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Selected ore deposits, igneous and metamorphic rocks from the Eastern Alps, Slovenia

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1. Field stop 1. The Idrija mercury mine

1.1 Short history of mining

The Idrija mercury deposit was discovered by chance in 1490. Mercury drops were found in the Carboniferous shale, in the centre of the town, where the church of St. Trinity stands today. Till the second half of the first decade in the 16th century, mining took place almost only in the Carboniferous shale. On 22nd of June, 1508, very rich cinnabar ore was found in the middle of the Triassic "Skonca" layers. With this finding several hundreds of years of prosperous mining began.

In 1575 the Court Chamber in Vienna took over the management of the mine. The mine plant was enlarged and modernized. At the end of 16th century, the mine was well known due to its highly developed technical equipment. With all the devices built up till 1652, the mine became technically the best equipped mine of the Austrin hereditary provinces. Its fame further increased in the 18th century and lasted till the beginning of the First World War. During the last decades under the Austrian management, several new mining devices and machinery have been tested. Modernization of the mine proceeded after 1956 and lasted just until the interruption of mine work in 1977, when mercury became an economically unnteresting element due to ecological reasons. The partial closing works started in 1988 and the mine was completely closed at the end of 2009.

From the early beginning of the work in the Idrija mine till the closing of mining, the crosscuts method with stowing and levels from down upwards was used. In the seventies of the 20th century, mining also reached the mechanically unsuitable shale with native mercury. At this time the underhand cut-and-fill method with reinforced backfill was used.

The Idrija mercury mine was the second biggest mercury mine in the world after Almadén in Spain. During the 500 years of its history the mine produced 12,757,730 t of ore with 1.13% Hg content. Thus the total amount of 144,725 t mercury produced corresponds to 3% of historic Hg output of the whole world. Considering the average 74.4% recovery, 107,692 t of Hg was economically produced. Approximately 37 thousand tons of mercury was lost during production, and this still has a large impact on the environment of Idrija and its surroundings, through Idrijca and Soča rivers towards the Bay of Trieste.

1.2 Geology and origin of the Idrija mercury deposit

The uniform Slovene carbonate platform broke into two parts approximately 238 million years ago, in the middle Anisian. The southern part of the platform, the so-called Dinaric carbonate platform, underwent complex tectonic and erosion processes that formed a trench in the area of Idrija during the Middle Triassic. Lower parts of the trench were filled up by

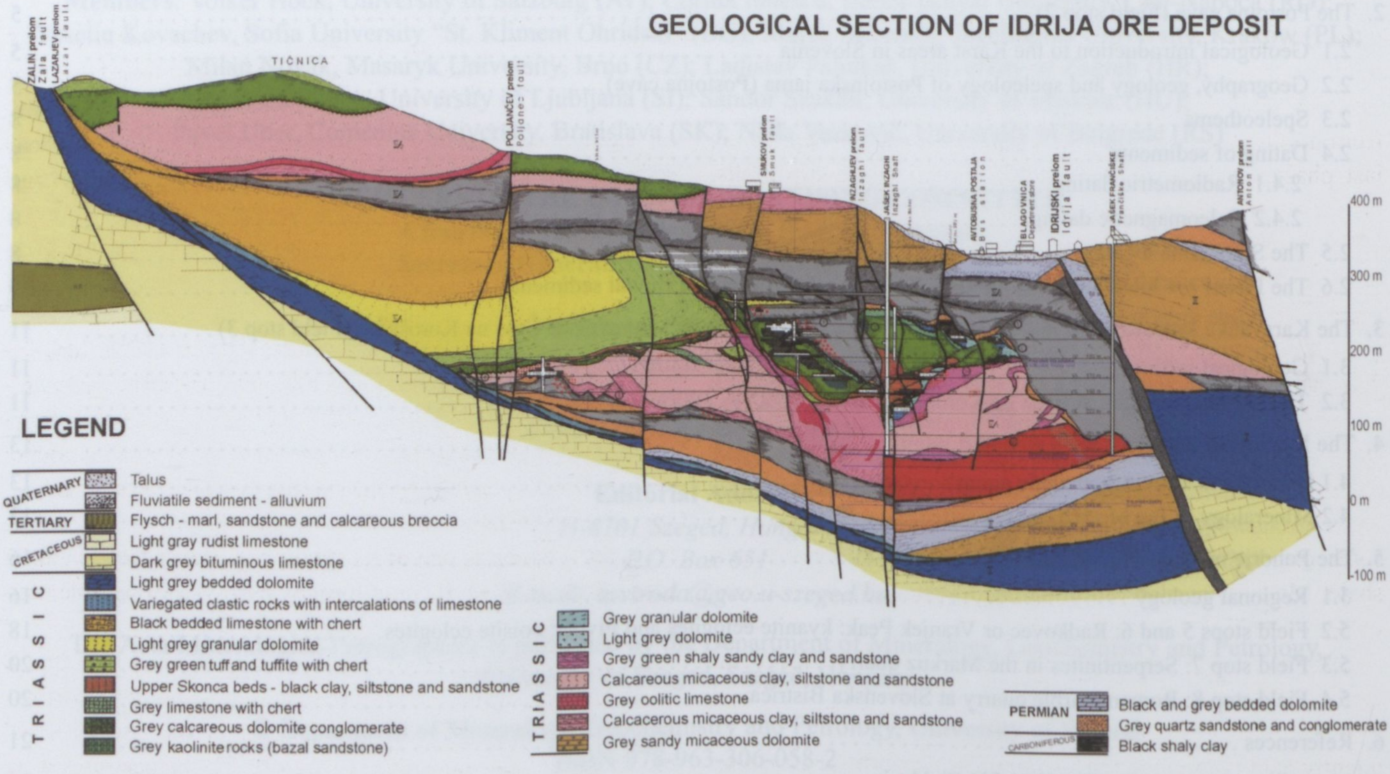

Fig. 1. Geological section of Idrija deposit (after Čar, 1985)

unusual coarse-grained clastic sediments of Ladinian age (~235 Ma), and then the trench was covered by biota-rich marsh, in which the so-called Skonca layers, consisting of bituminous shale, mudstone and sandstone, were formed.

The trench was bounded by deep, open faults that enabled the flow of mercury- and sulphur-rich hydrothermal fluids. The flow of ore-forming solutions was through faults and fractures in older rocks of Carboniferous, Permian, Scythian and Anisian age. Cinnabar mineral (HgS) replaced parts of the rocks and filled up numerous open cracks and faults that formed during the Middle Triassic. In this way a very rich epigenetic ore was formed. A very important part of the cinnabar ore was introduced into the marsh in the form of non-crystallized gel, which formed extremely rich (up to 78% of Hg) syngenetic sedimentary cinnabar ore in the Skonca layers. Where the amount of sulphur was not high enough, pure mercury precipitated and its drops impregnated different rocks, most commonly Carboniferous shale. Altogether 156 ore bodies became known during the long mining history of the deposit. 15 of them are in Carbonifeous shale, the other 141 ore bodies are hosted by Permian and Lower to Middle Triassic rocks. The ore bodies have variable shapes and sizes (from some 10 m^2 to more then 1000 m^2) and they are unequally distributed over the deposit.

After the cessation of Triassic tectonics and formation of the Idrija mercury deposit, the ore-bearing rocks were covered by an approx. 5500-m thick Mesozoic and Paleocene–Eocene sequence. During Oligocene–Early Miocene, the Alps were uplifted due to collision that followed the subduction of the Adriatic plate under the southern part of the Eurasian plate. This wide, complicated and long-termed process also affected the old tectonic trench and ore deposit within it at Idrija. The territory was severely folded and, due to a large scale thrusting, the Idrija mercury deposit was moved for about 36 km from northeast to the position where it is found today. In the last phases of tectonic movement, several strike-slip faults, parallel to the Dinaric course, cut the deposit (Čar, 1985). These complicated tectonic movements resulted in a "chaotic", extremely complicated structure of the deposit (Fig. 1).

1.3 Mineralogy of ore

In the Idrija mine, 29 different minerals became known up to date. The economically most important and main ore mineral was cinnabar (HgS). Elemental mercury (Hg) was found in some ore-rich parts of the deposit hosted by Carboniferous shale. Metacinnabarite (cubic HgS) occasionally also occurs. Other non-ore and secondary minerals found in the rocks of the deposit are pyrite, marcasite, dolomite, calcite, epsomite and idrialite; the latter mineral is a local specialty.

Mercury appears in the Idrija mine in two forms: most frequently as a compound with sulphur in the form of cinnabar, the main ore mineral (Fig. 2), and less frequently in the form of native mercury (Fig. 3). Both of these minerals can be found on the Achatius level as grains of cinnabar and droplets of native mercury. The latter are particularly attractive, and their glittering shine captures the eye of many a visitor. Small sections of the extremely diversified geological structure of the Idrija Mine can be observed along the path through the mine, featuring designations of various rock specimens, their age, tectonic and other particularities. Epsomite can be found growing in capillary hair-like forms (*Haarsalz*) or as stalactites in abandoned parts of the mine (Mlakar, 1975). Idrialite (first described as idrialine), is a soft, orthorhombic hydrocarbon mineral ($C_{22}H_{14}$). It is usually greenish yellow to light brown in colour with bluish fluorescence. It can be found mixed with clay, pyrite and gypsum associated with cinnabar. Its combustibility gave rise to the term "inflammable cinnabar", which is one of its synonyms. It was first found in Idrija Mine in 1832. It could form by pyrolysis of organic matter affected by hydrothermal solutions.

Fig. 2. Cinnabar ore, Idrija. Width of the picture is 20 cm

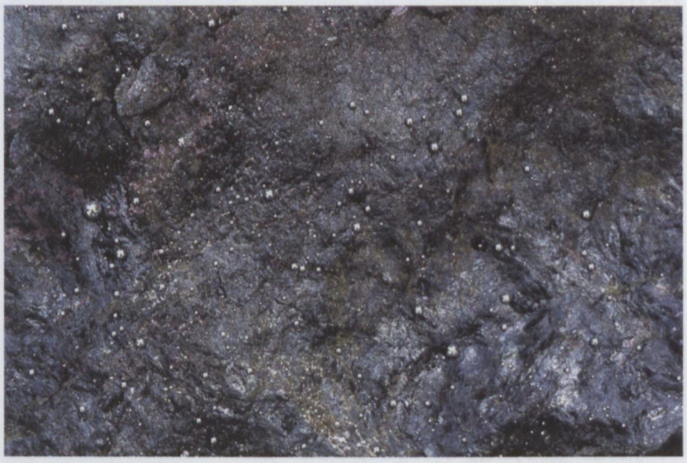

Fig. 3. Native mercury, Idrija. Width of the picture is 5 cm

Mine workers gave names to varieties of rich ore types, according to their colour, structure and mercury content. These names of course did not reflect mineral composition but the characteristic appearance of the ore. The richest ores were called *jeklenka* (after its resemblance to steel), *opekovka* (after its resemblance to brick), *jetrenka* (after its resemblance to liver) and *koralijevka* (coral ore, after the abundant brachiopod shells mistaken for corals). Old mineralogical textbooks may contain the German variants of these names (*Stahlerz*, *Ziegelerz*, *Lebererz*, *Korallenerz*). Among the specialities of the mine one can mention the so-called *karoli* ore (named after the Karoli ore body), consisting of different sedimentary ore and epigenetic ore in shale with high percentage of elementary mercury. For practical reasons, mine workers distinguished *jeklenka*, very rich ore, rich ore, poor ore and very poor ore (*bašperh*) according to the mercury content.

1.4 Mineral collections in Idrija

There are no written records of existing collections at the Idrija Mine up to the middle of the 18th century. In this period, mine employees already had their own smaller collections of Idrija minerals and ores. The famous mine physician and naturalist of European reputation, J.A. Scopoli, is known to have possessed quite an extensive and, for that time, well-arranged collection of minerals, rocks and ores, which he used for his lessons at the Idrija Technical School where he taught chemistry and metallurgy (1763).

Of major significance was also the collection kept by Balthazar Hacquet, which is mentioned in his encyclopedic work, *Oryctographia Carniolica* (1781). After his move from Idrija to Ljubljana, Hacquet took his collection, which also included samples from the Idrija Mine, with him.

When the reputed Slovene geologist, M.V. Lipold, took over the administration of the Idrija Mine in 1867, a rich collection of fossils and rocks had already been existed. Over the next few years, Lipold considerably enriched the collection, which, by its size and content, acquired national importance. In 1912, J. Kropáč, who was primarily interested in the geology of the Idrija ore deposit, wrote that it was largely owing to Lipold that the mine had a valuable collection, a small part of which is preserved today in the Municipal Museum in Idrija.

Following the establishment of the museum, mine experts set up a new, extensive stratigraphic-lithological, paleontological and mineralogical collection as well as an impressive collection of mercury ores in 1956. Over the next few decades, the collection was extended with several new samples, and today it comprises over 2000 specimens (Čar & Peljhan, 1999). In 1992, the collection was expertly renewed, considerably enriched and set up in newly renovated rooms in the Idrija Museum (Fig. 4).

The second important collection of preserved natural heritage is the Mine Geological Collection, which was created after the establishment of a geological department at the Idrija Mercury Mine. The collection comprises more than 800 specimens and is undoubtedly the most comprehensive professional collection of the Idrija Mercury Mine. Some of the samples were collected by mine geologists investigating the Idrija Mine and the broader surroundings of Idrija in the period 1955–2003. Owing to its complexity, the specimens are divided into seven thematic collections. Some of the specimens are quite unique and priceless. The samples represent individual geological elements relevant for the development and structure of the ore deposit (mineralogy, petrology, sedimentology, mineral geology, tectonics). As a whole, the collection encompasses the findings of several generations of geologists on the origin of the Idrija ore deposit, which represented a special challenge to many researchers. The decisions adopted during the preparation of the collection are based on exceptionally rich and preserved geological documents. The entire geological collection is also available on computer. The database contains an expert description, and defines the particularities and location (co-ordinates, map) of each sample in the ore deposit. Photos of the samples described have been added.

Fig. 4. Mineralogical collection of Idrija museum

The greater part of the collection is on display and available to researchers in the new administrative quarters of the Mercury Mine in the territory of Francisca shaft. Some of the most impressive specimens are also exhibited in the entrance building to Anthony Main Gallery, where they may be examined by visitors to the Idrija underworld.

The museum part of the mine open for tourist visits – Anthony Main Gallery – not only represents the preservation of history, technical and natural heritage, but also provides an opportunity to learn and discover something new in an authentic environment (Režun, 2006).

2. Field stop 2. The Postojna Cave

2.1 Geological introduction to the Karst areas in Slovenia

Karst has developed on carbonate rocks, limestone and dolomite, which cover about 8,800 km^2 (43% of the total surface) in Slovenia. It has been traditionally divided into three principal karst areas according to the general morphological and hydrological conditions, and the evolution history. These are the Alpine karst, the Dinaric Karst, and the Isolated karst (Fig. 5). Today there are more than 9,000 known karst caves, which are registered in the Cave Register of the Speleological Association of Slovenia and Karst Research Institute ZRC SAZU (Znanstveno raziskovalni center Slovenske akademije znanosti in umetnosti – Scientific Research Centre of the Slovenian Academy of Sciences and Arts).

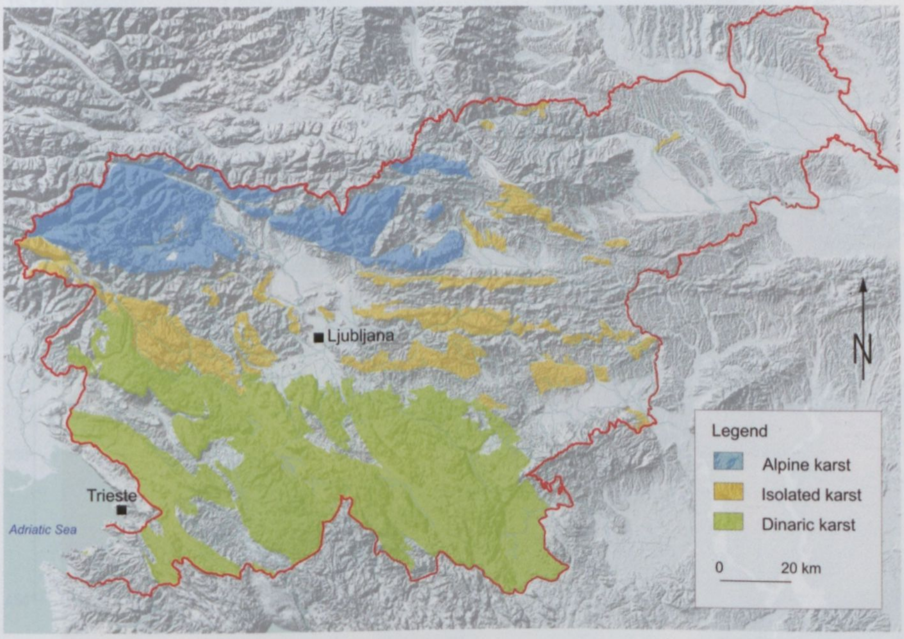

Fig. 5. Distribution of major karst areas in Slovenia

The Alpine karst or 'the karst of the high mountains' is characterized by extensive vertical gradients, and a mix of fluvial, glacial and karst elements in the landscape, resulting in deeply entrenched fluvial valleys in mountains and plateaus. Deep shafts and vertical cave systems are typical there. Alpine karst continuously covers large areas in northern Slovenia.

The Isolated karst occurs as small patches of karst surrounded by and developed under the impact of allogenic inflow from non-carbonate rocks, in the contrast to the large karstified areas in the Alps or Dinarides. Horizontal caves have been formed by sinking rivers, generally with high clastic sediment loads. Ponors and springs are common. The karst hydrology and features are principally defined by the position of each karst area, while the general evolution of the large-scale relief has been less important.

The Dinaric Karst (Dinarski kras) is the major karst area of Slovenia. The dominant relief features are rather extensive levelled surfaces at different elevations, large closed depressions (*e.g.*, poljes), and conical hills. Fluviokarst features like dells are common on dolomites. Karst rivers appear only in the bottoms of poljes, where they result from high level of karst water. Allogenic rivers flowing from non-carbonate regions either sink at the karst boundary forming blind valleys, or cross the karst through deep karst valleys and canyons. There are numerous extensive and complicated cave systems formed by sinking rivers and connected with the surface also by numerous vadose shafts. The surface karst morphology is typified by the abundance of karren, dolines of various diameters and depths, sometimes extensive collapse dolines, cave entrances, unroofed caves, etc.

2.2 Geography, geology and speleology of Postojnska jama (Postojna cave)

The Postojnska jama cave system is developed in the Postojnski kras, where the surface is at about 600 to 650 m a.s.l. (Fig. 6). The evolution of the Pivka Basin (flysch rocks) is defined by the altitudes of the ponors of Pivka river that drain into this cave. The gentle fluvial surface of the basin itself stands out in sharp contrast to the karst lands above the cave and to other higher karst plateaus, where there are no traces of fluvial valleys or other elements of the early fluvial relief today (Mihevc, 2002a). These surfaces are dissected with numerous dolines. Sixteen large collapse dolines developed above some parts of Postojnska jama, blocking certain passages. The thickness of bedrock overburden above the cave is 60 to 120 m. The cave was formed by the Pivka river. Its modern ponor is at 511 m a.s.l., and the terminal sump in Pivka jama is at 477 m a.s.l. There are still more than 2,200 m of unexplored galleries before the river reappears in Planinska jama at 460 m a.s.l.

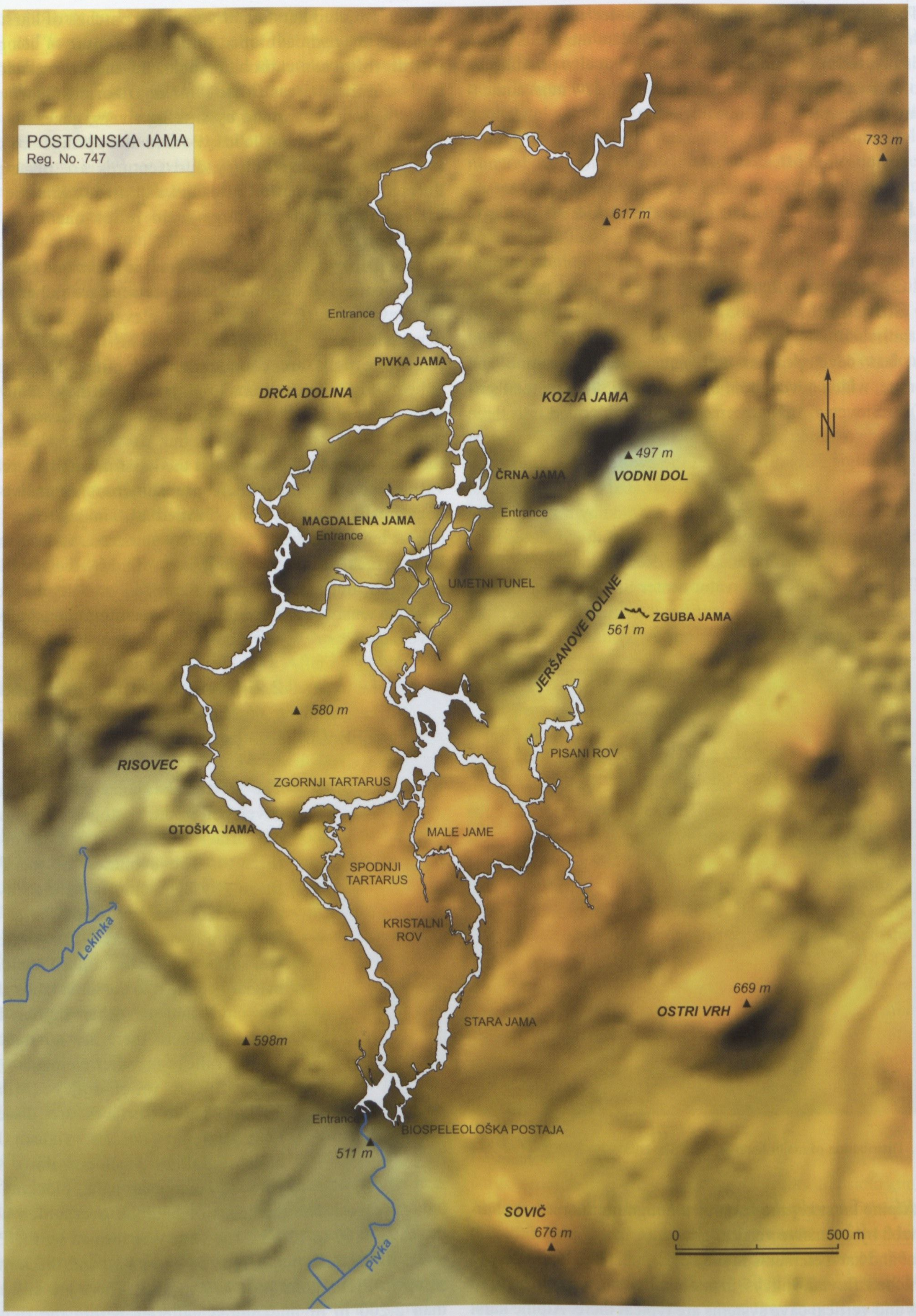

Fig. 6. Plan of Postojnska jama cave system projected onto surface topography

The historical entrance at 529 m a.s.l. is located above the modern ponor. Other entrances and parts of the system, *i.e.* Otoška jama, Magdalena jama, Črna jama and Pivka jama, are scattered on the surface above the cave (Fig. 6). All these caves are interconnected and form a cave system 20.5 km in length, the longest in Slovenia.

The entrance to Postojnska jama is situated near the contact between Eocene flysch and Upper Cretaceous limestones (Buser *et al.*, 1967). The entire cave system is developed in an 800-m thick sequence of Upper Cenomanian and Turonian to Senonian limestones.

The cave passages are formed in the Postojna anticline, which is oriented NW–SE (Gospodarič, 1976) and most of them being in its steeper south-western flank. The cave system is in the tectonic block confined by two distinctive dextral strike-slip fault zones in the Dinaric trend, the Idrija and Predjama faults (Buser *et al.* 1967, Placer, 1996). Habič (1982) explained different features, such as collapses and slumps in the cave, as the results of neotectonic movements. A geological survey of the cave passages was made by Gospodarič (1965, 1976) and Šebela (1998) added structural mapping in detail. The cave and the Pivka underground river have a general N–S trend.

The known passages were formed at two main levels (Fig. 7). The upper level is between 529 m a.s.l., at the main entrance to the cave and 520 m a.s.l. in the Črna jama. This level is composed of large passages, generally up to 10 m high and wide. Their profiles are more rounded and show also traces of paragenesis (levelled ceilings, side notches on the walls and scallops on the walls and ceiling). There are also remnants of cave fills indicating repeated fillings of the cave and successive erosion of the sediments. Speleothems were deposited in different phases above clastic sediments. The natural floor of the cave was modified for the construction of a railway during opening for tourists.

The second level is about 18 m below the upper one, where the modern underground Pivka river flows from its entrance. The riverbed has a low gradient and, except for some collapses and sumps, there are no natural barriers. It leaves the system through a terminal sump. The active river passages are mostly smaller than the higher ones. The riverbed is composed mostly of gravels derived from the Eocene flysch (Zupan Hajna, 1992). The mean annual discharge of the river is 5.2 m^{3}s^{-1}. The water level can rise 10 m during floods.

The cave is filled by several kinds of alluvial deposits characteristic to the internal cave facies, such as silts, sands, gravels. These are covered and/or intercalated by rich speleothems. The entrance cave facies consists of slope-derived debris mixed with the fluvial deposits. Pleistocene large mammal fauna such as hippopotamus, cave lion and cave bear, were found here (Rakovec, 1954) as well as Palaeolithic stone tools from the last glacial (Brodar, 1966, 1969, 1970).

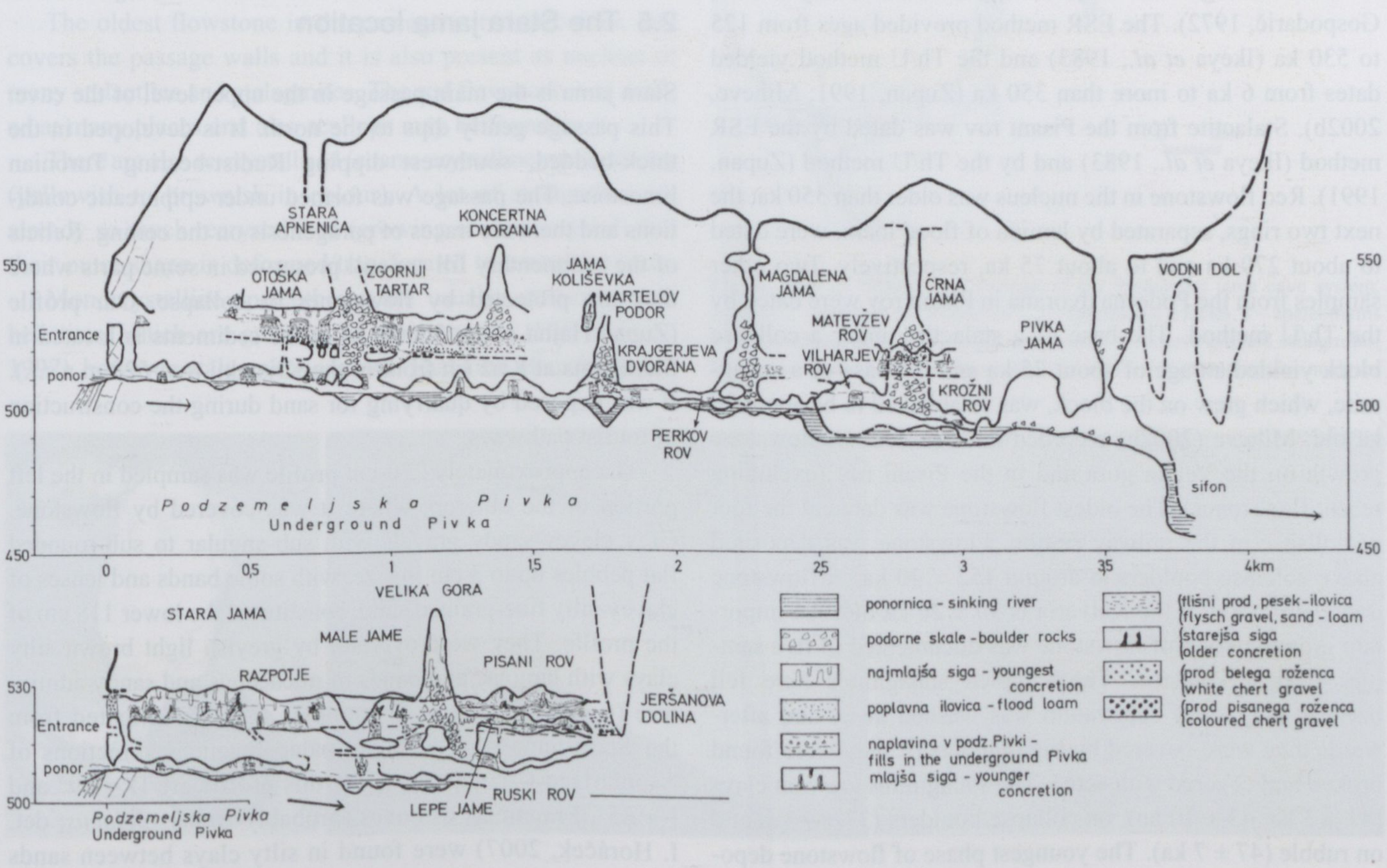

Fig. 7. Levels in Postojnska jama cave system filled by different sediments (from Gospodarič, 1976)

2.3 Speleothems

Intensive growth of flowstone is due to high annual precipitation (about 1700 mm), and high mineralization capacity of the percolating water. Calcite is the main secondary mineral in the cave and the abundance of other non-carbonate minerals is less than 1%. There are small regular crystals of calcite in the water pools, stalagmites and stalactites of all shapes and colours. The most beautiful speleothems are in Pisani rov ("Coloured passage") and Lepe jame ("Beautiful cave"). Also, draperies and cave pearls are well known from the cave, too. The oldest flowstone in the cave is the red one from the Pisani rov, which shows the traces of erosion on it and also scallops were found on it. In Pisani rov and Črna jama ("Black cave"), similar speleothems are black: it has not proven yet whether the black colouring is due to Mn oxides or organic material mixed in the solution. In some speleothems, between separate layers, flood loam was found. This suggests that flooding occasionally occurred during speleothem growing.

2.4 Dating of sediments

2.4.1 Radiometric dating

From the Postojna cave, different samples were analysed by radiometric dating (^{14}C, Th/U and ESR). Ages obtained by the ^{14}C method range from 7.5 to 39.5 ka (Franke & Geyh, 1971; Gospodarič, 1972). The ESR method provided ages from 125 to 530 ka (Ikeya *et al*., 1983) and the Th/U method yielded dates from 6 ka to more than 350 ka (Zupan, 1991; Mihevc, 2002b). Stalactite from the Pisani rov was dated by the ESR method (Ikeya *et al*., 1983) and by the Th/U method (Zupan, 1991). Red flowstone in the nucleus was older than 350 ka; the next two rings, separated by lamina of flood loam, were dated to about 270 ka and to about 75 ka, respectively. Two other samples from the Podorna dvorana in Pisani rov were dated by the Th/U method. The base of a stalactite under a collapse block yielded an age of about 75 ka and the base of a stalagmite, which grew on the block, was established to be about 20 ka old. Mihevc (2002b) recorded three periods of flowstone growth on the Velika gora and in the Pisani rov (excluding recent flowstones). The oldest flowstone was dated at the foot of collapse at the railway station. Flowstone was deposited above collapse boulders at around 152 ± 40 ka. A flowstone dome at the top of the Kalvaria is 70 ± 26 ka old. An important growth period of flowstone was documented in five samples from Pisani rov. The sampled stalagmites here fell because the clayey substratum was washed away and afterwards they were covered by big boulders or they were found broken and covered with scree. The stalagmites grew on clays (41 ± 3 ka, 43 ± 10 ka), on collapse boulders (37 ± 7 ka) and on rubble (47 ± 7 ka). The youngest phase of flowstone deposition is recorded in samples of grey crystalline flowstone and stalagmite (12 ± 5 ka and 6 ± 4 ka) covering all collapse blocks. The intensity of rock fall is low under the present conditions. These data, in spite of some errors, helped to distinguish some clear phases of collapse alternating with flowstone deposition. Collapses have been usually connected with colder climate, flowstone deposition with the warmer one.

2.4.2 Paleomagnetic dating

Šebela & Sasowsky (1999) did the first palaeomagnetic research on fluvial sediments from Postojnska jama (Male jame, Otoška jama, Partizanski rov = Umetni tunel). During the past years, since 2003, Zupan Hajna *et al.* (2008a, b), has completed paleomagnetic studies on selected sedimentary profiles within Postojnska jama, Zguba jama and Planinska jama. Results show that almost all samples from most profiles were normal polarized. Short reverse magnetozones (excursions) were detected in places only. Therefore most of the studied sediments are younger than 780 ka, belonging to the Brunhes Chron (paleomagnetic division of the Earth evolution). Older paleomagnetic signs were found in sediments in artificial tunnel between Postojnska jama and Črna jama and sediments in Zguba jama, only. There the sediments are about 2 Ma old or even older. Nevertheless this is only preliminary age estimation, as detailed statistical analyses of the palaeomagnetic parameters is still in progress.

2.5 The Stara jama location

Stara jama is the main passage in the upper level of the cave. This passage gently dips to the north. It is developed in the thick-bedded, southwest dipping Rudist-bearing Turonian limestone. The passage was formed under epiphreatic conditions and there are traces of paragenesis on the ceiling. Relicts of the sedimentary fill are still preserved in some parts where they are protected by flowstones or collapse. Our profile (Zupan Hajna *et al.*, 2008a, b) of the sediments is located in Stara jama at Križ (in front of the Kristalni rov; 528 m a.s.l.). It was exposed by quarrying for sand during the construction of tourist pathways.

The approximately 220-cm profile was sampled in the left portion of the outcrop, where it was covered by flowstone. Grey clayey-sandy gravels with sub-angular to sub-rounded flat pebbles up to 3 cm in size, with some bands and lenses of clayey-silty fine-grained sand, constituted the lower 118 cm of the profile. They were overlain by greyish light brown silty clays with laminae and bands of micaceous and sandy admixture (6 cm). A total of 26 samples were investigated from the Stara jama profile. Mean palaeomagnetic directions of N-polarized C-components for this profile are D = 19° and I = 65°. Fragments of bones (probably *Ursus spelaeus*; det. I. Horáček, 2007) were found in silty clays between sands in the right part of the outcrop. The palaeomagnetic results indicate that the age of sediments is younger than 0.78 Ma in the Stara jama profile. This interpretation is also supported by Pleistocene bear bones occurring on the top of the profile. The top part of the profile showing flaky disintegration could be disturbed by freezing, as this kind of texture is typical for cryoturbation processes.

2.6 The Pisani rov location: speleotherms, flowstone deposition and fluvial sediments

Pisani rov is the passage that deviates to the north from the main passage of the Stara jama (Fig. 8). It terminates below the slopes of the collapse doline of Velika Jeršanova where the bottom is filled by sediments at 535 m a.s.l. The passage was formed in the thick-bedded Turonian limestones with the strata dip towards west along bedding planes (Gospodarič, 1962). In Pisani rov, tectonically broken zones are in different directions of which those of N–W are the most frequent. Dinaric (NW–SE) and cross-Dinaric (NE–SW) directions are a bit less common (Šebela, 1992, 1998).

The Pisani rov (Coloured Passage) has been named for different speleothems of various colours and forms (Fig. 9). The evidence of floods above already existing speleothems is indicated by clay layers between dense calcite (sinter) layers and in porous layers (the best is seen in broken stalactites with alternating dense and porous laminations on the rightmost picture on Fig.9.)

The oldest flowstone in the passage is red in colour, and covers the passage walls and it is also present as nucleus of many stalactites and stalagmites. The red flowstone was eroded at many places and also scallops may be found on it.

There are also re-crystallised (coarse-crystalline) speleothems (yellowish to brownish in colour). A lot of stalagmites are already so much recrystallised (growing of monocrystal) that their outer shape is deformed/transformed to triangular form. Monocrystalline speleothems are usually stalactites and helictites, which are growing as monocrystals (Hill & Forti, 1997), however, stalagmites are rare. That kind of speleothems

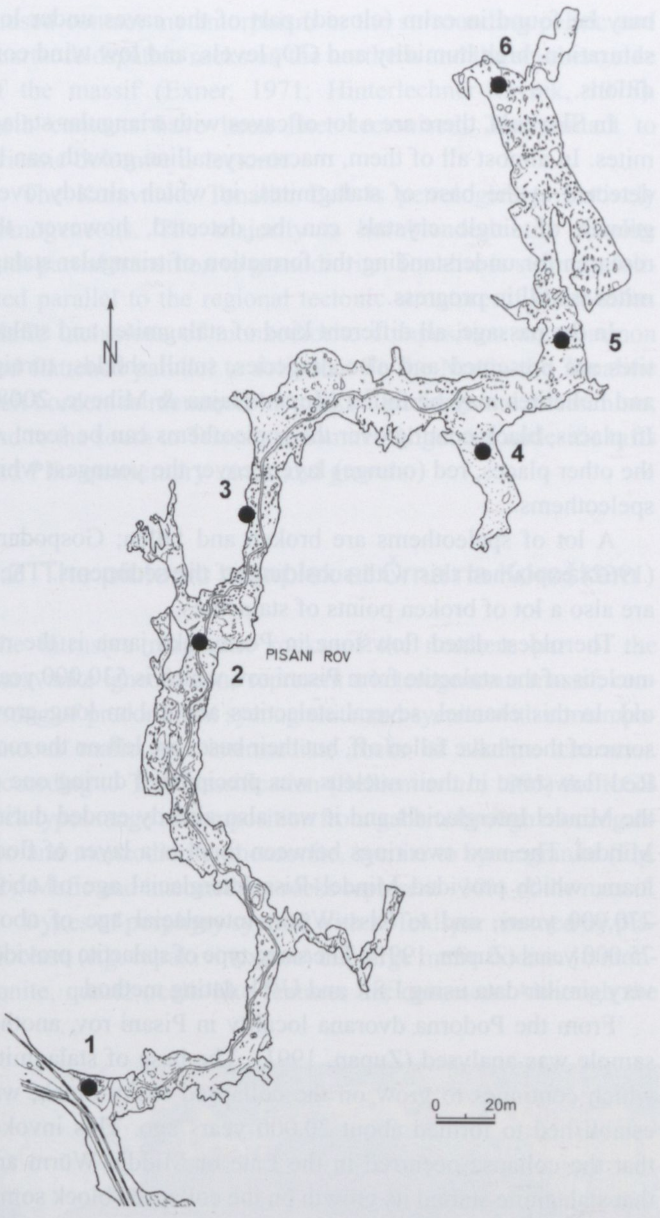

Fig. 8. Map of "Pisani rov" passage of the Postojnska jama cave system. Legend: 1 – entrance to "Pisani rov", 2 – corrosional trickles, 3 – speleothems with alternating dense and porous lamination, 4 – course-grained stalagmites, 5 – broken speleothems, 6 – location of the profile for paleomagnetic analyses

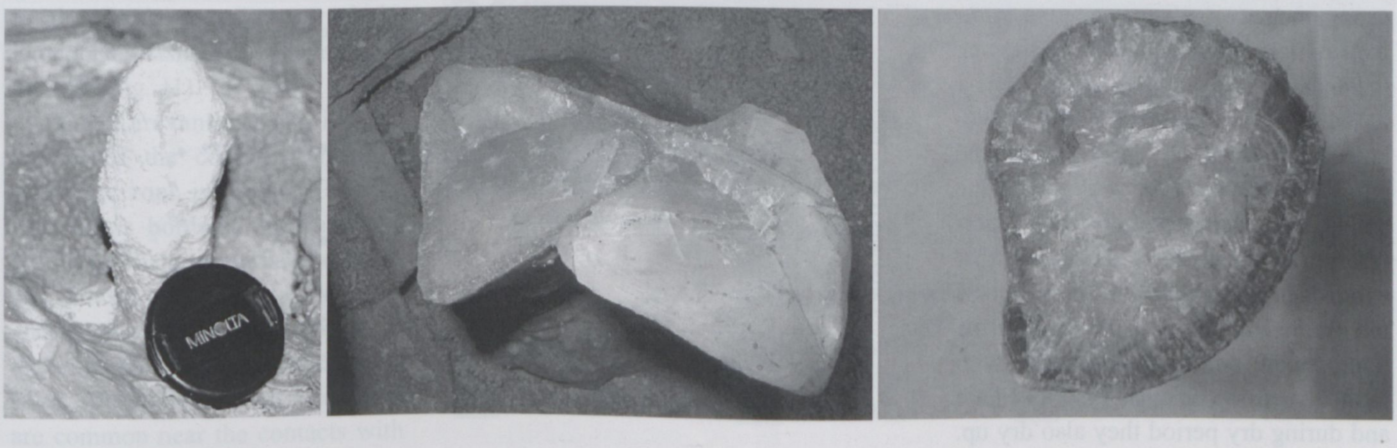

Fig. 9. Triangular stalagmite (left), cross-section of two triangular stalagmites (centre) and re-crystallised stalagmite (right; photos by N. Zupan Hajna)

may be found in calm (closed) part of the caves under low saturation, high humidity and CO_2 levels, and low wind conditions.

In Slovenia, there are a lot of caves with triangular stalagmites. In almost all of them, macro-crystalline growth can be detected at the base of stalagmites, in which already overgrowth of single crystals can be detected, however, the research for understanding the formation of triangular stalagmites is still in progress.

In the passage, all different kind of stalagmites and stalactites are presented and also draperies, small shields, turnips and helictites may be found (Zupan Hajna & Mihevc, 2008). In places, black coating over the speleothems can be seen. At the other places, red (orange) layers cover the youngest white speleothems.

A lot of speleothems are broken and fallen; Gospodarič (1962) explained this with subsiding of the sediments. There are also a lot of broken points of stalactites.

The oldest dated flowstone in Postojnska jama is the red nucleus of the stalactite from Pisani rov, which is 530,000 years old. In this channel, several stalactites about 1-m long grow, some of them have fallen off, but their bases are left on the roof. Red flowstone in their nucleus was precipitated during one of the Mindel Interglacials and it was also already eroded during Mindel. The next two rings between them is a layer of flood loam, which provided Mindel–Riss Interglacial age of about 270,000 years, and to Riss–Würm Interglacial age of about 75.000 years (Zupan, 1991). The same type of stalactite provided very similar data using ESR and U/Th dating method.

From the Podorna dvorana locality in Pisani rov, another sample was analysed (Zupan, 1991). The base of stalagmite, which continues to grow on the collapsed rocky block, was established to formed about 20.000 years ago. This invokes that the collapse occurred in the Late or Middle Würm and that stalagmite started its growth on the collapsed block sometimes during the Würm Interglacial.

In the extensively decorated Pisani rov, tiny drippings with low discharges and relatively low variations prevail. After rains, the percolating water forms gentle water pulses with very slow decrease and bigger or smaller retardations confirming strong retardation of precipitation influence through the cave ceiling. This is also reflected in the relatively small oscillation of hardness of water during the year. An important role is played by the ceiling that retains and directs the percolation of water. One can conclude that calm drippings prevail without abrupt or quick changes in the Pisani rov. Some larger trickles are connected with faults: their discharges also oscillate and during dry period they also dry up. They resemble the trickles in Planinska jama by fast reaction to rain and by forming expressive water pulses that show distribution and precipitation quantity.

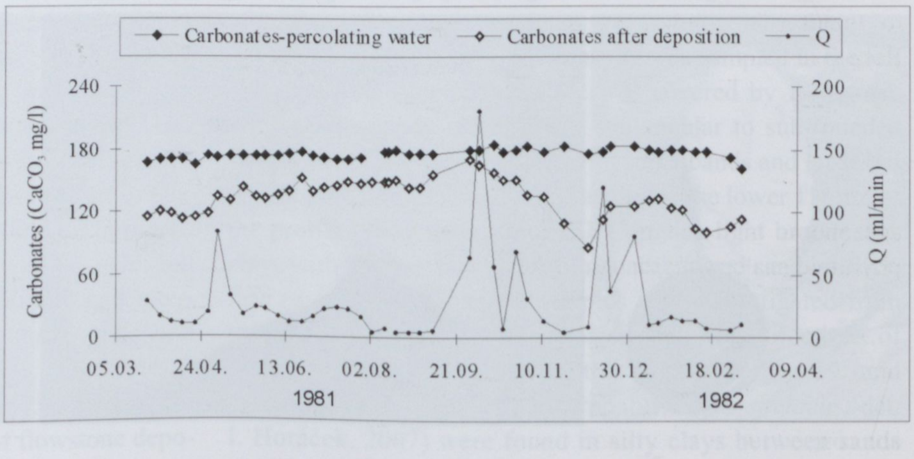

Fig. 10. Diagram of sinter deposition in Pisani rov

It is clear that the structure of the ceiling has the greatest impact on the discharge regime; larger differences among neighbour trickles can be explained by different system of inflow and different percolation as sometimes it is connected with joints and fractures. So one can also explain the different types of trickles located in immediate vicinity: one with percolation of saturated water, from which flowstone is deposited and the other more aggressive undersaturated water corroding rocks and old speleothems.

Nicely coloured speleothems in Pisani rov reflect diversified deposition of flowstone in the past. Today this passage is climatically very steady. Most of waters have high carbonate hardness (190–240 mg HCO_3^-) and deposits flowstone.

Discharge and carbonate hardness measurements are carried out in every week and the series of data explain the way of flowstone deposition during the whole year (Fig. 10). Data enabled a rough calculation of the amount of deposited carbonates at observation points: results indicate that permanent drippings would yield 0.5 mm flowstone per year. During the low discharge, the deposition of carbonates increases but the quantity of deposited carbonates in a defined time (the discharge rarely exceeds 100 ml min^{-1}) mostly depends on the quantity of percolation water. Evidently it is important how water flows on a speleothem; there are many asymmetrically grown speleothems because the flowstone deposition can change during a year even if other conditions are quite constant. The extremely steady conditions in Pisani rov show that the flowstone is deposited constantly during the whole year, thus completing the old speleothems.

Along the whole passage, the grey loam originated from weathered flysch rocks can be find at various places: on the bottom, between flowstone layers, incorporated into the stalagmites and stalactites, on walls and ceiling. The profile of fluvial sediments situated at the end of the Pisani rov (529 m a.s.l.), was studied by Zupan Hajna and others (Zupan Hajna *et al.*, 2008a, b). Fine-grained sediment covers the collapse boulders and massive flowstone. The roughly 145-cm thick Pisani rov profile is composed of yellowish brown silts to clays with dark stains and schlieren and an olive-green horizon and more finely laminated sediments in the lower third part of the sequence. The upper part of lutites shows cubic to columnar disintegration with Fe stains on the fractures. The profile is covered by two layers of flowstone. The lower one contains broken stalagmites and their remnants are lying on flowstone surface. The second layer was developed only in places and is covered by limestone clasts. A total of 65 samples have been investigated for their palaeomagnetic properties. Mean palaeomagnetic directions of N polarized C-components for this profile are D = 6° and I = 64°. The profile showed N polarized magnetization only, and a palaeomagnetic direction which is very close to the present magnetic field; therefore we assume that deposition occurred within the Brunhes chron (<780 ka).

3. Field stop 3: The Karavanke igneous zone and a bimodal Triassic alkaline plutonic complex at Črna na Koroškem

3.1 Geological setting

The central Karavanke magmatic zone is located along the Periadriatic Lineament in north and northeastern Slovenia and consists of two parallel elongated massifs: the Northern Karavanke Granitic Belt (Granitic Belt), and Southern Tonalitic belt. These belts are related to distinct magmatic events (Faninger, 1976). The massifs are separated by a thin belt of metamorphic rocks. The Karavanke magmatic zone also outcrops in Austrian areas, where it is represented by the "Eisenkappel (Karawanken) Granite" and "Karawanken Tonalite Gneiss". It extends for about 35 km, from the Slovenia-Austria border on the west to the Tertiary sediments of the Pannonian basin near Plešivica to the east (Fig. 11).

The Karavanke Granitic Belt (KGB) of the central Karavanke magmatic zone is of early Triassic age and is bordered by Paleozoic phyllitoid shales with diabase dykes and Triassic dolomite to the north and by a metamorphic complex to the south (Mioč & Žnidarčič, 1978; Mioč, 1983). Metamorphic xenoliths are common near the contacts with the country rocks. Granite intrusions caused contact metamorphism in the surrounding pelitic and quartzofeldspathic rocks on the northern and the southern side of the massif (Exner, 1971; Hinterlechner-Ravnik, 1978). Both contacts have been later tectonised. The contact to Triassic dolomite is tectonic.

The Karavanke Tonalite Belt is petrologicaly relatively homogeneous. The majority is hornblende-biotite tonalite with partial transition to granodiorite. Tonalite is strongly foliated parallel to the regional tectonic structure of Karavanke. Mafic inclusions of monzodiorite composition are common and flattened parallel to foliation. To the North, the Tonalitic Belt borders to metamorphic rocks – gneisses and micaschists, and to the south to Triassic dolomite, Oligocene andesitic tuffs and Plio-quarternary sands and gravels.

3.2 The plutonic complex at Črna na Koroškem

The intrusive magmatic rocks of the northern part of the Karavanke igneous zone represent a heterogeneous massif, consisting of predominant syenogranite and syenite with contemporaneous mafic and intermediate rocks of alkaline character. According to TAS classification (Bellieni *et al.*, 1995) the KGB rock types range in composition from gabbro through monzogabbro and monzodiorite, monzonite, syenite to syenogranite (Fig. 12). Mafic and intermediate rocks represent ~30% of the massif.

Dykes of porphyry syenite with K-feldspar rimmed by plagioclase (*e.g.* rapakivi texture) cut large mafic bodies. In monzonite, quartz ocelli-like features are common. Although the

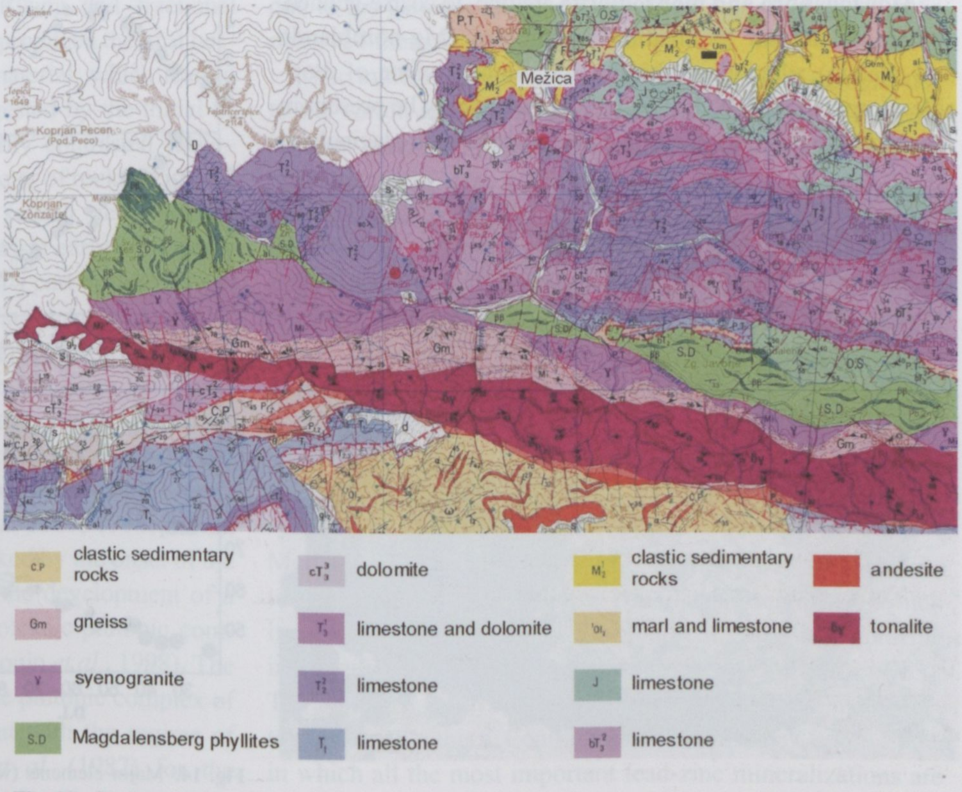

Fig. 11. Geological map of Karavanke – Mežica region (scale: squares correspond to 5×5 km)

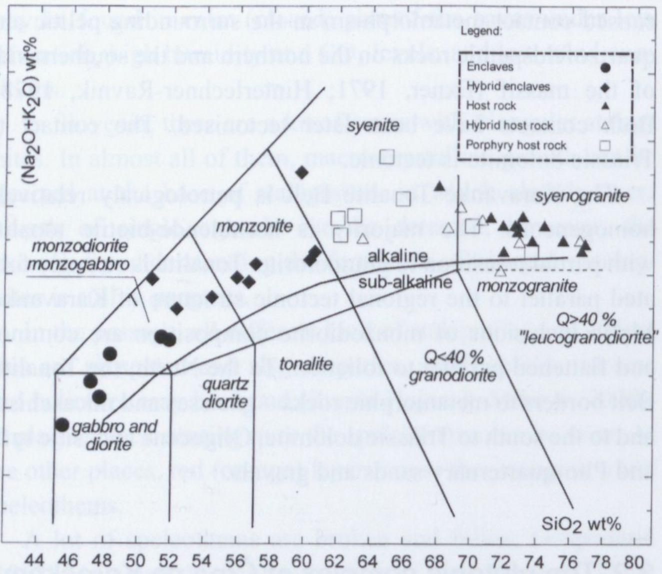

Fig. 12. Classification of rock types in the Karavanke Granite Belt (Bellieni *et al.*, 1995)

succession of rocks had been interpreted as the result of the evolution of the same parental magma (Exner, 1971, 1976; Faninger, 1974), features like plagioclase mantled K-feldspars, quartz ocelli and intrusive breccia features indicate some interaction between mafic and felsic magma (Fig. 13). Short description of rock types:

Gabbro is fine to medium grained, containing normal to alkaline amphibole, plagioclase (An_{45-70}), orthopyroxene (Fs_{22-31}) and olivine (Fo_{73-79}).

Monzogabbro and monzodiorite are fine- to coarse-grained, containing normal to alkaline amphiboles (Mg-hornblende and edenite), plagioclase, biotite and clinopyroxene of diopside composition ($Wo_{48}En_{35}Fs_{17}$). K-feldspar may be present in monzodiorite forming worm-like overgrowths with plagioclase.

Fig. 13. Mafic enclaves and rapakivi texture in syenogranite, Črna na Koroškem

Monzonite is fine-grained, consisting of plagioclase (An_{30}), K-feldspar, quartz of two generations, Mg-hornblende and biotite. Quartz of first generation forms rounded grains surrounded by fine grained hornblende, biotite and plagioclase, and features described as quartz ocellies (Blundy & Sparks, 1992).

Porphyry syenite has fine-grained matrix of anhedral plagioclase, hornblende, biotite, K-feldspar and quartz. Phenocrysts consist of biotite (annite 60-50%), plagioclase (An_{15-20}), quartz and euhedral perthitic K-feldspar (Or_{90}) which is usually rimmed by vermicular overgrowths of plagioclase (An_{20}) and quartz. Euhedral K-feldspar mantled by oligoclase represents rapakivi texture *sensu lato* (Rämö & Haapala, 1995). The cellular growth of plagioclase and infilling of voids with quartz may be a consequence of magma mixing (Hibbard, 1981). Phenocrysts of hornblende occur as well.

Syenogranite is fine- to coarse-grained, containing plagioclase (An < 3%), K-feldspar, quartz, biotite and Fe-hornblende.

Geochemical characteristics of rocks (Figs. 14–15) suggest that some of the most mafic and some of the most felsic rocks could be consistently linked by crystal fractionation only. Rocks

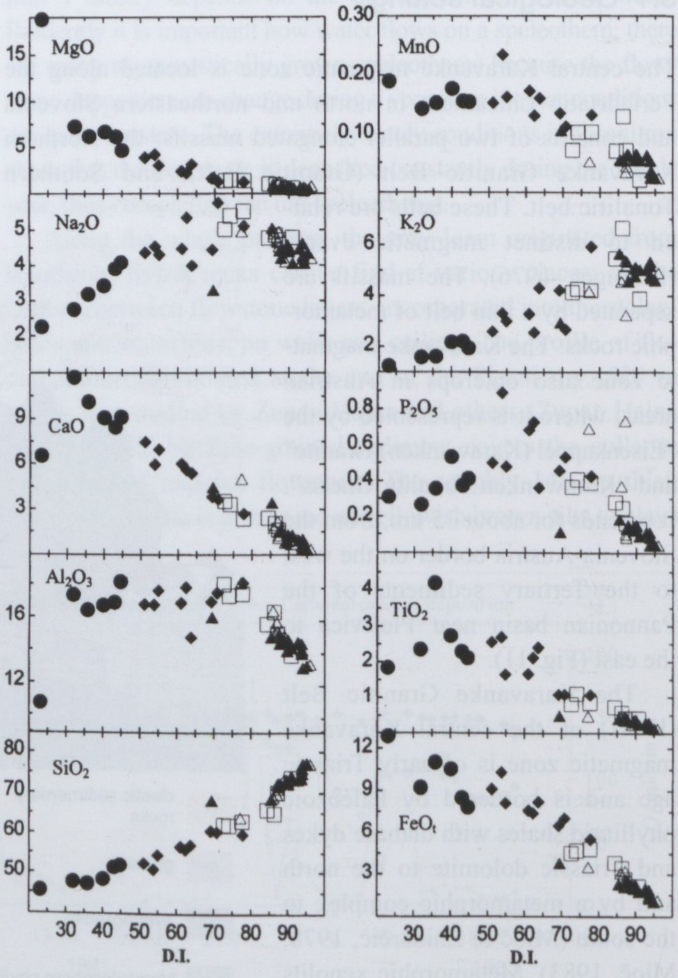

Fig. 14. Major elements (wt%) *vs.* D.I. for rocks of the Karavanke Granite Belt. Legend as in Fig. 12.

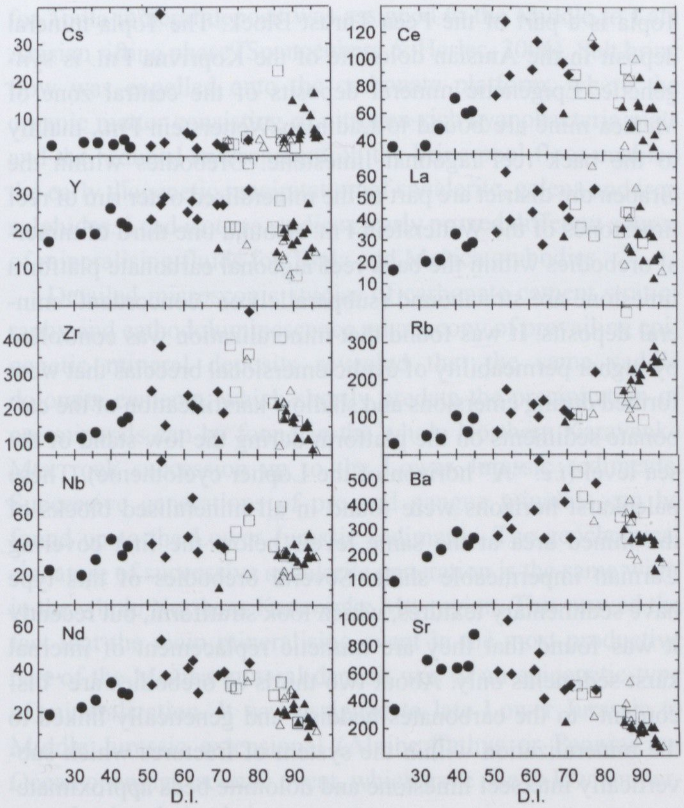

Fig. 15. Trace elements (wt%) *vs.* D.I. for rocks of the Karavanke Granite Belt. Legend as in Fig. 12

of intermediate compositions are the result of a different degree of interaction between the two end-member magmas. Chemical and mineralogical compositions indicate that the mafic rocks represent the mantle-derived magma. Rising and fractional crystallization of mafic magma probably produced the heat necessary to trigger the melting of crustal material, which lead to the formation of a felsic magma as suggested by the initial Sr isotopic data (Dolenec, 1994). The highly contrasted felsic–mafic relationships and the alkaline character of rocks fit into an anorogenic to post-orogenic tectonic setting according to Pitcher (1993). The Late Permian to Triassic early anorogenic A-type plutonic-volcanic complexes form a part of the Western Mediterranean province. The large alkaline magmatic activity of the Western Mediterranean province is related both to post-orogenic continental consolidation of the European plate containing fragments of Gondwana accreted to Laurasia and to precursory stages of the formation of the Neo-Tethys oceanic basin created from the Paleo-Tethys ocean and propagating westwards within Gondwanaland (Bonin *et al.*, 1987, 1998; Bonin, 1997). The Triassic (245–200 Ma) is marked by the onset of the Neo-Tethys ocean basin spreading with the development of a large rift system and emplacement of volcanic-plutonic complexes related to strike-slip fault zones (Bonin *et al.*, 1998). The Triassic early anorogenic bimodal alkaline plutonic complex of the Karavanke Granitic Belt is consistent with the regime of incipient rifting suggested by Bonin *et al.* (1987) for the Western Mediterranean Magmatic province.

4. Field stop 4: The Mežica Pb-Zn mine

4.1 History and current status of mining

Mining in the Northern Karavanke Mts. has more than 340 years long history. Mining activities took place in the area of almost 10 km^2, however, the area of all ore occurrences and prospects is 64 km^2. Around 350 orebodies were mined. The adit made at the highest altitude was just below the Peca Mt., at 2060 m a.s.l., and the deepest adit in the Graben ore district is at the level of 268 m a.s.l.

Until the year 1874, only galena ore was mined, production of sphalerite concentrate started only afterwards. Until their closure, Mežica mines produced altogether 19 millions tons of ore from more than 1000 km of adits and shafts. The more than 1 million tonnes of lead and 500,000 tons of zinc metal production placed Mežica mine among the important European Pb-Zn deposits. During the 2nd World War, due to the German demand for molybdenum, more than 3000 t of wulfenite ($PbMoO_4$) concentrate was also produced. Unfortunatelly many spectacular wulfenite samples were crushed, and used for canon's steel production. Due to low market prices, Mežica mine was closed in 2004. RSCM-Gradbeni materiali d.o.o. (CPM – Building Materials Ltd.) still operates parts of the ore processing plant of the former mine and produces building material from the ore gangue. As a part of this venture, there is a Tourist Mine and Museum, in this way a part of the mine is still open for the public, students and research. Three mine districts: Moring, Helena and Topla are still accessible due to the geosites and technical cultural heritage that can be observed there.

The mineral paragenesis of the Mežica mine is unique due to the varied appearance and crystal morphology of the constituent minerals. Mežica mineral deposits rank among the most important sites of the technical-cultural and geological-mineralogical heritage of Slovenia. We must preserve the most didactic and instructive outcrops and must maintain the accessibility of a part of the mine for the public and for future research. The Topla type zinc and lead mineralization represent a unique genetic environment, and we believe that it has a world-wide geoheritage importance.

4.2 Geology and origin of the Mežica ore deposit

Mežica and its surroundings (Fig. 11) belong to a larger geotectonic unit of the Alpine–Dinaric border zone, which includes the Northern and the Southern Karavanke and the intermediate zone of the Periadriatic line (Mioč *et al.*, 1983). The Northern Karavanke zone is divided into three major tectonic units: Southern, Central and Northern. The Central Zone, in which all the most important lead-zinc mineralizations are found, gives the northern Karavanke a high-mountain character.

The Peca and Uršlja Mountains are raised tectonic horsts and are mostly composed of Wetterstein limestone (Štrucl, 1984).

The host rocks of the Mežica ore deposit consist of a 2000 to 2500 m thick sequence of Ladinian, Carnian, Norian and Rhaetian beds overlying rocks of Anisian age (Fig. 16; Štrucl, 1984). The economically most important ore bodies are found in Ladinian rocks, mostly represented by so-called Wetterstein Limestone. The Wetterstein Limestones in the Northern Karavanke formed as coral reef and back reef facies in the Ladinian and in the lower Carnian. The coral reef facies is macroscopically difficult to distinguish from the lagoon facies. The difference is reflected in the fossil inventory and the microstructural and textural characteristics of limestone. Sediments deposited as fore-reef facies are called Partnaške layers and are represented by clayey carbonate rocks (Štrucl, 1984).

The Wetterstein Limestone Formation is 1000 to 1200 m thick, and its lower half consists of mainly dolomite, while the upper half is composed by limestone. Dolomite is sometimes also present in the upper half of the sequence. The Wetterstein beds are very heterogeneous. Often there is an interchange of microbreccias, macrobreccias, stromatolite and oncoide beds, dolomites of different grain size and chemical compositions, and aphanitic and crystalline limestone (Štrucl, 1984). According to Štrucl (1984), the most significant strata are black breccias, which are located about 12, 25 and 65 meters distances from the first slate. They are important marker horizons because they show a very wide lateral distribution, and they were found at the same levels at the Uršlja Mountains and in Bleiberg in the Gailtal Alps, Austria (Štrucl, 1984). The major part of the Wetterstein limestone sequence was formed in a shallow sea and represents lagoon sediments significantly protected from the sea waves (Štrucl, 1984).

Most of the lead and zinc mineral deposits (99%) are within the Northern Karavanke Thrust Block. Only a small, but zinc- and lead-rich mineral deposit with three orebodies at Topla is a part of the Peca Thrust Block. The Topla mineral deposit in the Anisian dolomite of the Koprivna Fm. is syngenetic. Epigenetic mineral deposits of the central zone of Mežica mine are bound to Ladinian Wetterstein Fm., mainly to the back reef lagoonal limestone. Orebodies within the Graben ore district are part of the mineralised outer rim of reef limestones of the Wetterstein Fm. Around one third of mineral orebodies within the back reef lagoonal carbonate platform limestone are stratabound (subparallel) or "concordant" mineral deposits. It was found that mineralization was controlled by higher permeability of cyclic emersional breccias that were formed during emersions and shallow karstification of the carbonate sediments on the platform during the low stand of the sea level (*i.e.* "A" horizon of the Lopher cyclotheme). These paleokarst horizons were found in all mineralised blocks of the mined area at the same levels below the first covering Carnian impermeable shale. Several orebodies of this type have sedimentary textures, which look stratiform, but recently it was found that they are mimetic replacement of internal karst sediments only. About two thirds of orebodies are "discordant" to the carbonates bedding and genetically linked to the mineralization within the system of fractures which subvertically intersect limestone and dolomite beds approximately in the meridian direction. Numbers of mineral orebodies are of the combined type. Some irregularly shaped orebodies are also strongly controlled by the permeability of the host rock. Columnar breccia ore bodies are collapsed hangingwall lagoonal carbonates above previously formed karst caves.

Apart the up to 7 m thick syngenetic ore deposit in the Anisian units of the Topla orebody, almost all epigenetic ore deposits are confined to the upper 600 m of the Wetterstein Fm. The whole succession of Anisian, Ladinian, and Upper Triassic platform carbonates is 2000–2400 m thick.

Sulphur, oxygen, and carbon isotopes, trace, and rare-earth elements studies disproved any magmatic or volcanic fluid source for both genetic types of deposits. The first mineralising event

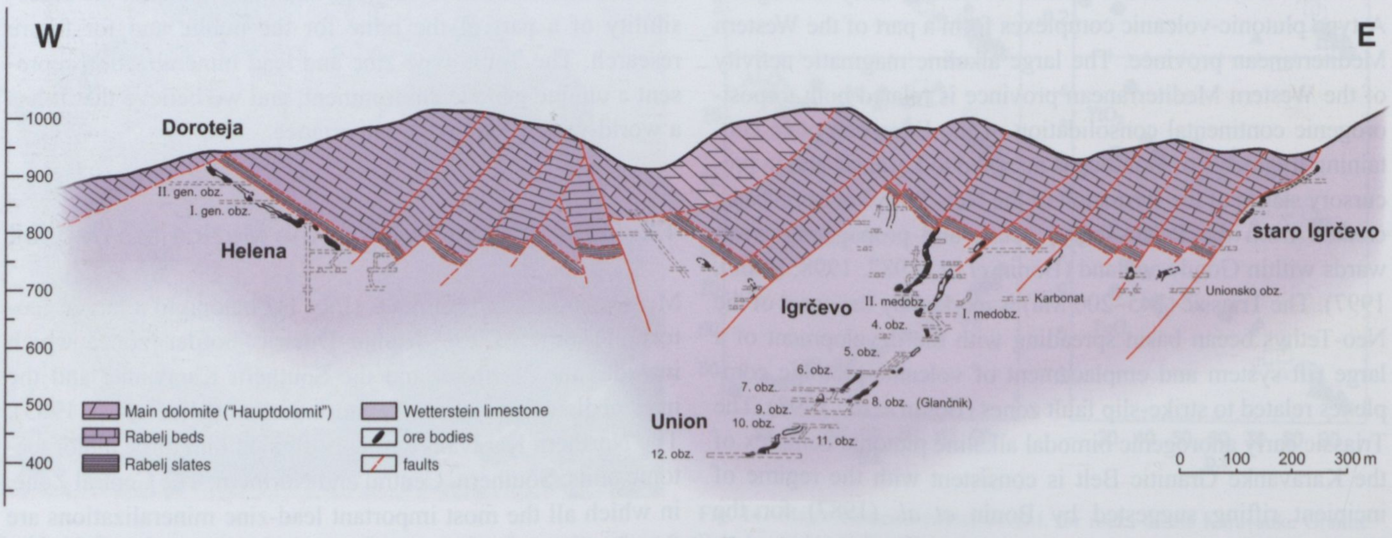

Fig. 16. W–E profile through the central part of the Mežica mine. Legend to the Slovenian text: ge. obz. = main level; medobz. = sublevel; obz. = level

for Topla mineral deposit was assigned to the Middle to Late Anisian rifting phase (Spangenberg & Herlec, 2006). Salt brine flow was expelled onto the carbonate platform, where the organic matter consisting of nitrogen-rich cyanobacteria mats and the reduced environment on the brine pool floor enabled the early diagenetic precipitation of sphalerite, galena and iron sulphides. Lead isotope studies clearly proved different source of mineralising fluids for Topla and Mežica orebodies.

Detailed microscopic studies of carbonate cement stratigraphy and cathodoluminescence microscopy of prevailing epigenetic mineral deposits revealed that the same saddle dolomite cements, which shortly predate the precipitation of ore minerals can be found in the whole Northern Karavanke Mts. rock succession up to the Lower Jurassic sediments. Successive generations of ore and gangue minerals can be found up to the Lower Jurassic sediments. The geochemical signature of successive sphalerite generation is the same within the whole Northern Karavanke Mts region. This proved the fact that the main mineralising event in the most productive part of the Mežica mineral deposit was of an epigenetic type of mineralization. It was assigned to late Lower Jurassic to Middle Jurassic extensional (Alpine Tethys or Penninicum Ocean opening) tectonic event, which gave rise to low temperature lead and zinc brines.

4.3 Mineralogy of the Mežica ore deposit

Minerals found in the Mežica mine are as follows: calcite (Fig. 17), galena, sphalerite, marcasite, pyrite, "melnikovite-pyrite", cerussite, wulfenite (Fig. 18 and 19), limonite, anglesite, smithsonite, hemimorphite, greenockite, gypsum, fluorite, descloizite, hidrozincite, native sulphur, wurtzite, ferrimolybdite, chalcocite, arsenopyrite, baryte, molibdenite, jordisite, ilsemannite, minium (Pb_3O_4), litharge (α-PbO) and massicot (β-PbO) (Jeršek, 2003).

The main ore minerals are galena and sphalerite, followed by pyrite and marcasite, which are generally not very common. Colloform sphalerite, galena and carbonates often form spectacular cockade ore textures within selectively dissolved carbonate rocks. Cubo-octahedral crystals of galena up to three cm are rare. Sphalerite is tectonically fragmented and multiply twinned, and of little interest from collectors' viewpoint. Small crystals of fluorite and barite with up to a few mm in size are seldom.

From the mineralogical point of view, secondary minerals, which are result of oxidation of the primary mineral assemblage due to tectonic uplift of the mineralised succession and inflow of the oxygen-rich meteoric water from the surface, are more interesting. Secondary mineralization is easily recognisable by the presence of iron oxide. Quite often, there are anglesite, cerussite, hydrozincite, and gypsum in the secondary paragenesis.

Anglesite was formed by the oxidation of galena. Crystals up to 5 cm are rare. Anglesite was followed by cerussite in


Fig. 18. Tabular wulfenite, Mežica


Fig. 17. Calcite, Mežica


Fig. 19. Bipyramidal wulfenite, Mežica

presence of carbonate in the water. It has typical prismatic or pyramidal habitus, and commonly shows twinning. Crystals can be up to 5 cm in height. The most common secondary zinc mineral is fine-grained hydrozincite, which forms tiny snow-white colloform overgrowths on limestone or dolomite. Smithsonite is also common as the product of sphalerite alteration.

Calcite of the area is known by its various morphologies. Several types of crystals were studied in detail. Scalenohedra up to several tens of cm are not rare. They were often overgrown by a successive generation of prismatic calcite crystals. In the last phase of calcite precipitation, crystals with steep rhombohedron and scalenohedron faces were developed.

Wulfenite is the best-known mineral of the Mežica mine. The source of molybdenum was most probably sphalerite, which was dissolved by the meteoric water and zinc sulphate was washed away. Molybdenum reacted with lead of the less soluble galena and formed wulfenite. At the lower levels of the mine thinner tabular crystals of wulfenite have been found, while thicker tabular crystals with pyramidal habit are common on the upper levels. Most crystals are twinned. Colour of wulfenite is yellow, orange, brown, green yellow, colourless or black. The largest crystal that has been found is up to 7 cm high. On the highest mine levels, wulfenite is overgrown by the last, recent calcite generation.

5. The Pohorje Metamorphic Massif

5.1 Regional geology

The Periadriatic Fault Zone represents a major, E–W trending Tertiary shear zone crosscutting the entire Alpine edifice from the Western Alps to the Pannonian Basin (Schmidt *et al.*, 1989). All along its strike it is associated with Paleogene igneous bodies, the so-called Periadriatic intrusions (Laubscher, 1983) (Fig. 20).

The Pohorje Mts. (NE Slovenia) represent the south-eastern margin of the Eastern Alps (Fig. 20). On the west it is confined by the Lavanttal fault and by the Periadriatic line on the south (Mioč, 1978, 1983; Mioč & Žnidarčič, 1977, 1989; Mioč *et al.*, 1983). To the north, the mid-Miocene Ribnica

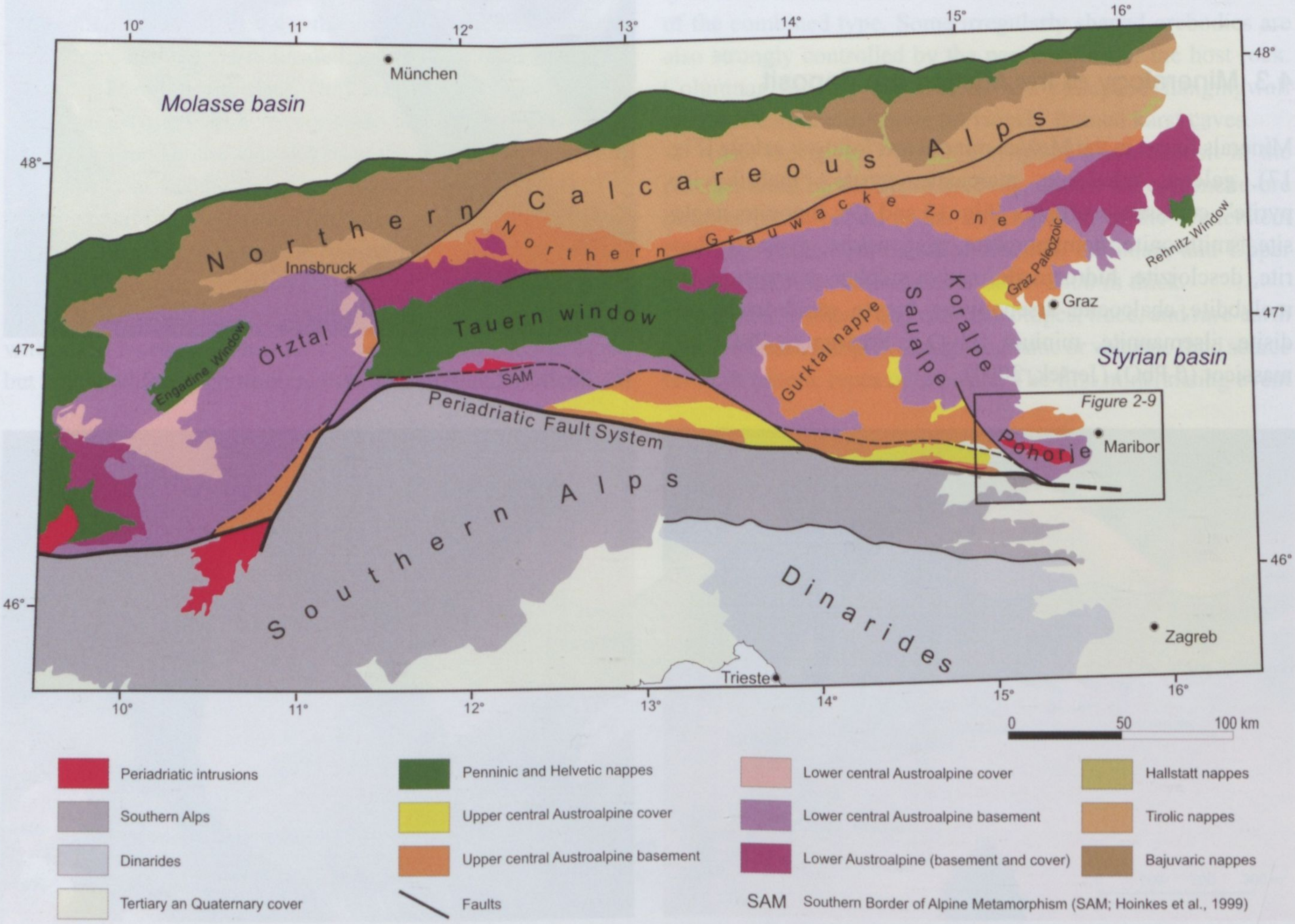

Fig. 20. Tectonic map of the Eastern Alps (modified after Schmidt *et al.*, 2004)

trough separates Pohorje from Kozjak, where rocks of similar lithology and structure occur.

The Pohorje Mts. consist of basement and cover sequences of the Austroalpine nappe system formed during the Eoalpine orogeny (Frank, 1987; Schmidt *et al.*, 2004; Fodor *et al.*, 2008). The deepest tectonic unit – Pohorje nappe (Janák *et al.*, 2006) – corresponds to the Lower Central Austroalpine Unit (Janák *et al.*, 2004). It is mainly composed of medium-grade metamorphic rocks – ortho- and paragneiss, micaschists and amphibolites – intercalated with marble and quartzite. These rocks form a strongly foliated matrix along sporadic eclogite lenses and two main serpentinite bodies (Hinterlechner-Ravnik, 1971, 1973; Mioč, 1978). The foliation and orientation of the lenses are parallel to the upper boundary of the Pohorje nappe.

Eclogites form bodies, lenses and bands of different sizes, up to 1 km long and several tenths of meters thick (Hinterlechner-Ravnik *et al.*, 1991a). They are found within country rocks north and south of the granodiorite body. Numerous lenses, boudins and bends of eclogites also occur within the metaultrabasite (serpentinite) body located near Slovenska Bistrica (Fig. 21).

Metaultrabasites form a body of 5×1 km. Some outcrops occur further to the west (Fig. 21). The main protoliths of the Slovenska Bistrica ultramafic complex are harzburgites and dunites. Because of extensive serpentinisation, only a few less-altered garnet peridotites, garnet pyroxenites and coronitic metatroctolites are preserved (Hinterlechner-Ravnik, 1978, 1991b).

The timing of HP/UHP metamorphism in the Pohorje nappe is Cretaceous, as documented by dating eclogites with garnet Sm-Nd and zircon U-Pb ages of 91 Ma (Miller *et al.*, 2005). Almost identical ages have been obtained from dating of garnet (Thöni, 2002) and zircon (Cornell *et al.*, 2007) of gneisses and micaschists. Tertiary K-Ar mica ages (19–13 Ma) as well as apatite and zircon fission track ages (19–10 Ma) were obtained from the country rocks of eclogites and metaultrabasites in the Pohorje nape (Fodor *et al.*, 2002). This suggests that the peak of metamorphism was attained during the Cretaceous and final cooling occurred in the Early to Middle Miocene. The final stage of exhumation to the surface was achieved in the Miocene by east- to north-east-directed low-angle extensional shearing associated with the main opening phase of the Pannonian basin and leading to the core-complex structure of the Pohorje Mts. (Fodor *et al.*, 2003). The Miocene shearing event reactivated and overprinted the nape boundaries in the Pohorje area (Janák *et al.*, 2006).

The Pohorje nappe is overlain by a nappe composed of weakly metamorphosed Palaeozoic rocks, mainly low-grade metamorphic slates and phyllites. The uppermost nappe is built up of Permo-Triasic clastic sedimentary rocks, prevailingly sandstones and conglomerates. The two latter nappes represent the Upper Central Austroalpine Unit.

The entire nappe stack is overlain by early Miocene sediments, which belong to the syn-rift basin fill of the Panonian Basin (Fodor *et al.*, 2003).

The Miocene (18–19 Ma; Trajanova *et al.*, 2008; Fodor *et al.*, 2008) Pohorje Igneous Complex is a more than 40-km long and 7-km wide calc-alkaline suite, extending in WNW–ESE direction. It consists of a larger central granodiorite body and a smaller dacite part in its north-western section (Dolar Mantuani, 1935; Faninger, 1970; Zupančič 1994a, b).

At the southern margin of the granodiorite massif, close to the village of Cezlak, there is a small quartz monzogabbro body, locally called "cizlakite" (Nikitin, 1939). It is the only locality of this rock type.

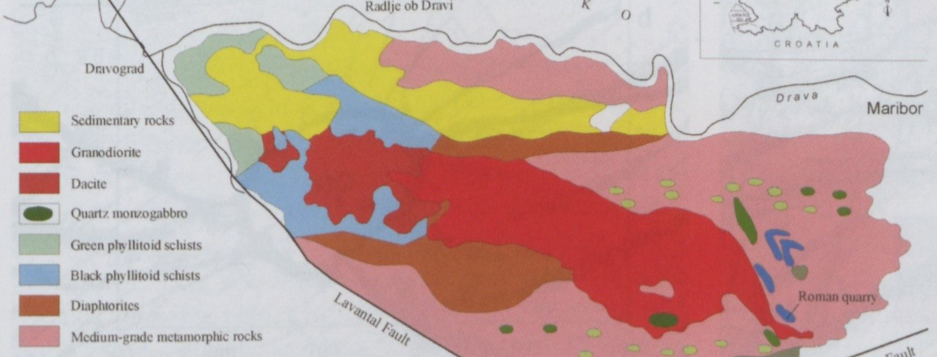

Fig. 21. Simplified geological map of Pohorje and adjacent areas with the location of the field trip stops (after Mioč & Žnidarčič, 1977)

Granodiorite and cizlakite are crosscut by several generations of pegmatite and aplite dykes (Činč, 1992) and by lamprophyres (called malchite in older literature). In the southwestern part of the Pohorje, lamprophyric veins intrude metamorphic rocks and exceptionally granodiorite and pegmatite (Germovšek, 1954; Zupančič, 1994a, b).

Dacite intrudes low-grade metamorphic schist. Its contact with the granodiorite is covered, but gradual transition from one rock type to another could be noted. According to the texture, some authors classify the transitional rock as diorite porphyry (Benesh, 1918; Dolar Mantuani, 1938a, b), tonalite porphyry (Dolar Mantuani, 1938a, b, 1939; Germovšek, 1954; Faninger, 1970; Mioč, 1978) and porphyrytic granodiorite (Zupančič, 1994a, b).

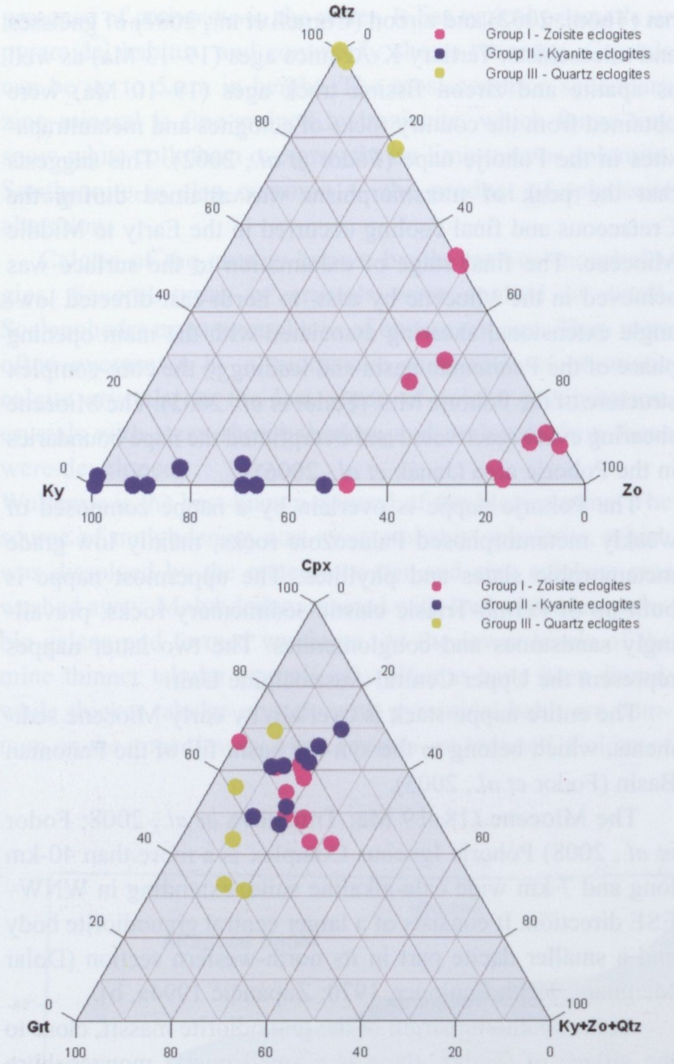

Fig. 22. Modal compositions of Pohorje eclogites shown in the (a) kyanite – zoisite – quartz and (b) garnet – (kyanite + zoisite + quartz) – clinopyroxene triangle. Based on these compositions, the rocks can subdivided into three groups: zoisite-, kyanite-, and quartz eclogites, which can be clearly distinguished in diagram (a). Cpx – clinopyroxene, Grt – garnet, Ky – kyanite, Qtz – quartz and Zo – zoisite

5.2 Field stops 5 and 6: Kyanite eclogites at Radkovec or Vranjek Peak and zoisite eclogites at Pivola

Eclogites contain large distinctive grains of garnet surrounded by omphacite matrix often accompanied with elongated grains of blue kyanite. Based on modal mineralogy, the eclogites can be divided into three distinct groups (Fig. 22):

- zoisite eclogites, found in ultramafics and continental crustal rocks. They contain also some kyanite and quartz;
- kyanite eclogites hosted by ultramafic, quartz-free rocks, which may contain some zoisite;
- quartz eclogites found mainly within continental crustal rocks. Some zoisite may be present.

Garnets are texturally uniform, unzoned, and nearly homogeneous in composition with 27–55 mol% of pyrope, 25–45 mol% of almandine and spessartine and 18–27 mol% of grossular and andradite content (Vrabec, 2007); thus they belong to the almadine–pyrope–grossular series with high pyrope content, as is common for UHP metamorphic rocks (Chopin, 1984). Garnet rims are commonly reserved by amphibole + plagioclase symplectite resulted from retrogressive reaction between garnet and omphacite with additional water.

Omphacite also shows uniform grains and almost homogeneous composition. Jadeite component varies between 18–37% (Vrabec, 2007). The total cation deficiency and excess of Al in the octahedral site suggest the existence of non-stoichiometric pyroxenes, indicative of high-pressure conditions (Gasparik & Lindsey, 1980).

Kyanite forms frequently twinned subhedral grains and small rod-like inclusions within garnet and omphacite. Its formation is connected to the disappearance of the plagioclase from the protolith of basaltic composition (Raymond, 2002). Retrogression of kyanite is expressed by development of complex coronas of sapphirine + corundum + spinel + anorthite. Sapphirine is a rather uncommon mineral because it requires

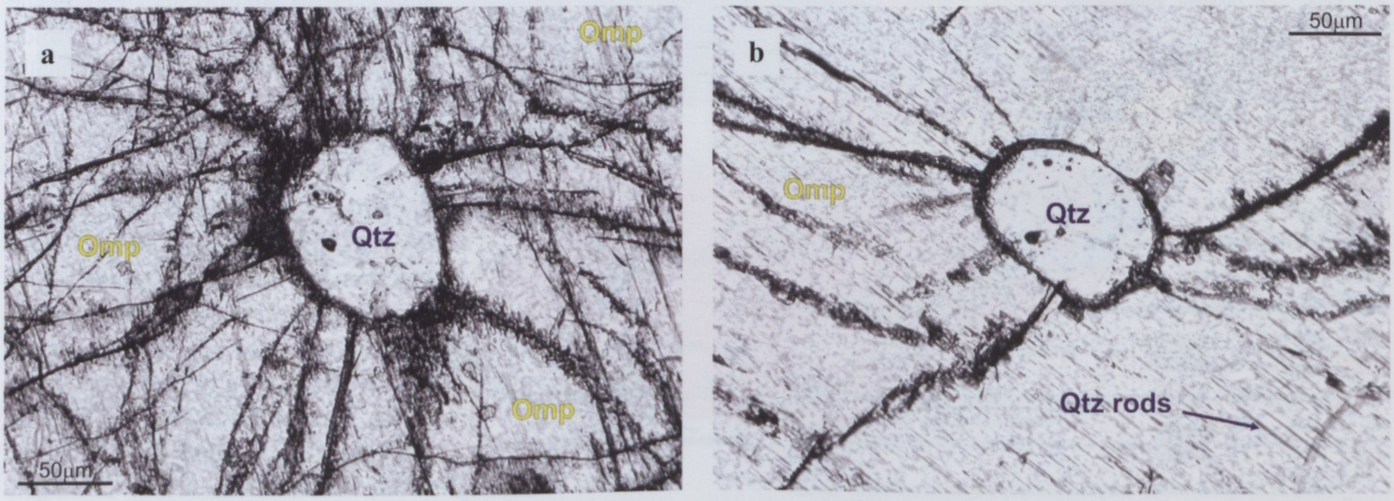

Fig. 23. Radial fractures surrounding quartz inclusions in omphacite under plane-polarized light. In picture b quartz inclusion surrounded by radial fractures is hosted by omphacite with tiny quartz exsolutions. Omp – omphacite, Qtz – quartz

bulk composition rich in both Mg and Al. Its formation is confined largely to high-grade metamorphic terrains formation of granulite facies (Akermand *et al.*, 1975). Pohorje sapphirines are clearly peraluminous. They formed most probably during decompression at lower temperature conditions (Vrabec, 2007).

Zoisite is present in eclogites from all localities. It mainly forms individual elongated grains but may also be found as minor inclusions in garnet and omphacite (Vrabec, 2007). Its formation is explained by the reaction (Raymond, 2002):

$$\text{anorthite} + H_2O \rightarrow \text{zoisite} + \text{kyanite} + \text{quartz}$$

Quartz inclusions are present in garnet, omphacite and kyanite. They are frequently surrounded by radial fractures (Fig. 23), which may imply the possibility for the existence of former coesite and are therefore indicators of possible UHP conditions (Gillet *et al.*, 1984).

Metamorphic conditions for the formation of eclogites have been calculated from a combination of the garnet–clinopyroxene Fe^{2+}-Mg exchange thermometer (Krogh Ravna, 2000) with the net-transfer reactions equilibrium in the garnet + clinopyroxene + phengite ± kyanite ± quartz/coesite system, calibrated as thermobarometers by Krogh Ravna & Terry (2001, 2004).

Estimated peak pressure and temperature conditions for Pohorje eclogites are in the range of 3.0–3.1 GPa and 762–824 °C (Vrabec, 2007; Fig. 24). These pressure and temperature values correspond well to the ultrahigh-pressure stability field of coesite. There is almost ideal fit between the garnet-clinopyroxene-kyanite-coesite and garnet-clinopyroxene Fe^{2+}-Mg exchange thermometers.

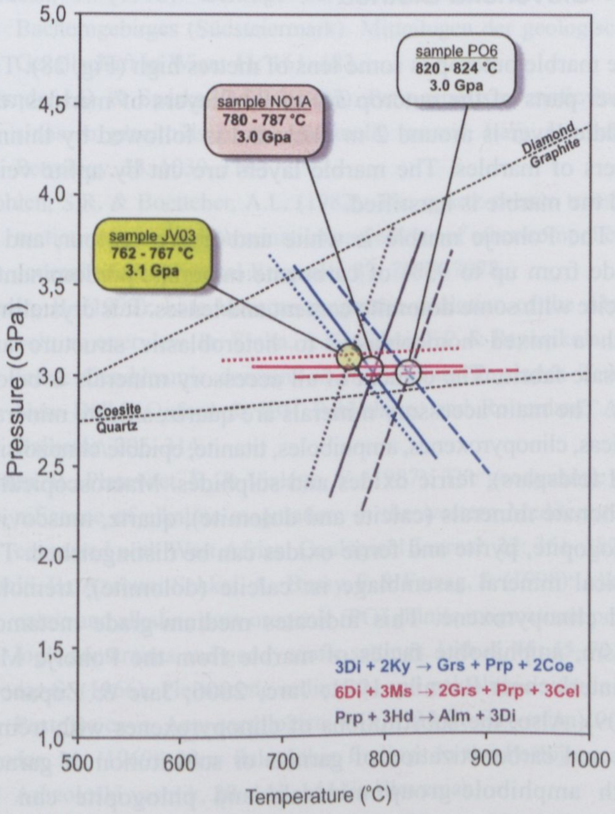

Fig. 24. Estimated peak pressure and temperature conditions for Pohorje eclogites from three different localities. Calculated pressures and temperatures of 3.0–3.1 GPa and 762–824 °C are well within the coesite, *i.e.* the ultra-high-pressure stability field

The Pohorje eclogites mainly originated as plagioclase-bearing (gabbroic) cumulates from depleted mantle-derived melts that crystallized at low pressures within the plagioclase stability field and later underwent various degrees of partial melting (Vrabec, 2007).

Accoding to the proposed tectonic scenario the closure of the Meliata Ocean by continent–continent or arc–continent collision was followed by intracontinental subduction of the Pohorje nape, belonging to the Lower Central Austroalpine, towards the SE under the Upper Central Austroalpine, which allowed subsequent exhumation of the UHP rocks by slab extraction (Figs. 25–26, Vrabec, 2007).

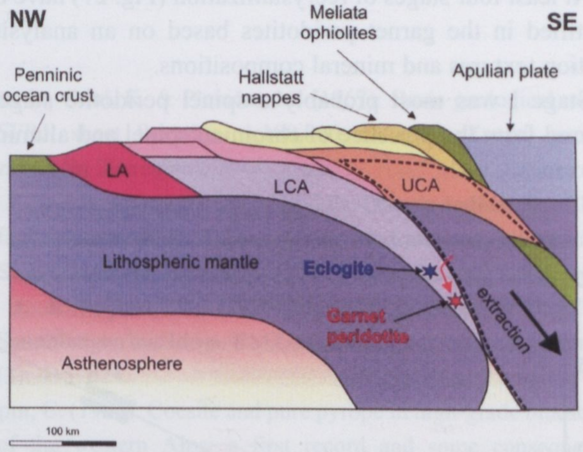

Fig. 25. Hypothetical cross-section of the Austroalpine orogen at ~100 to 90 Ma. Pohorje garnet peridotites and eclogites are deeply buried in an intra-Austroalpine subduction zone. The peridotites were incorporated from the overlying mantle wedge and carried down to UHP depth. Exhumation was accommodated by later extraction of the Upper Central Austroalpine lower crustal and mantle wedge. The dashed line delineates the extracted wedge. It comprises lithospheric mantle and lower crust of the Upper Central Austroalpine, as well as oceanic crust of the Meliata ocean (after Janák *et al.*, 2006). LA – Lower Austroalpine, LCA – Lower Central Austroalpine, UCA – Upper Central Austroalpine

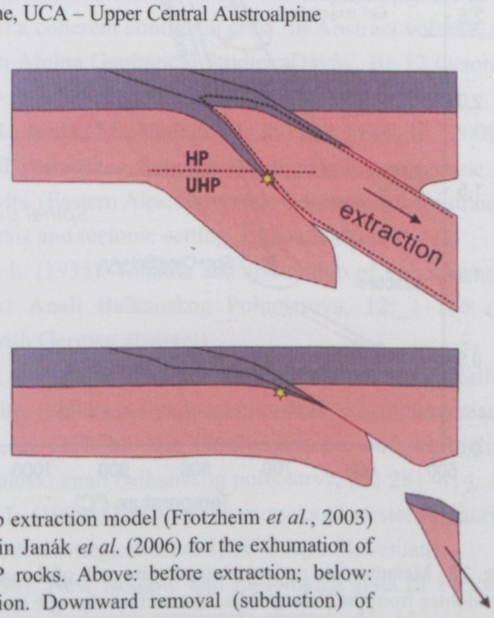

Fig. 26. Slab extraction model (Frotzheim *et al.*, 2003) as proposed in Janák *et al.* (2006) for the exhumation of Pohorje UHP rocks. Above: before extraction; below: after extraction. Downward removal (subduction) of lower crustal and mantle wedge enables significant exhumation without necessitating any erosion

5.3 Field stop 7: Serpentinites in the Markuz Quarry

An evidence for ultrahigh-pressure metamorphism (UHPM) in the Eastern Alps is reported also from garnet-bearing ultramafic rocks (De Hoog *et al.*, 2009). The garnet peridotites are closely associated with UHP kyanite eclogites. These rocks belong to the Lower Central Austroalpine basement unit of the Eastern Alps exposed in the proximity of the Periadriatic fault. Ultramafic rocks have experienced a complex metamorphic history. On the basis of petrochemical data, garnet peridotites could have been derived from depleted mantle rocks that were subsequently metasomatized by melts and/or fluids either in the plagioclase–peridotite or the spinel–peridotite field.

At least four stages of recrystallization (Fig. 27) have been identified in the garnet peridotites based on an analysis of reaction textures and mineral compositions.

Stage I was most probably a spinel peridotite stage, as inferred from the presence of chromian spinel and aluminous pyroxenes.

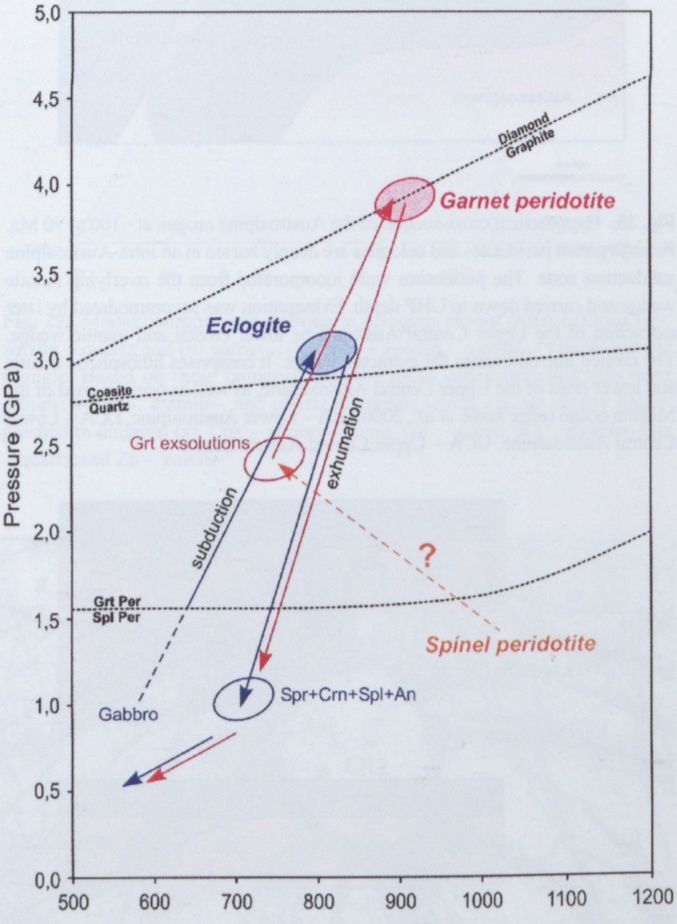

Fig. 27. Metamorphic pressure-temperature path of the eclogites and garnet peridotites from the Pohorje Mts. Shown for reference are equilibria for diamond–graphite (Bundy, 1980), coesit-quartz (Bohlen & Boettcher, 1982) and spinel-garnet peridotite (O'Hara *et al.*, 1971)

Stage II is a UHPM stage defined by the assemblage garnet ± low-Al orthopyroxene ± clinopyroxene ± Cr-spinel. Garnet formed as exsolutions from clinopyroxene, coronas around Cr-spinel, and porphyroblasts.

Stage III is a decompression stage, manifested by the formation of kelyphitic rims of high-Al orthopyroxene, aluminous spinel, diopside and pargasitic hornblende replacing garnet. Stage IV is represented by the formation of tremolitic amphibole, chlorite, serpentine and talc.

Geothermobarometric calculations using (i) garnet–olivine and garnet–orthopyroxene Fe-Mg exchange thermometers and (ii) the Al-in-orthopyroxene barometer indicate that the peak of metamorphism (stage II) occurred at conditions of around 900 °C and 4 GPa. These results suggest that garnet peridotites in the Pohorje Mts. experienced UHPM during the Cretaceous orogeny. UHPM resulted from deep subduction of continental crust, which incorporated mantle peridotites from the upper plate, in an intracontinental subduction zone. Sinking of the overlying mantle and lower crustal wedge into the asthenosphere (slab extraction) caused the main stage of unroofing of the UHP rocks during the Upper Cretaceous. Final exhumation was achieved by Miocene extensional core complex formation.

5.4 Field stop 8: Roman marble quarry at Slovenska Bistrica

The marble outcrop is some tens of metres high (Fig. 28). The lower parts of the outcrop are of thin layers of marbles; the middle layer is around 2 m thick and is followed by thinner layers of marbles. The marble layers are cut by aplite veins and the marble is karstified.

The Pohorje marble is white and/or grey colour, and is made from up to 95% of carbonate minerals, predominantly calcite with some dolomite content and lenses. It is crystalline, with a mixed homeoblastic to heteroblastic structure and mosaic fabric. The content of all accessory minerals is below 5%. The main accessory minerals are quartz, silicate minerals (micas, clinopyroxenes, amphiboles, titanite, epidote/clinozoisite, and feldspars), ferric oxides and sulphides. Macroscopically, carbonate minerals (calcite and dolomite), quartz, muscovite, phlogopite, pyrite and ferric oxides can be distinguished. The typical mineral assemblage is: calcite (dolomite), tremolite and clinopyroxene. This indicates medium-grade metamorphism, amphibolite facies of marble from the Pohorje Mts. (Hinterlechner-Ravnik, 1971; Jarc, 2006; Jarc & Zupancic, 2009). Also, the substitutions of clinopyroxenes with tremolite and carbonatization of garnets or substitution of garnets with amphibole-group minerals and phlogopite can be observed in thin sections (Jarc, 2006). This could be the result of retrograde metamorphism which had been already established for other Pohorje metamorphic rocks (Hinterlechner-Ravnik *et al.*, 1991).

The maximum grain sizes exhibit great variability and the values of MGS (maximum grain size) are up to 6 mm, as characteristic for medium- to coarse-grained marble.

The isotopic signatures throughout the massif show very high oxygen depletion (–15.62 to –6.45‰ β^{18}O PDB and from –12.03 to –7.82‰ β^{18}O PDB for Roman marble quarry, respectively), whereas the values of β^{13}C are between 0.11 and 2.3‰ and 0.18 to 0.7‰ for this locality (Jarc, 2006). The isotopic values of marbles throughout the Pohorje massif are very similar to those of the Austrian marbles from Carinthia (Kärnten) and Styria (Steiermark) (Müller & Schwaighofer, 1999).

Fig. 28. Roman marble quarry, Slovenska Bistrica

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Appendix – Itinerary for IMA2010 SI1 Field trip

Tuesday, August 17, 2010 (Day 1)

Ljubljana: arrival to Ljubljana airport or railway / bus station, optional tour around the town, accommodation

Wednesday, August 18, 2010 (Day 2)

08:00	Departure for Idrija
10:00	Field stop 1. Visit to Idrija mine (1 hour walk in the part open for tourists; ~100 staircases)
12:00	Visit to the museum (cinnabar, native mercury, idrialite in sedimentary rocks)
13:30–14:30	Lunch
15:30	Departure for Postojna
16:00	Filed stop 2: Visit to Postojna cave: karst features (train and 1 hour walk through part open for tourists)
18.00–19.30	Ljubljana: dinner and accommodation

Wednesday, August 19, 2010 (Day 3)

08:00–12.00	Ljubljana: Departure for the Karavanke igneous zone. Field stop 3: Rapakivi granite (15 minutes light walk)
12:00–13:30	Lunch
13:30–16:30	Field stop 4: Visit to Mežica mine (Pb-Zn hydrothermal and sedimentary deposit – 1 hour light walk) and visit to the museum (sphalerite, galena, wulfenite specimens)
16:30–18:00	Maribor: accomodation and dinner

Friday, August 20, 2010 (Day 4)

08:00	Maribor: Departure for the Pohorje area
09.00–13.00	Pohorje area (Field stops 5–8): Radkovec or Vranjek peak: kyanite eclogites; Markuž Quarry: serpentinites; Pivola: zoisite eclogites (20 minutes uphill walk); Slovenska Bistrica
13:00–14:30	Lunch
15.00–17:00	Slovenska Bistrica: Roman quarry (calcitic marble; 30 minutes uphill walk)
17:00	departure for Budapest