of light rare earth elements (REEs) in relation to heavy REEs, indicating the possible genesis of spilites in back-arc basins (Fig. 5.6). Similar results were observed in the analysed dolerites and diabases from other localities in the Central Ophiolite Dinaride Belt (LUGOVIĆ et al., 1991).

EXPLOITATION OF CRUSHED STONE IN THE LASINJA QUARRY

According to BOLČIĆ (1954), exploitation of crushed stone in the Lasinja quarry (Kremešnica quarry) began in 1923 and proceeded with periodic interruption (e.g. between 1941–1945) until today. It is used as base material for roads. Beton-Lučko Ltd. use spilites from this quarry for the production of aggregate to form concrete.

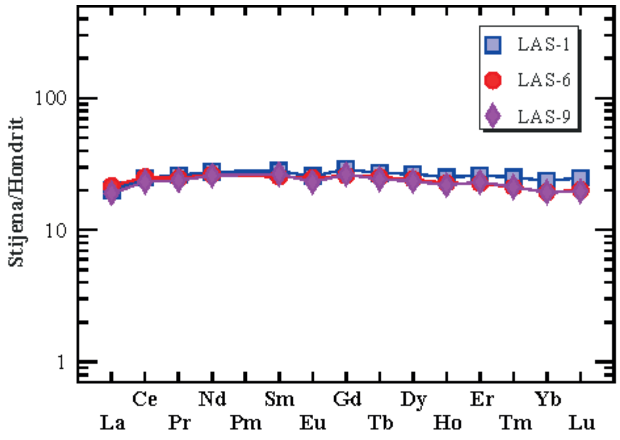

Fig. 5.6. The distribution of chondrite normalized concentrations of rare earth elements in spilites from Lasinja quarry. Normalised values are from SUN & McDONOUGH (1989).

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Zaprešić
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Rakovica
Vrbovec
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Strmec
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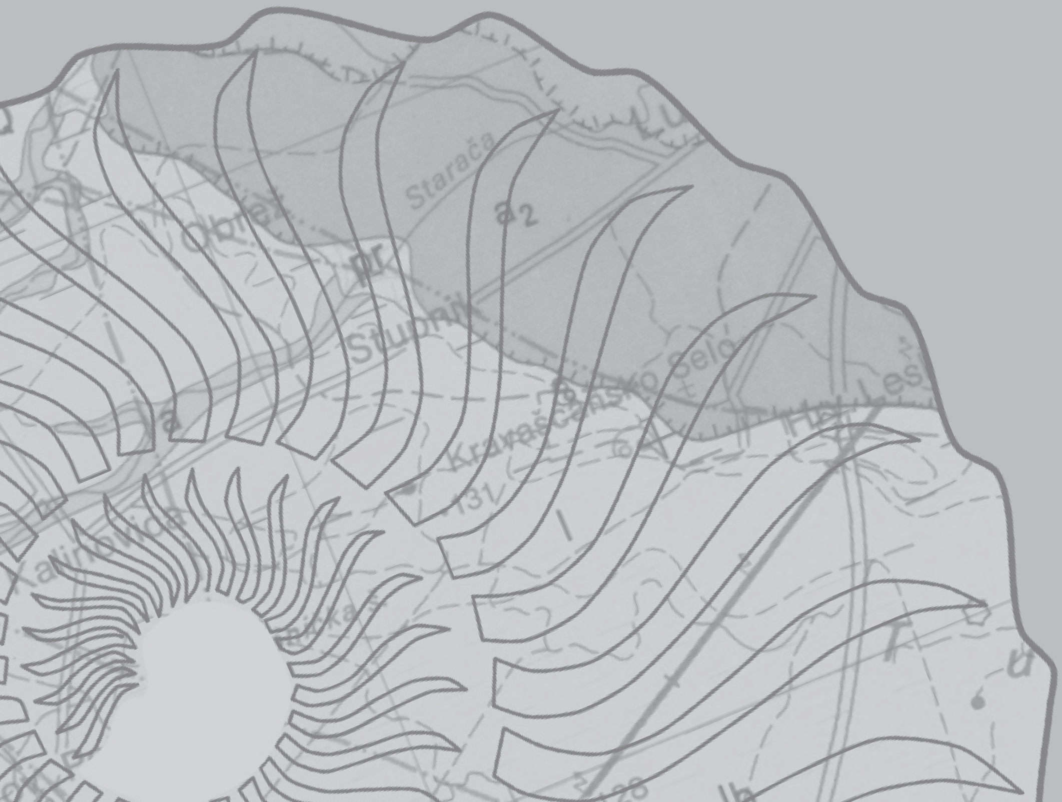
EXCURSION 2
Hrvatsko Zagorje



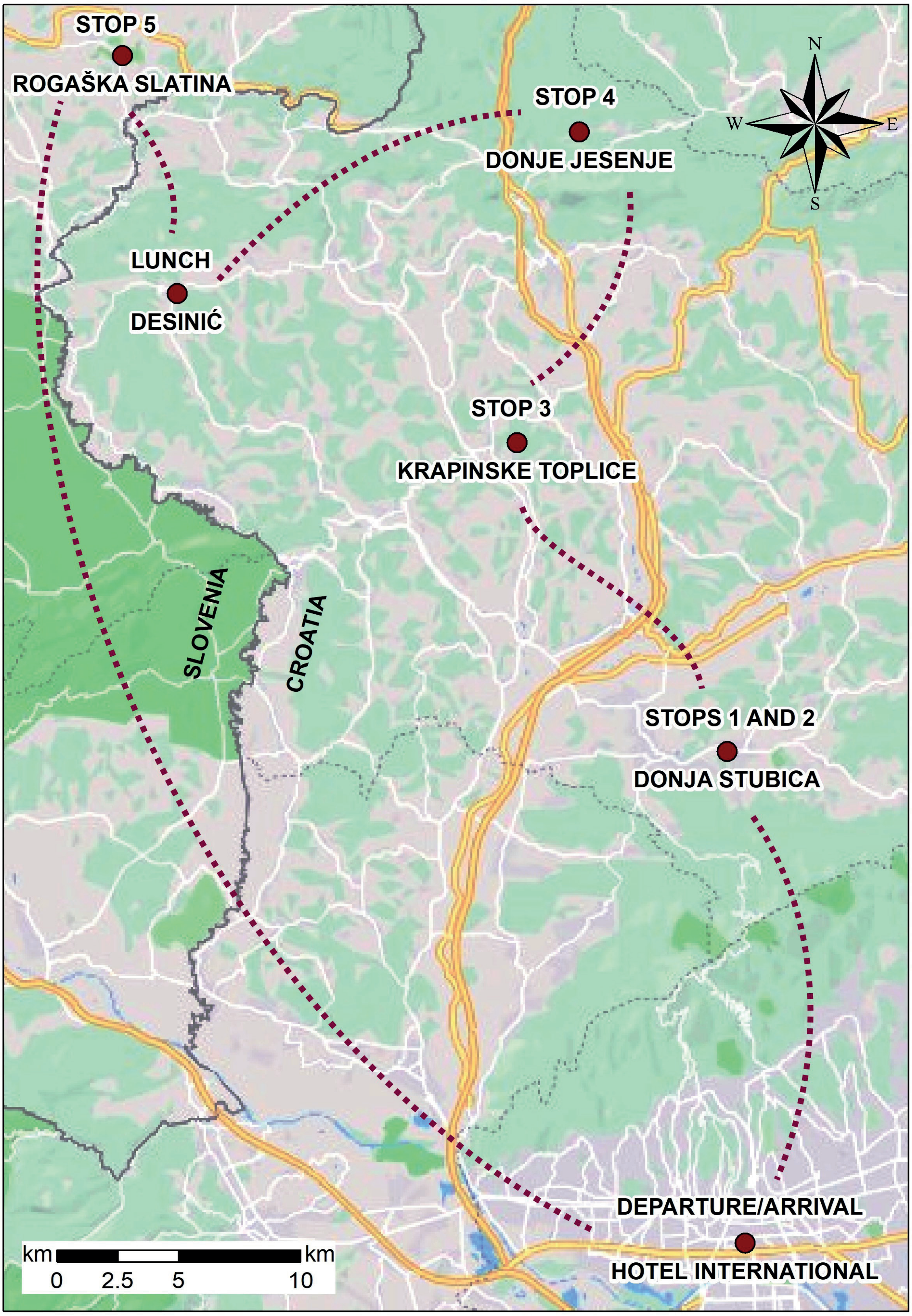


Fig. A. The Hrvatsko Zagorje area and excursion route with stops: 1. & 2. Donja Stubica (Mirti / Hruševec), 3. Krapinske Toplice, 4. Donje Jesenje, 5. Rogaška Slatina.

Foreword

Dear participant,

On behalf of my colleagues and myself, I welcome you to this field trip. It has been organized through the collaboration of many institutions: the Croatian Geological Survey, the University of Zagreb, the Faculty of Science, University of Zagreb, the Faculty of Mining, Geology and Petroleum Engineering and the Geological Survey of Slovenia.

This trip will take you to the area of the Hrvatsko Zagorje, across the border with Slovenia to the Rogaška Slatina area (Fig. A). The Hrvatsko Zagorje is located in the north-western part of the Republic of Croatia and occupies a total area of about 1900 km^2. It is a hilly terrain surrounded by the Medvednica and Kalnik Mts to the south, the Varaždin-Toplica, the Ravna Gora and Macelj Mts to the north, and the Sutla and Drava Rivers to the west and east, respectively. There you can see sedimentary, volcanic, magmatic, metamorphic rocks from the Palaeozoic to the Quaternary, different geological structures, faults, folds… and geothermal water occurrences. In the area of the Rogaška Slatina, where geology defines the land use, e.g. vineyards predominate in the southern parts where andesitic tuff and marls outcrop and where geothermal water occurs. Unlike the geothermal waters from the Hrvatsko Zagorje part which are all thermal; these waters are thermomineral and mineral.

In both countries, Slovenia and Croatia, thermal and mineral water production is important both economically and for tourism.

Tamara Marković

Mirti – Lake Pannon Middle Age – Transdanubian Forced Regression

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INTRODUCTION

A small abandoned sandpit is located alongside the Mirti road in the village of Hruševec, 2 km N of the city of Donja Stubica, on the northern slopes of Mt. Medvednica. It exposes deposits of the Andraševec Formation (KOVAČIĆ et al., 2009), comprising the brackish-water, endemic Lake Pannon mollusc fauna of the Transdanubian (middle Pannonian, Late Miocene) *Paradacna abichi* Zone (BAKRAČ et al., 2012). The outcrop was studied in detail by KOVAČIĆ et al. (2004).

The succession dips 20° to the north and belongs to the southern limb of the Konjščina Syncline. The lower part of the 50 m thick succession (Fig. 1.1) is composed of marls with sandy and silty intercalations (Facies F1). Its upper part exposes strongly deformed sandy and silty deposits (Facies F2).

Facies F1

Marls of this interval form massive or bioturbated beds and may be intercalated with sands and silts. Sandy and silty beds are centimetres to several decimetres thick. Sands are fine-grained, well sorted showing either horizontal lamination with a gradual upward transition to thin sandy silts and overlying marl, or vertical grading followed by gradual transition to marl. Less represented are current-ripple laminated sands followed by horizontally laminated sand. The mollusc association includes *Paradacna abichi* (Fig. 1.2), *P. lenzi*, and *Amygdalia czjzeki*.

Occasional intercalations of sands and minor silts with sharp to erosional bases, the overall grading and vertical sequences of structures are comparable to the T b d e, T a e, T d e and T c d e turbidite sequences of BOUMA (1962). They record a distal, infrequent sediment delivery to the relevant part of the lake bed. The mollusc assemblage in the marls represents the quiet brackish-lacustrine environment

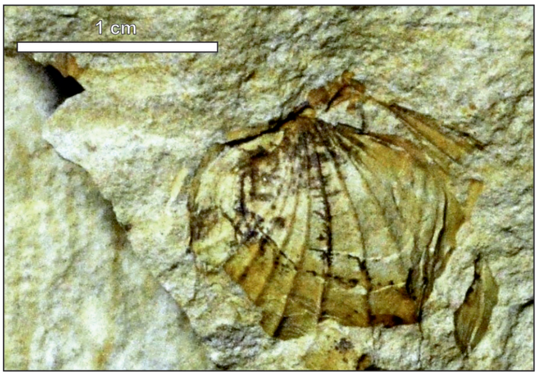

Fig. 1.2. Paradacna abichi from the lower part of the succession at Mirti. It indicates a deep brackish lake environment and Pannonian age (abichi beds) of F1 facies.

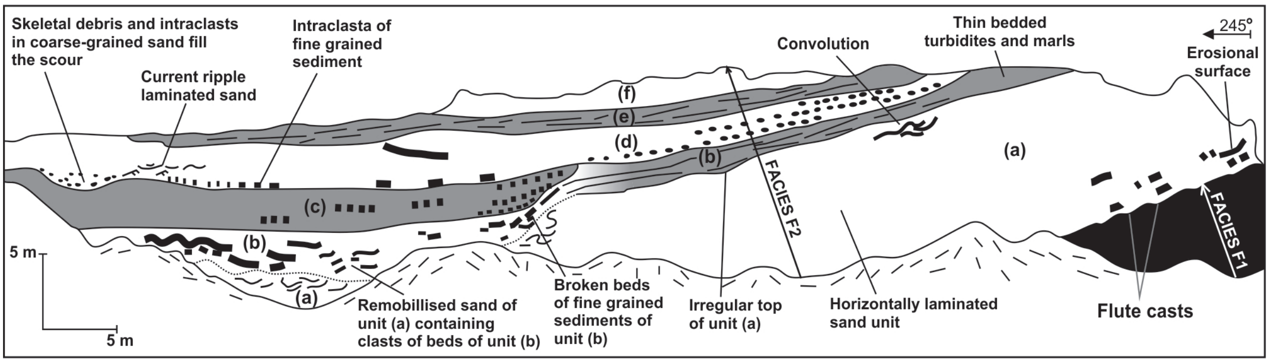

Fig. 1.1. A sketch of the outcrop of Late Pannonian deposits at the Mirti locality displaying a vertical section of sediments of facies F2, and a small proportion of the underlying facies F1 in the lower right corner. The orientation of the outcrop section is 65°–245°, which is approximately diagonal to the palaeotransport directions shown by flute casts (average = 95°) at the base of the sand body (a), and current ripples (SE) in the thin turbidites of the unit (c).

and a water depth below 50 m (MAGYAR, 1995). Such a depth suggests a quiet, uniform suspension settling of fine-grained material to the lake bed where these burrowing bivalves lived.

Facies F2

The upper and main part of the succession consists of three thick sandy units separated by alternating sands and marls (Units a–f in Fig. 1.1).

Unit a is 10 m thick. It consists of fine to medium sand characterized by horizontal lamination (Fig. 1.3 A). Large scale convolutions, erosional surfaces as well as marl and laminated silt clasts occur within the sand body. The basal surface of the lower unit contains flute casts directed towards the E-SE.

Unit b is about 1–2 m thick. It consists of gently deformed, locally disrupted thin beds of sands, silty marls and marls. In the western part of the outcrop, the unit occupies a depression more than 20 m wide showing a diffuse basal contact with highly deformed sands. Unit b is represented here by massive sand containing scattered angular clasts of thin marl and silt beds, which may be deformed (Fig. 1.3 B).

Unit c is up to 2.6 m thick and more than 25-m-wide at the outcrop. The infill of the depression consists of an alternation of thin sands and marls (Fig. 1.3 C). Some sands contain marl clasts. Current-ripple lamination in the sands is directed towards the SE.

Unit d consists of fine-grained sand <3.5m thick. The erosional base of the unit truncates Units b and c, and includes a 1.2 m deep and 5 m wide scour in the western part of the outcrop (Figs. 1.1, 1.3 D). The scour is infilled with coarse sand containing intraclasts of fine-grained sediment, as well as mollusc debris. Other parts of the basal surface are covered by intraclasts of fine-grained sediment.

Unit e comprises alternating thin-bedded sands and marls, while **Unit f** is represented by sand. Units e and f are not accessible for close inspection.

The deposition of **Unit a** probably started at a depth greater than 50 m, as implied by molluscs in the underlying Facies F1. Basal flute casts and crude horizontal lamination, together with the presence of marl and silt intraclasts, reflect erosion by turbulent flow and deposition under upper-stage plane bed conditions. The great thickness of this sand suggests deposition by gradual aggradation from a quasi-steady turbidity flow sustained by a prolonged river flood-stage. A tentative depositional setting would be the slope-base or the lowermost delta slope.

The succession of alternating marls and thin sands of **Unit b** reflects the alternation of fine-grained background deposition and deposition from low-density turbidity currents. Laterally occurring massive sand, containing intraclasts in the western part, reflects sliding and sand flow. Internal structures in sand, the alternation of graded sand and marl, as well as the vertical association of these sediments suggest

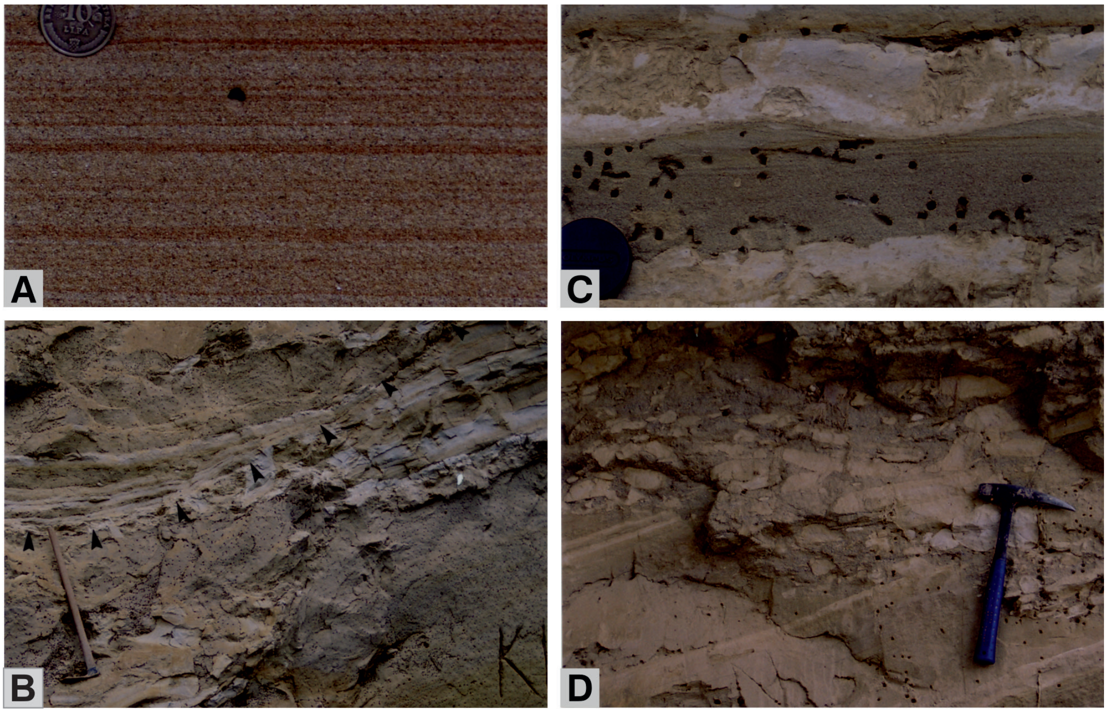

Fig. 1.3. Specific outcrop features of lacustrine late Pannonian delta slope facies at the Mirti locality. A – Horizontally laminated sand in the lower unit (a) of facies F2. The coin is 2 cm in diameter. B – Partly deformed sand of unit (a) in the lower right is overlain by unit (b) consisting of thin-bedded turbidites including hemipelagic marls (upper right). In the lower left, the massive sand contains disrupted beds of silty marl and thin-bedded turbidites. The truncation surface (arrows) representing a slump scar (or erosional surface) is overlain by alternating thin-bedded turbidites and marls of unit (c). The hoe for scale is 1 m long. C – Alternation of sands (dark) and marls (light) of unit (c). Internal structures represent Bouma T b c d e sequences including hemipelagic marl. Current ripples migrated towards the SE. The lens cap is 5 cm in diameter. D – Erosionally truncated alternation of sands and thin marls of unit (c) in the lower part and overlying basal portion of unit (d) showing intraclasts in a sand matrix. The hammer is 31 cm long.

an alternation of turbidity-current deposition and slow, fine-grained lacustrine deposition. The depression probably acted as a channel for the basin-ward sediment transport and was subsequently infilled by thin-bedded turbidites.

The origins of **Units d**, **e**, and **f** are probably similar to comparable units occurring in the lower part of the exposure.

Conclusively, the sediments of **Facies F2** are related to fast, sustained, hyperpycnal flows, which scoured the bottom upslope. The sediment features indicate the deformation and sliding of different sediment types, liquefaction and flows of remobilised sand, as well as closely related scouring and channelling. These processes occurred in close succession, thus indicating an unstable slope setting connected to the mouth of the river, very rich in sand.

Also their chute and ridge morphology indicates depositional dynamics described from recent submarine delta slopes (eg. PRIOR & BORNHOLD, 1989, 1990). The packages of alternating thin turbidites and fine-grained sediments may have been deposited either on interchute areas as overbank sediment or within chutes and slide scars. They have also been involved in sliding.

The slope was facing E-SE based on the directions of flute casts and current ripples. Sliding and deformation/liquefaction events were probably induced by seismic activity.

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Stops 2 & 3 Utilization of geothermal waters in Hrvatsko Zagorje

Geothermal Waters of the Stubičke Toplice & Jezerčica & Geothermal Waters of the Krapinske Toplice

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INTRODUCTION

Geologically, Croatia is situated at the intersection of three major European regions: the Alps to the north-west, the Pannonian basin to the north-east, and the Dinarides to the south-west. The majority of Croatia's geothermal potential is concentrated in the Croatian part of the Pannonian Basin System (PBS) which represents the south-western margin of the PBS. With regard to geothermal characteristics, Croatia can be divided into two regions: the Pannonian Basin area to the north and the Dinarides to the south. The area of the Pannonian basin has a significant geothermal potential where the average geothermal gradient is 0.049 °C/m and in places reaches values of more than 0.07 °C/m. The terrestrial heat-flow density is also high – 76 mW/m^2. Compared to the Dinarides area where the average geothermal gradient is 0.018 °C/m and the terrestrial heat-flow density flow is 29 mW/m^2 (BOŠNJAK et al., 1998) (Fig. 2.1).

The average geothermal gradient of Europe is 0.03 °C/m (BOŠNJAK et al., 1998) (Fig. 2.1).

In the area of Hrvatsko Zagorje, located in the western part of the Pannonian basin, the geothermal gradient varies from 0.020 to 0.060 °C/m (Fig. 2.2). The highest values are observed in the area were geothermal waters occur.

Previous research on the geothermal waters in the Hrvatsko Zagorje area proved that springs are located in the tops of anticlines that are fractured in different directions by transverse faults and cracks that usually represent an environment with high permeability which in this case enables the upwelling of heated water at depth to the surface (ŠIMUNIĆ, 2008). Most of the aquifers in this area are composed of Triassic dolomites and limestone (MARKOVIĆ et al., 2019). Geothermal water in the Hrvatsko Zagorje is mainly used for rehabilitation, balneology, recreation, space and individual heating, greenhouse heating and sanitary water. A few years ago it was also used for bottled water and fish farming but not anymore. The water temperatures of the utilized geothermal waters vary from 30 to 60 °C.

Fig. 2.1. Schematic division of the Croatian territory according to geothermal features (modified from BOŠNJAK et al., 1998).

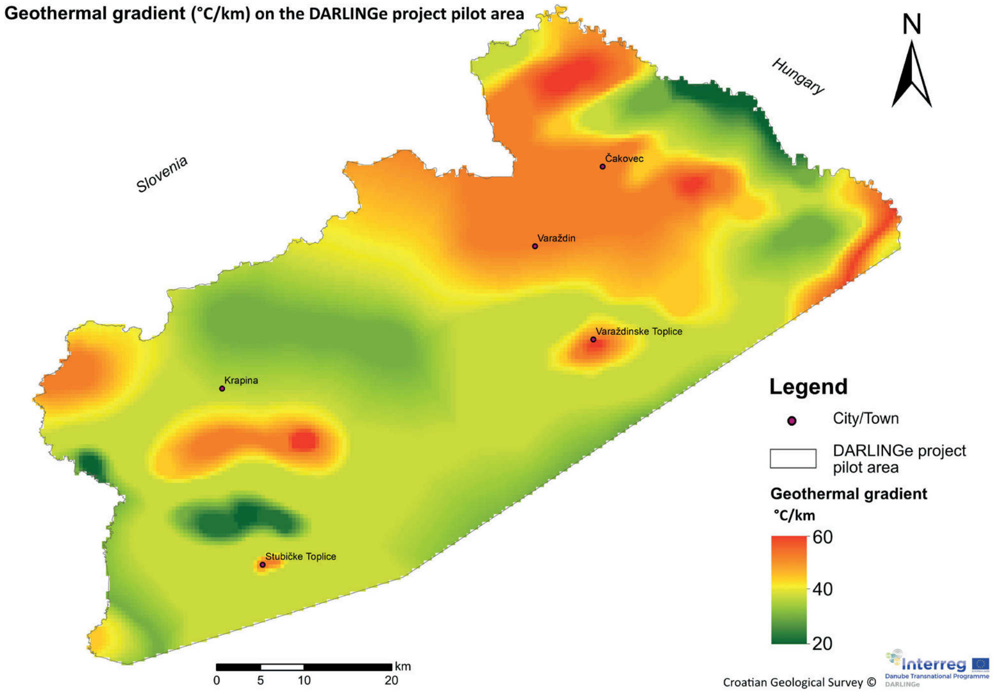

Fig. 2.2. Map of the geothermal gradient in the Hrvatsko Zagorje area according to MARKOVIĆ & ŠOLAJA, 2019.

Stop 2 Geothermal Waters of the Stubičke Toplice and Jezerčica

The largest and most famous health and tourist spa of the Hrvatsko Zagorje is Stubičke Toplice (Fig. 2.3). In 1811 archbishop Maximilian Vrhovec became its owner. At that time, the first indoor swimming pool was built, along with two rooms with baths for several persons and several individual spa chambers. The geothermal springs had consisted of two major and several smaller springs, but they dried up when deep wells were drilled and put into operation. The only spring which did not dry up, is the spring near the hospital, but this spring is mixture of geothermal and cold water and the water temperature is 35 °C. The water temperature in the wells varies from 56 to 60 °C. The surrounding area of the Stubičke Toplice spring/wells comprises clastic carbonate sediments, dolomite, alluvial, proluvial-deluvial deposits and siliciclastic rocks. The geothermal aquifer consists of carbonate sediments (dolomite and limestones). The geothermal water belongs to a CaMgNa-HCO_3SO_4 mixed type. A high content of CO_2 is observed – 101.49 mg/L (https://bolnicastubicketoplice.com).

Today geothermal water is utilized by the Special Hospital for Medical Rehabilitation, Stubičke Toplice and the hotel Matija Gubec (Fig. 2.4). The Special Hospital for Medical Rehabilitation uses well B-1 which was drilled in 1963. The operational depth of the well is 51 m although the drilled depth was 201.73 m (GLAVINIĆ, 1963). The average yield of the well is 2.7 l/s. The water is used for recreation, balneotherapy and space heating and sanitary water. The hotel Matija Gubec uses the second well ST-2 and the water is used for recreation.

There was another geothermal spring only a few kilometres east of Stubičke Toplice, in the Jezerčica area (Fig. 2.5). However, when during the late sixties when the well was drilled and put into operation, the spring dried up. The spring was called *Jezerišće* and according to the old literature, the water temperature was between 28–34 °C. The water temperature at the head of the well is around 38.5 °C and it does not vary which is an indicator that the geothermal water is not in direct contact with "cold" water which is the case at the previously mentioned site (MARKOVIĆ et al., 2019). The geothermal aquifer consists of carbonate sediments (dolomite and limestones). The geothermal water belongs to a CaMg-HCO_3 type. Today, the geothermal water is utilized by the Terme Jezerčica and is used for recreation and balneotherapy.

During the DARLINGe project, both sites were intensively investigated from hydrochemical and hydrogeological perspectives. Many chemical and isotopic analyses were performed including determination of the ratio of the stable isotope oxgen-18 and deuterium (Fig. 2.6). It was observed that waters at both sites have a meteoric origin.

Fig. 2.3. The Special Hospital for Medical Rehabilitation, Stubičke Toplice (https://zagorjehealth.hr/clanice/specijalna-bolnica-za-medicinsku-rehabilitaciju-stubicke-toplice).

Fig. 2.4. The hotel Matija Gubec (https://www.visitzagorje.hr/objekt/hotel-matija-gubec).

Fig. 2.5. The hotel and camp Terme Jezerčica (http://terme-jezercica.hr).

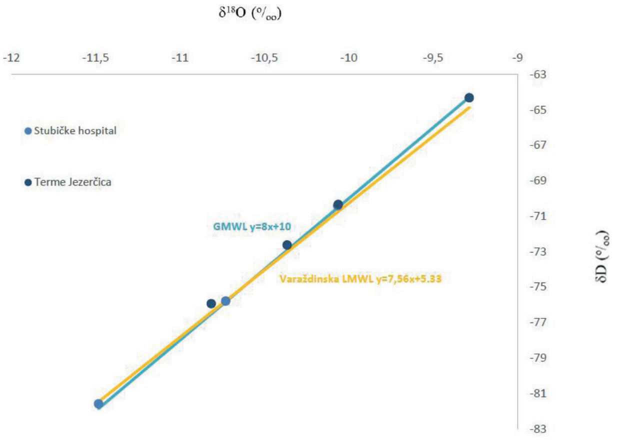

Fig. 2.6. The ratio of stable isotope oxgen-18 and deuterium in the geothermal waters of Stubičke Toplice and Jezerčica.

The thermal springs of Krapinske Toplice have been known since the time of the Romans, when a settlement called *Aquae vivae* existed here. The *modern* development of tourism began in the 18th century and from the very beginning, it was based on the use of the thermal springs in the area. The first bath, called Dubrava, was built in 1772, followed by the Rukavina spa in 1808. However, the real momentum behind the development of tourism started in 1857, when Jacob Badel bought the existing baths and started to build new baths, a hotel, and health resorts. In that period, Krapinske Toplice became a modern health resort within the Austro-Hungarian Monarchy and attracted a significant number of tourist visitors. The more recent era of modern tourism began in 1956, when a hospital department for rheumatic diseases and orthopaedic rehabilitation was established (Fig. 3.1).

Geothermal springs occur in the narrow valley of the Topličica stream where there are three main springs and a few springs of lower yield. The main occurrence of the thermal springs is in the area of Pučke and Jakobove kupelji. The average yields of the springs are: Pučka kupelj – 36.8 L/s and Jakobova kupelj – 10.3 L/s. The water temperature in Pučka kupelj varies from 40.5–41.7 °C and in Jakobova kupelj from 42.2–43.1 °C. In 1985, a deep well was drilled about 250 m north of the thermal springs. The well passed through limestone and dolomite before terminating in calcarenites and shale at a depth of 861 m (ŠIMUNIĆ, 1986). The well was tested with a yield of 30 l/s and the water temperature was 45 °C. The geothermal aquifer consists of carbonate sediments (dolomite and limestones).

The water by its ion composition belongs to the CaMg-HCO_3 type of water. Hydrochemical facies are the result of the dissolution of carbonate minerals in the thermal aquifer. It is also noticeable that the type of water, or hydrogeochemical facies, has not changed over the years. The site was also part of the DARLINGe project and here as in the two previous sites the ratio of stable isotope oxgen-18 and deuterium in the geothermal waters showed a meteoric origin.

Today in Krapinske Toplice, the geothermal water is used in:

- the Special Hospital for Medical Rehabilitation Krapinske Toplice: for therapeutic treatments, swimming pools and for space heating of the hospital using the heat pumps
- the Magdalena clinic next to the Special hospital: for space heating
- the Waterpark Aquae vivae, that extend to 18 000 m^2 of closed space, for swimming pools and for heating entire complex
- the Villa Magdalena hotel: for whirlpools in the hotel rooms and as sanitary hot water

Geothermal water is used in the water supply distribution system connecting 271 households.

Also, 5 km away from the geothermal springs in Jurjevac village, Samek Ltd. uses geothermal water from the well for heating greenhouses for tomato production.

The Special Hospital for Medical Rehabilitation, in accordance with the concession, uses a total amount of 534 500 m^3/y of geothermal water (with up to 183 950 m^3 for the water supply, up to 287 300 m^3 for technological needs, and up to 63 250 m^3 for health and recreational use). The hospital has heat pumps: a GEA HAPPEL type EUWH 240FSD – year 1992 – COP 3.6 – which uses thermal water (water from 40°C is heated to 60 °C – T= 20 °C) for space heating but only at night and during the wintertime.

Fig. 3.1. The Special Hospital for Medical Rehabilitation Krapinske Toplice (https://www.visitzagorje.hr).

The Waterpark Aqua Vivae (Fig. 3.2) uses thermal water for swimming pools and heating the entire 18 000 m^2 complex. The water temperature at the inlet of the park is around 40.5 °C. The temperature of the outlet water (wastewater) is 28 °C. Water used for the swimming pools first goes to the hottest pool, then to a warm pool, ending in the coolest swimming pool. The heating in the water park is performed in the way that the heating condensators (accumulators) (Fig. 3.3) use the bottom plate of the water park in which 50 km of pipes were built-in for under-floor heating. The bottom plate is made of concrete, and has a mass of 5000 tons and a volume of 2700 m^3. It is heated during the night (when the prices for electrical energy is lowest) to a temperature of 33 °C, and during the day it cools down to 30 °C. The thermal energy is stored at the lowest part of the premises thereby ensuring that the natural circulation of hot air occurs from floor to ceiling, where the air conditioning chambers suck in the heated air and transport it to the previously mentioned recuperators. Roof and wall thermal insulation reduces mechanical and static losses of heat to a minimum. The primary construction goal is to achieve a building complex with an integrated thermal insulation system that ensures very low thermal conductibility. The insulation of the outer walls is designed in such a way as to achieve a very high coefficiency in the passing of warmth through the wall's material. This coefficiency is = 0.26 W/m^2K. On the vertical walls, we have 60 mm thick glass bricks, with a coefficiency of 0.9 W/m^2K. The roofs are composed of a laminated wood construction and are insulated in such a way that they have a coefficiency of 0.2 W/m^2K. The glazed areas of the roof are designed with triple-glazing to lower emission so that the coefficiency of the passing of heat in that part of the roof is 1.1 W/m^2K. The heat leaving the water park, still has a temperature of 28 °C and can be cooled by another 20 °C so that another 2.2 MWh energy can be obtained for some other project. The water temperature is exploited to a temperature of 8 °C when it can no longer be used.

All the apartments at the Villa Magdalena Hotel (Fig. 3.4) have jacuzzis in rooms heated by the thermal water from the spring with water temperatures of around 39 °C. This results in an annual consumption of thermal water of 4000 m^3 for this purpose. Unfortunately, the Villa Magdalena spa and wellness centre has no built infrastructure to use the thermal water to heat the whole building.

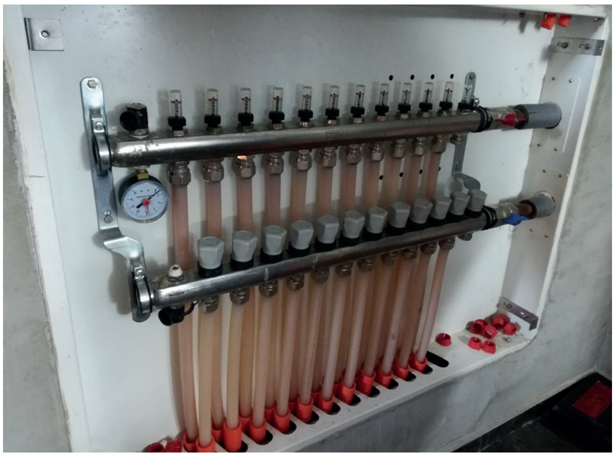

Fig. 3.3. The heating system in the waterpark (photo by I. Bobovečki).

Fig. 3.2. The Waterpark Aquae vivae (photo by M. Crljen).

Fig. 3.4. The hotel Villa Magdalena (https://www.villa-magdalena.net).

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Pyroclastic Rocks of Donje Jesenje and Their Alteration Products

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Pyroclastic rocks that occur in the abandoned quarry near Donje Jesenje are of Early Miocene (Eggenburgian) age and belong to the Vučji Jarek Mb. of the Macelj Fm. (ŠIMUNIĆ, AN. et al., 1995; AVANIĆ, 2012). The Donje Jesenje deposit was developed within the Hrvatsko Zagorje Basin (HZB), which was part of the Central Paratethys characterized by marine deposition from Egerian to Sarmatian (AVANIĆ et al., 2018a and references therein). Collision of the Adriatic microplate and the European foreland during the Oligocene and Miocene (SCHMID et al., 1989) caused regional stress characterized by a main NS compression axis with EW extension. Dextral strike-slip fault systems were formed, representing the eastern continuation of the Periadriatic lineament. Associated with these fault systems is the occurrence of synsedimentary volcanism in the Egerian (andesite and pyroclastic rocks), Eggenburgian and Ottnangian (tuffs, tuffites and bentonites). In the Macelj area there are numerous outcrops of sediments containing variable quantities of volcanic material; however, due to exploitation the best outcrops of tuffs (*sensu lato*) can be observed in the Donje Jesenje quarry (ŠIMUNIĆ, AN. & PAMIĆ, 1993; TOMLJENOVIĆ & CSONTOS, 2001; AVANIĆ et al., 2018a).

The thickness of the pyroclastic rocks in the quarry, as determined by exploration drilling, is approximately 60 m (GOLUB & BRAJDIĆ, 1969; MARKOVIĆ, 2002). The tuff was first exploited as an ornamental construction stone, but this stopped because it was unsuitable for exterior applications. Later, it was used as pozzolanic material in the cement industry, and most recently as zeolite raw material used as a soil additive, litter additive and in wastewater and sewage water purification. Due to their abundance and low cost, natural zeolites have widespread applications in environmental protection and remediation, in agriculture for soil treatment, as pet litter, additives in animal nutrition, and as construction material etc. Estimated zeolitized rock reserves are in the order of 3 000 000 tonnes (KRUK et al., 2014). The Donje Jesenje quarry was abandoned in the first decade of the 21st century.

DESCRIPTION

Pyroclastics are lateral correlatives of the upper part of deposits belonging to the horizontally and cross-bedded glauconitic sandstones facies. The deposits are mostly horizontally bedded, with bed thicknesses between 1 and 30 cm (Fig. 4.1). Some beds are thicker, reaching up to 5 m in thickness. Trough cross-bedded pyroclastics of sandy grain-size occur in just a few beds.

Tuffs are the predominant type of pyroclastic deposits. They show vertical alternation of vitroclastic, vitrocrystalloclastic, crystalloclastic and crystallolithoclastic types (GOLUB & BRAJDIĆ, 1969; ŠIMUNIĆ, AL. et al., 1988). Pumice characterized by hollows that are irregularly dispersed or parallel to the bedding plane occurs within the pyroclastics. The hollows are empty or filled with clayey material produced by the devitrification of volcanic glass (Fig. 4.2). Volcaniclastic rocks have variable primary composition; the main constituents of vitroclastic and crystalloclastic tuffs are volcanic glass, plagioclase feldspars (andesine) and biotite, while amphibole and quartz are rare. Lithoclastic tuffs are composed of tuff and effusive rocks fragments, and, in smaller quantities, mineral fragments and glass. In the quarry, the SiO_2 content varies between 65–70 %; therefore the tuff was determined as being of dacito-andesitic composition.

The rocks contain various alteration products of volcanic glass (Fig. 4.3), including zeolites, clay minerals (smectite, authigenic mica), SiO_2 phases (opal-CT, opal-C, and quartz) and authigenic feldspars (TIBLJAŠ, 1996; TIBLJAŠ & ŠĆAVNIČAR, 2007).

Fig. 4.1. Facies of horizontally and cross-bedded pyroclastics (photo by R. Avanić).

Clinoptilolite (based on the Si/Al ratio) is the most abundant zeolite, however analcime and mordenite are also present. The type of exchangeable cations in clinoptilolite is variable; therefore, clinoptilolites present in the quarry were divided into two subgroups: Ca-K- (present in the upper part), and Na-rich (present in the lower part). Clinoptilolites present in the younger sediments that crop out in the Šeprun and Jamno areas (except those from the borehole sample which are Na-rich), belong to the Ca-K group while those from the Hromec area are rich in divalent cations. The clinoptilolite content in the volcaniclastic rocks discovered in the Macelj area varies significantly: in some rocks it is the dominant component, in others it is present only in traces. In the Donje Jesenje quarry the variations, although present, are not as conspicuous, and the average content of clinoptilolite is approximately 50 wt.%.

Authigenic mica occurs in thin veins (Fig. 4.4) and as coatings within vesicles in the glass shards (Fig. 4.5). An X-ray powder diffraction pattern with widened but still relatively sharp reflections is characteristic for lM micas, with an Fe-rich octahedral sheet. The observed d(060) value is 1.508 Å. The IR spectrum is characterized by sharp absorption bands in the OH stretching region, with the two strongest bands at 3580 and 3600 cm^{-1} ascribed to Al-Fe^{3+} and Al-Mg cationic environment of the OH groups. Microprobe analyses revealed that this is an interlayer-deficient dioctahedral mica, with Al as the dominant cation in the octahedral sheet, $^{VI}M^{3+}>1.2$, and low tetrahedral substitution (TIBLJAŠ et al., 2004), with quite a peculiar chemical composition that does not correspond ideally to any member of the mica group as defined by RIEDER et al. (1998). It can best be classified as an interlayer-deficient alumino-celadonite.

Bentonite deposits have also been investigated in the area. Exploitable amounts were found in Šeprun and Šaša, in the area around Bednja. These deposits were formed by the alteration of vitroclastic tuff and volcanic glass of Early Miocene age (MARKOVIĆ, 2002). The immobile microelements composition suggests felsic to intermediate volcanism.

The clay pit in Šaša was active, although not continuously, from 1926 when surface excavation began, until the 1990s when the reserves were depleted. Bentonites from Šaša was used in castings, as its quality was deemed unsuitable to be used in drilling fluids. The deposit is 10 to 35 m thick, plate-shaped, occurring within the layer of coarse-grained arenites of Early Miocene age (BRAUN, 1991). The dominant mineral in the deposit is a high-charge montmorillonite with a high Fe-content. The main interlayer cation is Na. Other minerals present include plagioclase, quartz, opal-CT and trace amounts of kaolinite, calcite and zeolite from the heulandite-clinoptilolite series. XRD data showed some degree of interstratification with 10-20% of illite layers. The CEC values have been determined at 85 meq/100g (AVANIĆ et al., 2018b).

Chaotic pyroclastics showing slumping occur in the upper part of the succession (Fig. 4.6). They consist of tuffs with dispersed fragments of lapilli composed of volcanic

Fig. 4.2. Dark clasts of devitrified pumice fragments in pyroclastics as an indicator of synsedimentary explosive volcanic activity (photo by R. Avanić).

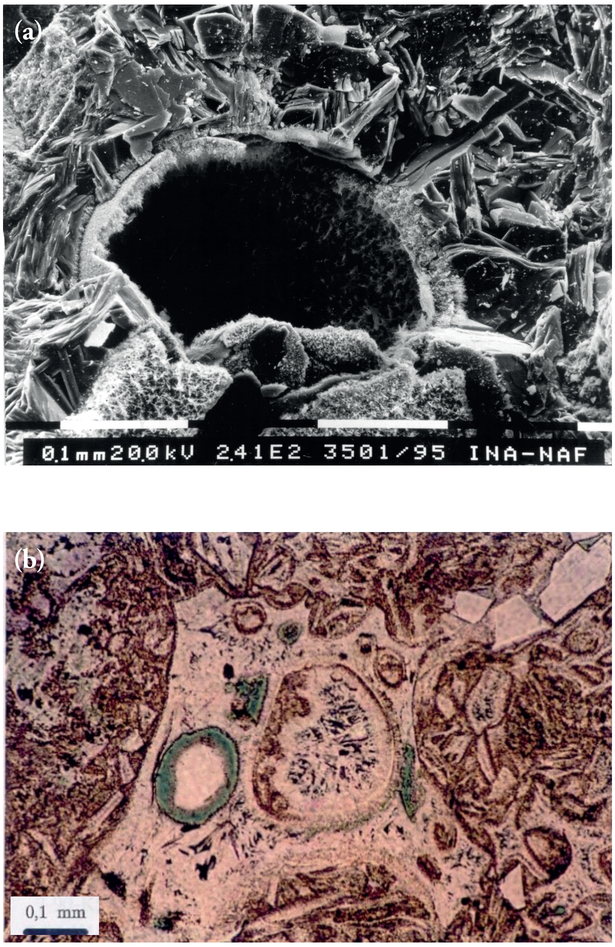

Fig. 4.3. (a) SEM photomicrograph of a volcanic glass shard altered to platy clinoptilolite. The vesicle within the shard is lined with laths of authigenic mica (photo by R. Slavković); (b) Photomicrograph of a tuff from the Donje Jesenje quarry showing a glass shard altered to platy clinoptiloite and authigenic mica (celadonite) present as a vesicle lining (diameter of the vesicle is ca. 0.1 mm) (TIBLJAŠ et al., 2004).

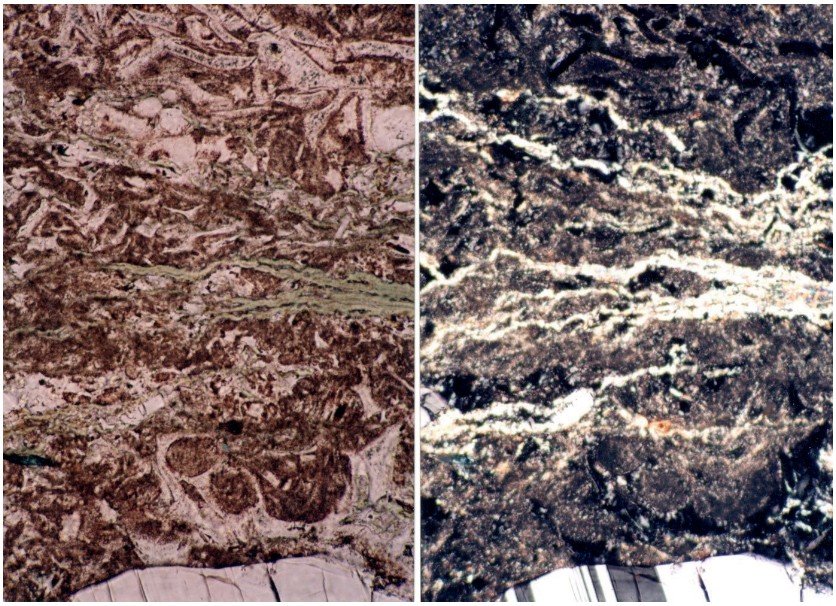

Fig. 4.4. A photomicrograph of a veinlet filled with a green mica mineral in a tuff containing glass shards, altered to clinoptilolite, and plagioclase phenocrysts in a fine-grained matrix. The black line is 0.1 mm long. Left – plane-polarized light; right – cross-polarized light – veins with authigenic mica are clearly visible due to their second order interference colours (TIBLJAŠ et al., 2004).

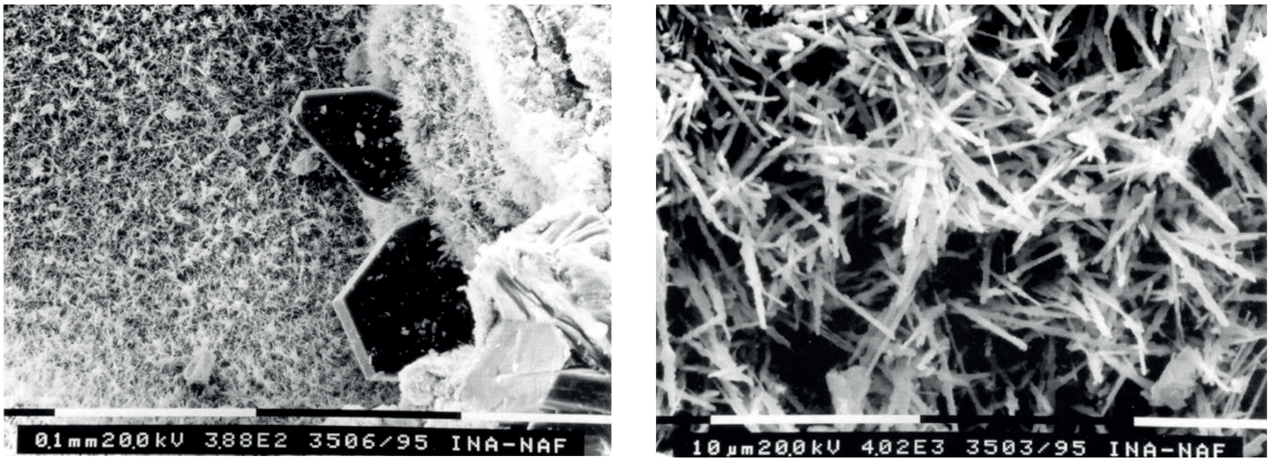

Fig. 4.5. An SEM photomicrograph showing two platy crystals of clinoptilolite within a vesicle of altered volcanic glass shard in the tuff from Donje Jesenje quarry. The surface of the vesicle is lined with lath-shaped authigenic mica (left); a higher magnification SEM photomicrograph of authigenic mica (app. 0.1x0.25x10 µm) (TIBLJAŠ et al., 2004) (right).

glass, lithoclasts and crystalloclasts. The lithoclasts are composed of andesite or tuff. Rounded tuff blocks up to 5 m in diameter rarely occur (Fig. 4.6). The uppermost part of the succession is characterized by tuffs that have been strongly affected by modern weathering processes that resulted in alteration into a sandy material.

INTERPRETATION

The pyroclastics were probably deposited in a marine environment. This is indicated by pumice with hollows formed parallel to bedding planes reflecting rapid cooling of volcanic ash in water, and relatively quick deposition (WHITHAM & SPARKS, 1986; McPHIE et al., 1993; CAS & WRIGHT, 1995). This interpretation is supported by cross-bedded pyroclastics that suggest subaqueous dune migration facilitated by currents in a shallow marine environment (ASHLEY, 1990). Chaotic pyroclastics in the upper part of the succession are interpreted as a result of density flows generated by seismic events that caused liquefaction and destabilization of the pyroclastic material produced by submarine eruptions (sensu CAS & WRIGHT, 1995). The thickness of the pyroclastics indicates a relatively long-lasting explosive sequence of volcanic activity. This activity was characterized by a variable intensity. High intensity produced crystalloclastic tuffs and a high accumulation of pumice, while low intensity activity resulted in vitroclastic tuff and a low accumulation of pumice (ŠIMUNIĆ, AL. et al., 1988; McPHIE et al., 1993).

Alteration of volcanic glass is the result of burial diagenesis. Different alteration products are most probably due to temperature increases with increasing depth of burial. Clinoptilolite was transformed to mordenite and analcime, while opal-CT changed to opal-C and recrystallized to quartz. However, the different immobile elements content of the rocks containing various alteration products indicates that alteration was probably also dependent on the chemical composition of the rocks. In some instances the type of alteration product was, most probably, also dependent on the grain size of the primary material. Huge reserves of volcanoclastic rocks make them economically interesting, nevertheless, planning particular applications of them should be done bearing in mind the properties of the raw material i.e. zeolite content and chemical composition.

Fig. 4.6. Chaotic pyroclastics indicate the proximity of the volcano (photo by R. Avanić).

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Stop 5 Rogaška Slatina

Natural Mineral Waters in Rogaška Slatina

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The landscape near Rogaška Slatina is hilly with altitudes 220–350 m and composed of sandy marl which quickly weathers producing a favourable soil for agriculture. Vineyards predominate in the southern parts where andesitic tuff and marls outcrop. On the northern edge, the slopes steeply rise and reach heights of 400–550 m. The Boč mountain range (the eastern extension of the Karavanke Mts.) reaches 978 m (Fig. 5.1).

The oldest known written sources of mineral water in the area of Rogaška Slatina date from the 12th Century. Initially, mineral waters named Tempel and Styria were exploited from natural sources and shallow wells. In 1908, the mineral water was captured in a 10 m deep drainage Knetteum, in which highly mineralised mineral water of the new Donat type was captured for the first time. After 1950, under the leadership of Josip Bać and Anton Nosan, the period of capturing mineral waters from boreholes began in Rogaška. The research was extended eastwards to Rogatec and west to Gabernik. The Donat mineral water was captured in deep wells V-6/67 in Rogaška Slatina, V-3/66-70 in Podplat and K-2/75 in Spodnja Kostrivnica. Due to the high content of magnesium (over 1 g/l), the brand was officially supplemented with Mg to Donat Mg in 1976.

The geological structure of the Rogaška Slatina area is very complex (NOVAK et al., 2010; TRČEK et al., 2011) (Fig. 5.2). The oldest rocks are claystones, quartz sandstones and conglomerates of Carboniferous age (C) which were encountered in the RT-1/92 geothermal well underlying a mixed carbonate-clastic-volcanic Pseudogailltal series of formations ($T_{2,3}$). In the area of Boč and Dreveniška

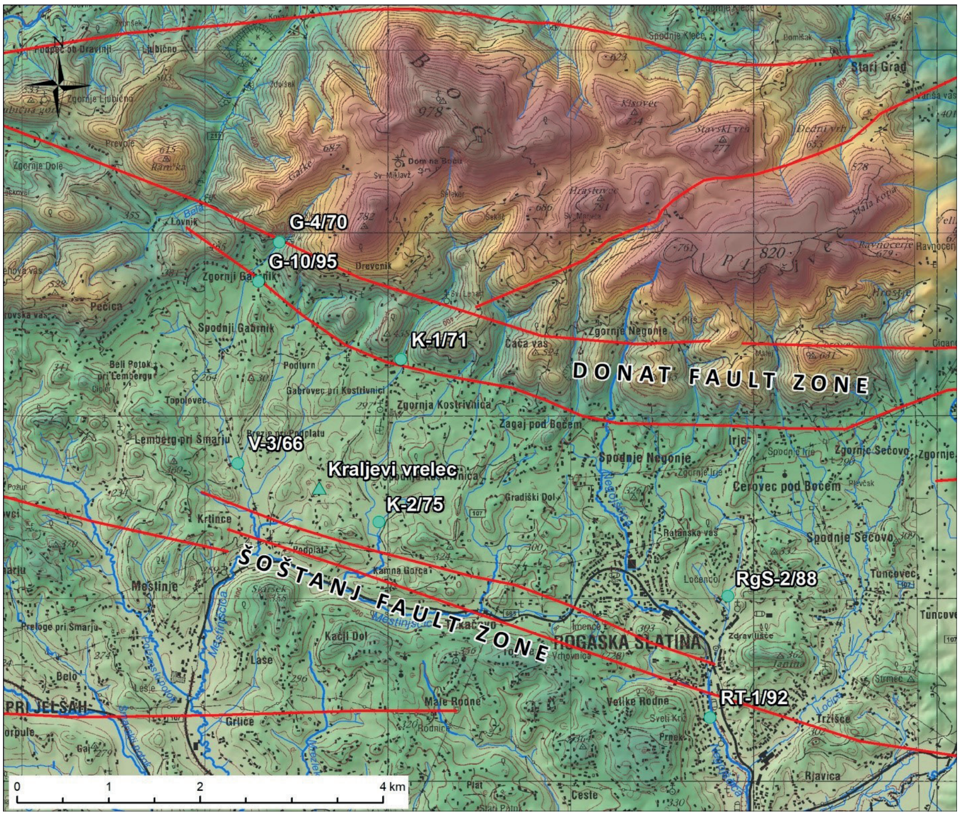

Fig. 5.1. Main fault zones in Rogaška Slatina area and locations of mineral water wells.

gora, and along the Donat fault zone from Kostrivnica to Zg. Negonje (the northern andesite belt), rocks of Middle Permian age outcrop. These are massive limestones (Pa), sandstones, conglomerates, claystones (Pk), and Tarviso breccia (TB). The Middle Permian rocks are overlain by black marly limestones of Lower Triassic age (T_1), massive limestone (T_2^1a) and the massive dolomite (T_2^1d) of the Middle Triassic age in the Boč Mts. In fault zones, erosion residues of the Upper Eocene nummulitic limestone (E_3) are observed. The Donat Mg mineral water aquifer consists of a pyroclastic rock series – andesite tuffs, tuff breccias and tuff sandstones ($^2Ol_1$), in which a thick layer of andesite (α) is also deposited.

Diverse geological settings, deep-seated faults, different retention times of groundwaters and other settings result in chemically varied waters (TRČEK et al., 2011; TRČEK & LEIS, 2017). Groundwaters from the northern carbonate massif are of a Ca^{2+}-Mg^{2+}-HCO_3^- type with mineralization of 0.5 g/l. Mineral water tapped in the northern and central part of the andesitic tuffs are of a Na^+-Ca^{2+}-$Mg^{2+-}HCO_3^-$-SO_4^{2-} type and with mineralization of 6–9 g/l (wells G-10/95, K-1/71, Kraljevi vrelec). Mineral waters from the southern part of the andesitic tuffs, (brand Donat Mg), have a characteristic water type of Mg^{2+}-Na^+-HCO_3^--SO_4^{2-} with mineralization about 14 g/l (wells V-3/66-70, K-2/75, RgS-2/88). South of the Šoštanj Fault, thermo-mineral water of Na^+-HCO_3^--SO_4^{2-}-Cl^- type and mineralization of 6 g/l is captured in the deepest well in the region, RT-1/92.

Stable isotopes of oxygen and deuterium in mineral waters are lighter than those in recent precipitation and show a distinctive left-shift due to the CO_2 effect (TRČEK & LEIS, 2017). Carbon-14 indicates a retention time of several thousand years but a reliable determination is difficult due to CO_2 gas and dissolution of carbonates. Noble gases prove a deep-seated permeable fault system with a huge contribution of mantle helium, having a very similar composition to the Radenci area waters (BRÄUER et al., 2016; RMAN et al. 2017). Tritium activity in these wells is very low, mostly below 0.02 TU. Carbon-13 indicates that all mineral waters dissolve carbonates, while this effect is not so evident in RT-1/92. Strontium and boron isotopes were also measured and show differences not only between mineral waters but also from the thermo-mineral water.

The natural mineral water aquifer in the Miocene andesite and andesitic tuff is separated from the geothermal reservoir with thermo-mineral water by Oligocene to Miocene clayey silt with lenses of tuff material and sandstones, reaching depths of 1.4 km.

The artesian mineral water has a thermo- and gas-lift with a dynamic wellhead pressure of 3.2 bar. Hydro-geochemically, the type of water is Na^+-HCO_3^--SO_4^{2-}-Cl^-, with mineralisation at 6 g/l, electrical conductivity of 5760 µSi/cm and 1.3 g/l of dissolved CO_2. Dynamic reserves are estimated to be 6 l/s. Stable isotopes of oxygen and deuterium are rather heavy and similar to those of freshwater from the dolomite (TRČEK & LEIS, 2017). Carbon-14 indicates a retention time of about 14 000 years by some interpretations. Noble gases show a characteristic distinction from the mineral waters (BRÄUER et al., 2016; RMAN & LAPANJE, 2017). Thermo-mineral water from RT-1/92 shows only 16 % of mantle helium while the mineral waters have more than 75 %. Due to CO_2 degassing it is not possible to calculate the infiltration temperatures.

In 2018–2019, a new borehole Ng-1/18 was drilled in the vicinity of Rogaška Slatina (Fig. 5.3) for the Atlantic group d.d. with the aim of capturing an additional source of Donat Mg natural mineral water. It was positioned between the Donat Fault zone in the North and the Šoštanj Fault zone in the South, where production wells V-3/66-70 and RgS-2/88-90 exist. The hypothesis was that the thickness of the andesitic tuff and andesite is considerable, and that this horizon is developed continuously in the area.

Despite deepening from the projected 700 m to a final depth of 802 m, the Ng-1/18 did not capture mineral

Fig. 5.3. Drilling site of a new research natural mineral water well Ng-1/18.

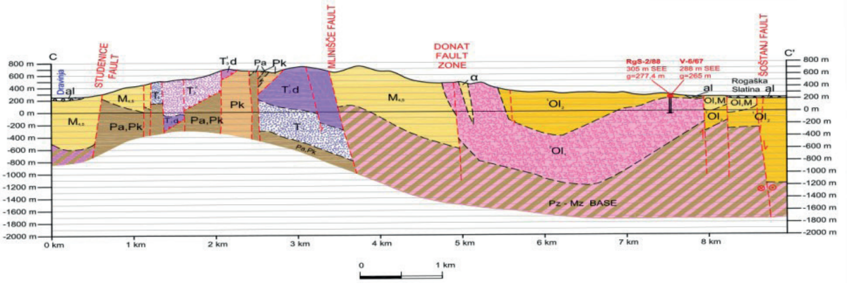

Fig. 5.2. Geological cross-section of the mineral water area (modified from NOVAK & CELARC, 2010).

water of the Donat Mg type in the depth interval between 300–700 m. The lithostratigraphy was significantly different from that predicted. The first occurrence of andesitic tuff was detected at a depth of 386 m (forecasted 270 m). The thickness of pure andesitic pyroclastites is very small (26 m in total) compared to the nearby RV-1/86 wells in Radanska vas (385 m) and T-1/75 in Tekačevo (183 m). In the interval between 386–802 m mudstone is dominant, with only 5–45 % of andesitic tuff and andesite. Frequent fragments of vascular calcite and dolomite in cuttings indicate that tectonically formed cracks are mainly cemented, and therefore no significant fracture porosity is expected. Analysis of the nannoplankton revealed an Upper Oligocene Chattian age (Ol_2) from 0 to cca. 200 m and a Lower Oligocene Rupelian age (Ol_1) below. While the area between the Donat and Šoštanj Fault zones obviously has a complex structure, detailed structural-geological and geophysical research is needed in future to be able to select an appropriate location for another research borehole.

Thermo-mineral water in the Rogaška Slatina is very different from the mineral water. A 1700 m deep geothermal borehole RT-1/92 was drilled in 1992 based on a geo-electrical survey and a thermometric borehole TR-3/90. Here, the ‘Pre-Tertiary’ relief drops steeply to south and exceeds a depth of 2000 m at the river Sotla. The water is stored in a complex of Ladinian Psevdozilian Series of Formations. Below this discordance, the Ladinian is a dark gray to black clay slate with diagenetic dolomitization down to 1600 m. The base of the well at 1700 m is in Carboniferous black clayey siltstone. The rocks are poorly permeable; geophysical measurements marked the section between 1506–1570 m in dolomitized clayey slate as water-bearing while the major thermal water inflows occur only in a few narrow cracks between 1507 and 1518 m. This water is used in the thermal pools of the Grand Hotel Sava and SLKI Co. 800 m away from the well, reaching an average discharge below 2 l/s and an average temperature of 57.2 °C (RMAN et al., 2018). Prior to utilization, the iron has to be removed in sand filters and the water cooled. Waste thermal water from the pool complexes is dechlorinated and discharged into the public sewage system, which is connected to the wastewater treatment plant in Rogaška Slatina.

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