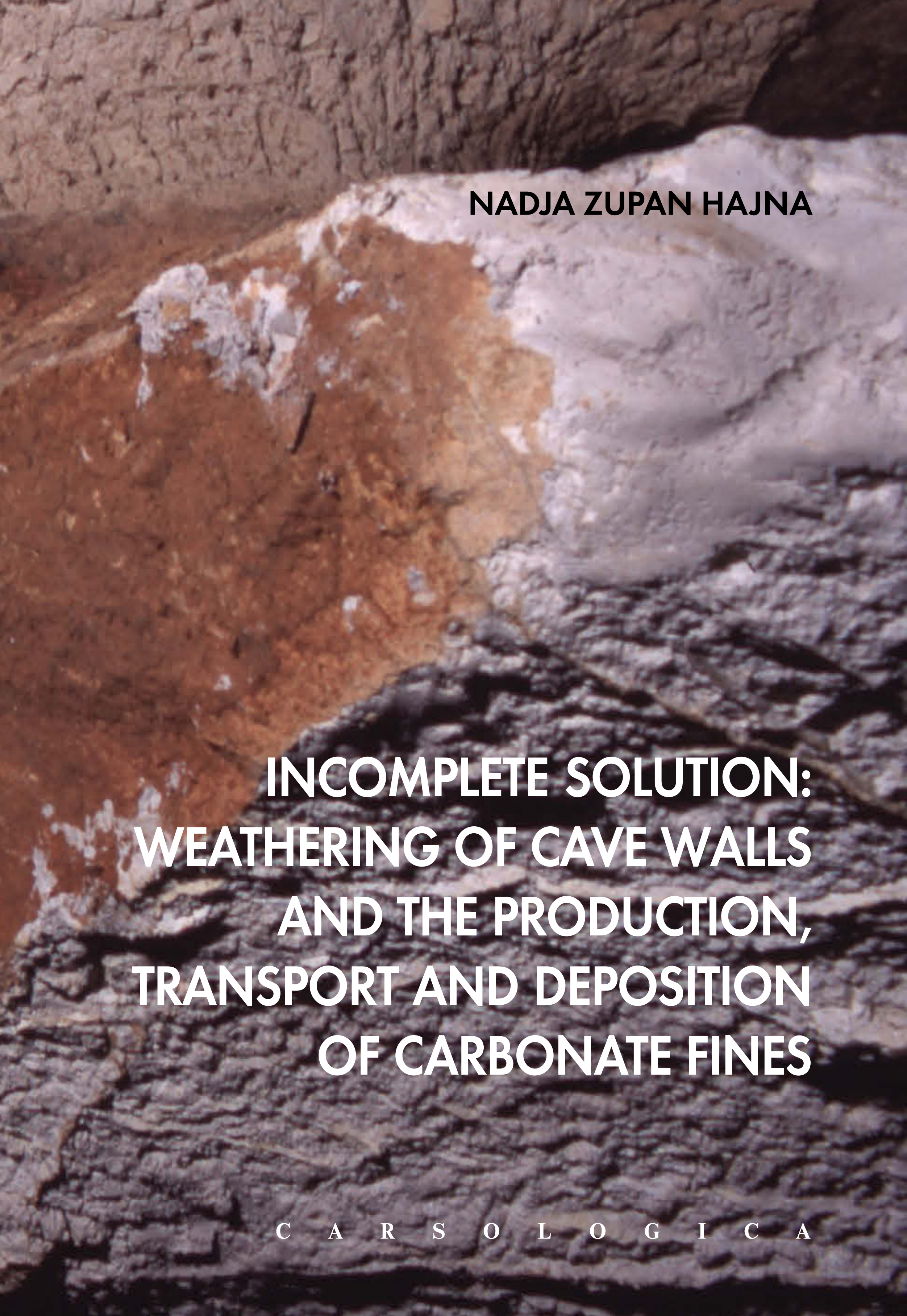

NADJA ZUPAN HAJNA

INCOMPLETE SOLUTION: WEATHERING OF CAVE WALLS AND THE PRODUCTION, TRANSPORT AND DEPOSITION OF CARBONATE FINES

C A R S O L O G I C A

Nadja Zupan Hajna is a researcher at the Karst Research Institute of the Scientific Research Centre of the Slovenian Academy of Sciences and Arts in Postojna, Slovenia. She graduated in 1987 at the Faculty of Natural Sciences and Technology, Department of Geology, University of Ljubljana with the title *Heavy minerals in stream sediments from the area of Ravne na Koroškem*. At the same faculty she finished her Master degree thesis *The origin and mineral composition of cave sands and loams* in 1990 and defended her doctoral dissertation *Relation between autochthonous chemical and mechanical erosion at cave passages formation* in 2002.

Her professional work dealt mainly with physical speleology and karstology, with emphasis on karst sediments, specially their mineral composition, origin and age. Her latest works are dedicated to weathering of limestone and dolomite in a cave environment. She is involved in several Institute's national and international research projects. She is a caver, member of the Slovenian Geological Society and actual president of the Geomorphological Society of Slovenia.

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INCOMPLETE SOLUTION: WEATHERING OF CAVE WALLS AND THE PRODUCTION, TRANSPORT AND DEPOSITION OF CARBONATE FINES

NADJA ZUPAN HAJNA

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FOREWORD

My studies investigated poorly researched subject of incomplete solution of limestones and dolomites in different caves. Before I decided to work on this research topic I was surprised by the high occurrence of fine carbonate clasts in cave sediments and also by the appearance of thick, soft zones of an unknown mineral found on the walls of cave passages.

Field work and laboratory work were mostly carried out at the Karst Research Institute of the Scientific Research Centre of the Slovene Academy of Sciences and Arts, partly as projects financed by Ministry of Education, Science and Sport, and partly as a doctoral research work entitled "Relation between autochthonous chemical and mechanical erosion at cave passages formation" supervised by Prof. Dr. France Šušteršič.

I thanks Dr. Tadej Slabe, Head of the Karst Research Institute ZRC SAZU, to give me an opportunity to research in frames of different Institute's projects.

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Analyses of weathered carbonate rocks were done with help of Dr. Matjaž Kavčič, Bsc. Tomaž Polak, Dr. Meta Dobnikar, Zoran Samardžija and Mateja Zadel. I am much obliged to all of them.

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And at last I have to thank my parents, Jure and children for all their support, help and understanding during my research.

INTRODUCTION

MAIN THEMES AND PREMISES

Karst is a unique part of the earth's crust for wich the most significant caracteristic is developing of underground water dreinage. The most important process in the formation of karst (karstification) is dissolution by carbonic acid. Its forms are produced by the chemical effect of water on relatively soluble rocks. The formation and development of karst is influenced by the lithological characteristics of rocks as well as by their effective porosity and a sufficient amount of atmospheric precipitation.

The main topic of this monograph is the weathering of carbonate rocks on the walls of cave passages. In general the rate of weathering depends on both rock decomposition and transportation of the resulting products. In the case of carbonate rocks it is taken as a rule that the rate of weathering depends solely upon the speed of dissolution. My research is demonstrating, however, that carbonate weathering is partly limited by the rate of transport as well.

I have discovered that all of the carbonate rock does not dissolve immediately: and is not carried away from its primary place in its ionic form, but that the disintegrated particles may remain on the cave passage walls. An incomplete dissolution may just prepare the carbonate rock for the mechanical transport of its particles by the flowing water. To what extent the carbonate rock dissolves at its secondary site or may get carried away in some other way, still remains unknown to us. The transported carbonate particles of silt or clay size may accumulate in the cave passages as clastic cave sediments.

I cannot be precisely certain if incomplete dissolution of carbonate rocks is an important factor or is one of the rare processes that occur in the formation of cave passages. This is because water may be incessantly washing away effected rock at the same time as it decomposes. We are able to detect strongly weathered limestone or dolomite on cave passages walls only where they are protected from further dissolution and mechanical erosion.

Mineralogical analysis have already shown that all carbonate rocks do not dissolve immediately, but are washed away by water in the form of particles. Some cave sediments contain a large proportion of carbonate clasts, as described by Newson (1971a), which originate from the cave passage walls (Zupan & Mihevc 1988). Carbonates in clastic cave sediments do not only occur as individual layers of flowstone or as a cohesive, binding elements; but also as minute fragments of the original primary rock, lithoclasts of silt or clay size.

The frequently used method of extracting all the carbonate from cave sediments before undertaking more serious analysis is in its' essence flawed. It ignores the important fact, that all carbonate rock does not dissolve completely on the cave passage walls.

The way in which the carbonate rock is carried away from its primary site depends mostly on its chemical and mineral composition and on the chemical and hydro-mechanical characteristics of the water, which in a karst environment is both the predominant natural solvent as well as the erosive and alluvial agent. Rock may be carried away from its primary site in the form of ions or mechanical particles, that is, by means of chemical or mechanical erosion, or in some cases by the combined action of both. The ratio between them is influenced by the water flow with all its characteristics, as well as by the structure and mechanical properties of the rock. However, biogenic corrosion may also interfere in the dissolution processes.

I have assumed that the mechanical alluvium of solid particles derived from crystallised and dolomitised limestones, which are composed of the sparry grains, is greater than that from fine-grained uncrystallised and non-dolomitised limestones. Similarly, when the carbonate rock is already tectonically significantly decomposed, tiny gravel will get washed mechanically away by water much more easily and will dissolve faster as well. Where it is not already decomposed, its disintegration is much more influenced by the process of dissolution. In this way its' mineral composition and texture becomes more significant. Dissolution firstly corrodes the edges and irregularities on the surface of grains. Whether the dissolution is carried out to completion, depends on many factors. The chemical process may just superficially intend the rock so that all the rest is performed by water, which may afterwards just wash the already intended particles away. There exist therefore, two forms of alluvial transport: dissolution and washing away.

In this monograph technical terms were following the karst terminology of Gams (1974) and Ford & Williams (1989), I do not intend to accompany them with any further explanations. In the text itself I elucidate only the terms that appeared less intelligible, but were, nevertheless, of considerable importance in understanding the paper.

CHARACTERISTICS OF CARBONATE ROCKS AND HOW THEY WEATHER

The characteristics of carbonate rocks are one of the most important factors in the process of cave passage formation. Sedimentary carbonate rocks are composed of carbonate minerals; predominantly the carbonates of calcium and magnesium. Of particular interest to me were the characteristics and peculiarities of the limestone and dolomite weathering processes.

As limestones are transferred from the depositional environment into one with different physical and chemical parameters, they start to weather. The course of the retrograde diagenesis of carbonate rocks is influenced by numerous factors, the most significant of them being temperature, pH, organic matter, CO_2 dissolved substances, the Ca/Mg ratio, the flow of the liquid, etc (Wolf & Chilingarian 1994).

Chemical processes may cause partial or total change in the rock. Chemical rock disintegration processes include: hydration, hydrolysis, oxidation, base-exchange, the effects of acids, dissolution and colloid formation.

Mechanical rock weathering processes include: crushing, cracking near the surface, tectonic fissuring, climate fluctuation, the growth of ice crystals and salts within cracks, and expansion which results from such growth.

The biological factors that impact on the rock weathering include the vegetation, with roots causing mechanical and chemical disintegration. Of some importance also is dissolution by organic acids, which are created mostly under the influence of bacteria and partly under the influence of plants and animals.

The dissolution of carbonate rocks by carbonic acid or corrosion, is a process characteristic of karst areas. The lithological properties of carbonate rocks, the type of porosity and the climate are of outstanding significance for karst development and also for the formation of caves.

Unsaturated meteoric waters get enriched with atmospheric CO_2 with CO_2 from the soil and with organic as well as other acids coming from the soil, and are thus able to dissolve carbonate rocks. Chemical processes and the kinetics of the carbonate rock dissolution are very complex phenomena that have been studied by different authors from various perspectives. Those of greatest significance are: Garrels 1960, Garrels & Christ 1965, Thrailkill 1968, Plummer & Wigley 1976, Bögli 1980, Plummer *et al.* 1978, Busenberg & Plummer 1982, Dreybrodt 1980, 1981, 1988, Reddy *et al.* 1981, Dreiss 1984, Sjoberg & Rickard 1984, Baumann *et al.* 1985, Buhmann & Dreybrodt 1985a, 1985b and 1987, Herman & White 1985, Trudgill 1985, 1986, Shopov *et al.* 1989, Morse & Mackenzie 1990, Dreybrodt & Buhmann 1991, Svensson & Dreybrodt 1992, Pingitore *et al.* 1993, Atkins 1995, Dreybrodt *et al.* 1996, Dreybrodt & Zaihua 1997, Eisienlohr *et al.* 1997, Eisienlohr *et al.* 1999 and Gabrovšek 2000a. The subject matter dealt with is dissolution at different pH values and temperatures, under stable conditions, with the addition of Mg ions, with impure calcium carbonate, in porous media etc.

The rate of dolomite dissolution and its dependence on temperature and pH have been investigated in some recent treatises (Purser *et al.* 1994, Gauteilier *et al.* 1999, Pokrovsky & Schott 2001), but nevertheless the kinetics of the dolomite dissolution is still not completely explained. In the research reported here I have given consideration to the findings of all these authors, whom I also refer to later; but I have not concerned myself with the dissolution kinetics of the calcite and dolomite.

Dissolution depends on the properties of the carbonate rock, the water, environment where the dissolution is taking place and the nature of reactions on the mineral's surface (Colman & Dethier 1986).

The rock itself influences dissolution by its mineral composition, the crystal lattice arrangement of the minerals in the rock, the texture, size and the shape of the grains, the contacts among them and by the type and degree of porosity. Of great significance in the environment itself are climatic conditions such as precipitation, temperature, pH, Eh, pressure and also the soil, vegetation, partial pressure of CO_2 and of course, time.

Water affects dissolution with its chemical composition and mechanical properties such as: the quantity and manner of the water flow as well as the nature and the extent of the contact with the rock. Rainwater, when absorbed through the ground, gets enriched with CO_2 and forms carbonic acid, which then dissolves carbonates. Carbonate rocks are also dissolved by other waters, which come in contact with them or are circulating in their fracture systems. The pH of karst water is approximately 8.0 where as ordinary rainwater reaches pH values from 5.6 to 6.4 and acid rain below 5.0 and in some cases, below 3.5.

The chemistry of the limestone dissolution generally involves the system H_2O – CO_2 – $CaCO_3$. It is accelerated by the presence of microorganisms, sulphur, etc. This system is of the highest importance and proves to be sufficient for the karst formation (Gabrovšek 2000a). Principally, this may be defined as a mass action, the result of which is the balanced diagram, where two extreme systems have been taken into consideration: namely the contact with the atmosphere and with it an open CO_2 system as well as phreatic conditions and with them, the closed CO_2 system.

Dissolution kinetics determines the rate of dissolution. The dissolution speed on the surface is described by an empirical rule, based on results of synthetic calcite experiments (Plummer *et al.* 1978). The dissolution rate is linear. With natural calcite, Gabrovšek (2000a) found that dissolution is linear only at the beginning of the reaction. Owing to impurities accumulated on the calcite surface (insoluble residue), however, it becomes non-linear. According to Dreybrodt (1988) and Gabrovšek (2000a) the overall dissolution speed is determined by dissolution on the crystal's surface, by the transportation of ions through the border layer as well as by the speed of the reaction $CO_2 + H_2O = H^+ + HCO_3^-$.

The grain size of a carbonate rock is one of the significant factors influencing the manner of its dissolution. The energy of edges (the Gibbs's free energy) is proportional to the volume, in case of smaller grains, greater than in case of the bigger grains, that is why the smaller grains prove to be more soluble (Borg & Dienes 1992). Solubility is inversely proportional to the crystal net energy that is why solubility influences the size of crystals. Small particles have, with regard to their rock mass, a larger specific surface. And for that reason the surface corrosion intensifies at places where the moisture remains longer and where the rock is tectonically crushed, with a lot of fissures, and is more porous and of smaller grains.

Such reasoning may lead to the logical conclusion that micritic limestones, with an increased primary porosity, and tectonically fissured carbonate rocks, with bigger surfaces for the solution reaction, will show greater solubility. Smaller are particles, more they are being crushed, faster they will dissolve. For this reason »accelerated« corrosion emerges in the areas with smaller rock particles, for example, in crushed and broken zones. In some cases this accelerated dissolution operates so strongly that it results in considerable differences in the relief of karst landscapes.

Selective dissolution, which appears due to the size difference of calcite granules, is described as “boxwork”. Boxwork got its name from its similarity with a confusing jumble of boxes (Hill & Forti 1997). Authors describe it as compact thin layers arranged into a lattice, which juts out from cave walls, ceilings, flowstone or cave floors. Palmer 1981 (after Hill & Forti 1997) defined boxwork as a phenomenon of selective weathering and explained its formation in three stages. The cave passage is formed in the flooded zone; as water flows away from the passage, cracks and pores of the limestone and dolomite in cave walls get filled with the air. CO_2 thus disappears in the weathered zone and the calcite partly fills up the open cracks. After the continuation of dissolution and weathering the boxwork juts out from the cave walls into the cavern. According to Lowe & Waltham (1995) boxwork is a three-dimensional grid made of thin mineral layers that jut out from the cave walls. Boxwork is the filling up of veins eaten out from the cave wall by the intermediate limestone dissolution.

In the Slovenian karst, boxwork is found on cave walls that were transformed by the condensation corrosion and at those parts of cave walls, where the limestone has been disintegrated in thick layers. However, we do not come across any boxwork of larger dimensions. Calcite veins jut out from indented cave walls up to several millimetres and the veins are not so thickly ramifying. During the formation of boxwork, the bedrock dissolves faster than the veins, which remain jutting out from the walls. The same happens to recrystallised fossil shells and their fragments, because, due to faster dissolution, micrite bases start to jut out from cave walls.

The majority of theoretical treatises on the dissolution and modification of carbonate rocks, as well as laboratory research, have concentrated on the properties of water. Particular emphasis has been given to its chemical and mechanical properties, its contact with the carbonate rock and to the manner and speed of dissolution. The purpose of my research was not however to determine the properties of the solution, nor the change in its composition during the dissolution, nor the influence of the changes in the rock on the dissolution. My principal interest was to study the manner of carbonate rock weathering on cave passage walls in relation to the characteristics of the rock.

In nature, limestones do not always dissolve in the way, predicted by laboratory tests. While limestone solubility is fairly well described and understood, dolomite dissolution, however, despite some recent research (Burger 1989, Purser *et al.* 1994, Gauteilier *et al.* 1999, Al-Asam & Packard 2000) is still comparatively poorly understood.

Dissolution in the karst takes place in different environments (Ford & Williams 1989). The upper part of the karst environment manifests is the vadose zone, where the prevailing processes are: diffuse stream flow, water migration through pores and channel flow. In the vadose zone, the pores in rock are, in the main, filled with air. This zone may be subdivided into two sub-zones: the infiltration zone and the filtration zone Water flows under the influence of gravity, which in the fissured rocks occurs very rapidly. The water that flows through the vadose zone contains atmospheric CO_2 as well as the CO_2 that originates from the soil and organic acids. Between the vadose zone and the permanently flooded or phreatic zone, where the atmospheric and hydrostatic pressure are identical, is the subterranean water table. The transition between the two zones is the capillary zone, where the water, due to the capillary action, rises above the subterranean water table. The second environment is the phreatic zone where all the pores in the rock are permanently flooded with water. In continental areas the phreatic zone descends downwards, passing into the deep flooded zone, which in proximity to the ocean mixes with salt water.

The intensity of the carbonate rock dissolution in karst differs mostly in the vertical direction; in the domain of the vertical sinking, as well as in case of the authigenic or allogenic water flow (Ford & Williams 1989 after Williams & Dowling 1979, Lauritzen 1990). Dissolution intensities in their dependence on various factors have been summarised by Ford & Williams (1989) in several synoptic tables. The extent of available data on the measurements of the vertical arrangement is very limited. Nevertheless, Gams (1962) and Ford & Williams (1989) point out that the majority of authigenic dissolution takes place at the top of the rock mass, especially at the contact with the soil. Where the karst is covered with the non-carbonate rocks it is protected from corrosion.

Measurements of weathering effects on the cave walls and on the karst surface have been done by many researchers (Gams 1962, 1965, 1980, 1995, 1997 and 1998, Gunn 1986, Ford 1988, Cucchi *et al.* 1987 and 1996, Smith *et al.* 1995, Gillieson 1997, Trudgill & Viles 1998). The weathering of gypsum however, has been significantly less studied (Forti 1996, Klimchouk 2000).

Due to secondary porosity development, which is caused by the corrosive expansion of fissures and by the lengthening and widening of the channels, the typical karst hydraulic system develops. The vertical denudation arrangement depends on two factors: the lay out of the streams and the disposition of concentrations of soluble matter.

Besides the manner and arrangement of water flow and the water's chemical properties, the most important factor in dissolution processes is the rock's mineral composition texture. Dissolution is influenced by the composition of the rock, as well as by the size of grains and their texture. Solubility of limestones and dolomites depends on their purity, that is, on the amount of insoluble matter they contain (Palmer 1995). The most frequent insolubles tend to be clay minerals and quartz. For this reason, karst located on limestones with 20 % to 30 % impurities tends to be less developed, because the abundant clay fills the initial channels (Ford & Williams 1989). The most suitable rock for the karstification contains more than 70 % of carbonate minerals.

In Slovenia, the majority of limestones are very pure, containing a very insignificant amount (1 –2 %) of insoluble residue (Gams 1974, Ogorelec & Rothe 1993). According to Herak (1972), the limestones from the Dinaric Karst contain different concentrations of $CaCO_3$ depending on the sedimentation conditions in a given period. Thus the Lower Triassic limestones contain from 80% to 95% of $CaCO_{3.}$ Lower Cretaceous between 95 % and 98 %, while Upper Cretaceous contain from 98 % to 100 % of $CaCO_3$.

Rock dissolution does not result only in lowering of the karst surface and enlargement of cave passages, but also forms the basis for the first phase of speleogenesis. For this reason I cannot completely avoid mentioning, the recently controversial topic of, the formation of karst conduits.

Organic activity may increase calcium carbonate solubility by producing carbon dioxide. During decomposition, caused by the activity of microorganisms, various substances may be produced. These substances increase the acidity or alkalinity of the environment, and this, in turn, accelerates the dissolution or precipitation of calcium carbonate. In cases where the activity of the organisms and microorganisms, participating in dissolution, is especially strong, or is sole cause of dissolution, the process is called biocorrosion (Gams 1973). It is usually the activity of microorganisms, for these are the main factor in the emergence of the chemical processes; for example in case of dissolution among roots.

The research literature gives clear evidence for the role of microorganisms in calcite dissolution and precipitation. Viles (1987), Hill & Forti (1997), Northup *et al.* (1997), Castanier *et al.* (1999), have provided clear evidence for the presence of microorganisms. They have also described those shapes in the rock that result from microbial action. However, very few authors have concerned themselves with the microbial processes and studied the ways in which microorganisms behave and act in particular situations (Jones 1994, Sterflinger & Krumbein 1997, Perry 1998, Bennett *et al.* 2000, Yee *at al.* 2000). The activity of microorganisms in the karst environment, which is rich in sulphides, and their contribution to the formation of cave passages have been recently investigated by Palmer and his collaborators (Hose *et al.* 2000) in the case of the Cueva de Villa Luz cavern in Mexico.

CAVE PASSAGE DEVELOPMENT AND THE WALL MORPHOLOGY

The shape of cave passages, from which their genesis may infer, is primarily the consequence of hydraulic conditions at the given areas. Passages may have been formed in the phreatic, epiphreatic or vadose zones (Bretz 1942, Gams 1973 and 1974, Bögli 1980, Maire 1980, Palmer 1982 and 1991, Trudgill 1985, Ford & Williams 1989, Šušteršič 1991 and 1999a, Slabe 1994 and 1995, Gabrovšek 2000a, Lauritzen & Lundberg 2000).

In the phreatic zone, the passages are formed by the action of pressurised, slow-moving, water flow below the karst water table. Water in the phreatic zone fills all the voids in the rock, and flow is regulated by the principles of hydraulic conductivity. Waters from the vadose zone, from other parts of phreatic zone and strong allogenic waters accumulate in this zone. In the epiphreatic zone, currents through the channels flow faster. In drought periods water covers only the bottom of the channel or the riverbed, but otherwise the channels are flooded. Fast water flows with free surface level or containing sinking water are frequently formed in the vadose zone. Channels, and also the rock of the vadose zone, are exposed to mechanical erosion, dissolution, condensation corrosion, moisture, biogenic corrosion, freezing and breakdown processes.

Due to surface denudation, over time cave channels become closer to the surface. Finally, they are left without a ceiling and are incorporated into the morphology of the karst surface. With the continuation of surface lowering even the last remnants of cave channels and sediments disappear (Mihevc 1996a, 2001).

Channel forms (Šušteršič 1991) that originate in the phreatic, flooded zone, have forms that are transitional between geological "discontinuities" and well-proportioned soda straw forms developed along bedding planes. Vertical channels may also develop; which are similar in plan to a shaft.

In the early phase of speleogenesis the dissolving water moves by diffusion and laminar flow. When flow through a fissure increases to such a degree that breakthrough occurs and turbulent flows are established, the channel will continue to grow steadily along its entire length (Gabrovšek 2000a). Dissolution under turbulent flow conditions is greater (up to 10^4) than under laminar flow (Ford & Williams 1989).

Flooded passages will grow until they are so large that the speed of waterflow falls and growth stops. Some researchers relate the cessation of the channel growth to deposition of alluvial sedimentary particles on the channel's walls. The stream, at maximum discharge may be no longer capable of tearing particles from the walls and so the particles remain attached to the channels' walls and slow down further channel growth. The period in the cave development, when such conditions have been established is called the paragenetic threshold (Worthigton 1991, Šušteršič & Knez 1995). Paragenesis, as understood by Renault (1968), Ford & Ewers (1978) and Mihevc (1991a), is enlarging of cave channels by the corrosion above deposited alluvial sediments.

As the level of karst water table falls cave channels pass into vadose conditions. In the vadose, unsaturated, zone the water (Šušteršič 1991) flows by gravity or by adhesive trickling down the walls, except in the case of suspended streams. These caves are oriented vertically the principal cave types being, chimneys and slightly altered shafts. Meanders are also formed, being carved out by suspended streams.

In the course of time, the primary phreatic channel shapes in the vadose zone undergo a transformation, which is effected in various ways. They may be transformed by flowing water, that is by a fast water stream with free surface, or by water carrying gravel, by percolation water, by condensed water, as well as by biogenic corrosion, by dissolution under sediments, by the wall crumbling, by breakdown, freezing, etc. Mechanical erosion, by all means, gains in significance when occurring in the form of the abrasive effects of the transport, carried by water, as well as by tearing off rock particles, which is due to viscosity of the water mass and by crushing processes and the freezing processes.

Cave passages may also be shaped by abrasion from the suspended load in flowing water (Gams 1959a, Newson 1971a) or by the water flow itself, when it runs fast enough to tear particles from surface of the cave walls (Trudgill 1985). Water will wash the particle away when its force is greater than the particle's resistance to movement (White *et al.* 1994). There is a critical speed for each type of particle, at which it is still capable of moving; this speed is called the critical erosion speed (Briggs 1977). Water carries the torn particles away and then accumulates them. How long the water is able to carry grains and roll them along channel depends on its speed, on the size of particles and on their specific weight.

The ratio between chemical and mechanical erosion is described by the prevalent hydrodynamic factor (Lauritzen & Lundberg 2000). The rate of chemical and mechanical erosion is measured experimentally using small plates of rock, the so-called tablets. Gams's tests (1959b) in Podpeška jama are a well-known example. He placed Lipica limestone tablets on clay in standing water, however he placed granite tablets in the rapids of a brook. In first case corrosion occurred, while in the second case there was erosion. After the experiment the Lipica limestone tablets were sent to different parts of the world. During a period of one year they were exposed to various conditions so that the results could be compared and prove suitable for calculating the rate of corrosion and mechanical erosion (Gams 1985). In recent times experiments with various limestones have been undertaken, therefore these results may not be directly comparable (Gams 1996). The only measurements of the ratio between corrosion and erosion using Lipica tablets was by Ford & Williams (1989) and their survey is the only one of its type in the world.

In recent years Mihevc (1993, 1996b) focused his research on corrosion and erosion measurement on cave passage walls. He measured the rates of both processes using a micrometer in Ponor of Odolina and in the Škocjanske jame. His measurements indicated that in the Škocjanske jame riverbed is a variety of shapes that alternate between those formed by corrosion and those shaped by erosion. This implies that different processes are acting on the rock at different water levels and at different positions in the riverbed. On the channel walls mechanical and chemical erosion frequently intermingle, both are significant for the growth and shaping of cave channels.

Recently, there has been a great deal of discussion on the importance of condensation corrosion in shaping cave walls. Its principal cause is condensed water, which accumulates on cave walls or ceilings, mostly in the areas, where the warm and cool air are mixing, especially in summer (Dublyansky & Dublyansky 2000). However, condensation corrosion does not transform only the cave walls (Cigna & Forti 1986, Hill 1987, Slabe 1988, Pavuza 1993) it also affects flowstone (Tarhule-Lips & Ford 1996, Hill & Forti 1997).

Cave walls are also strongly reshaped by the crushing processes related to the mechanical pressures in the rock (White & White 1969 and 1997, Brenčič 1993, Kortnik & Šušteršič 2000). The consequence of the destruction processes, are rock blocs, plates and smaller rock fragments. From the cave channel walls they break away in the form of single blocks, fragments or entire breakdowns. The breakdowns comprise the mass of the fallen stones with the cave roof of more than one layer. Breakdowns of the cave ceilings and walls may occur during the shaping period of the cave channels and during the changes of conditions of the flooded channels, as well as of those with free water level (White & White 2000). Last but not least, breakdowns represent also a part of the karst system degradation processes.

Breakdown in caves and the formation of larger breakdown chambers are genetically related to geological structures. Thus all the breakdown chambers in Postojnska jama are restricted in the areas of tectonic instability, that is, within a single fault zone or among many fault zones (Šebela & Čar 1991, Šebela 1998).

Frost and ice also exert a significant influence on cave passage transformation, especially in areas, where the ice and snow are continuously or seasonally present. Their importance lies mostly in their relationship with mechanical rock weathering in the cave entrance area and in those areas where caves have some connections with the Earth's surface. In such parts of cave passages we may detect an intensified mechanical disintegration of the cave walls, and weathering of wall surfaces and speleothems, mostly due to temperature fluctuations, when the bonds in mineral granules weaken due to temperature changes. Rock blocks have sharp edges and are of various size, condensation corrosion however, may make them rounder. In some cases caves passages become filled by the cryoclastic gravel, which formed in the Pleistocene, when mechanical rock disintegration was a more intensive process than dissolution and the gravel accumulated in large quantities. Nowadays, however, mechanical shaping of slopes or collapse dolines is negligible when compared with dissolution. Similarly stones that come rolling from the slopes also soon get dissolved. Smaller broken fragments, may be caused by mineral growth in cracks, usually by gypsum (White & White 2000) or ice.

Caves are thus the result of various speleogenetic factors, which operate in different conditions and are creating different speleogenetic forms (Lauritzen & Lundberg 2000). These forms, expressed in the micro and macro scale, reflect the functions of the principal and less significant speleogenetic factors. Medium and micro- forms are caused by corrosion and erosion, yet are influenced at the same time by lithological and tectonic factors.

Cave passages are not only formed by described processes, but also in other ways. An example of such alternative mechanisms of formation is "*in situ*" weathering of limestone. The rock's texture remains the same; the mineral composition however, changes (Vergari & Quinif 1997). The weathered parts of limestone, which have irregular shapes and situated in the centre of the rock mass are called »the phantom rock«. The weathered parts are much more porous than the unaltered rock and water may easily wash them away and thus excavate a sort of cave. Caves may thus be of »pseudo-endokarst« origin (Vergari 1998), the remnant of limestone dissolution is in this case the quartz microcrystal lattice (Kaufmann *et al.* 1999).

There are various speleogenetic processes that act on the surfaces of carbonate rocks and carry away their products. These processes include - corrosion, erosion with the laminated and turbulent flow, subterranean corrosion, condensation corrosion, ice, frost, etc. In his dissertation, Slabe (1992) classified the processes that influence the rock as point, linear and planar processes.

Slabe (1992, 1994, 1995) named the forms, which reflect different processes as rock features. The rock features on the cave passages walls interconnect themselves into the typical rock relief. Various processes taking place in the rock create various rock features, which are incised below the base level of the rock surface. From their form we may infer the processes that shaped them, for they are primarily the consequence of the continuous ways in which the carbonate rock has been carried away and acted upon (Slabe 1995).

The surface texture of the rocky features, which may be smooth or coarse, depends on the rock's composition and the effectiveness of the process that is acting upon it.

Dissolution and mechanical polishing of rock by flowing streams creates a smooth, bruised (longitudinally incised) or "beaten" surface. The rock is frequently polished also by fine-grained alluvial material, ice and also by the influence of strong condensation corrosion. Linear indentations are caused by weaker condensation corrosion and biogenetic processes (Slabe 1994).

AUTOCHTHONOUS CARBONATE CLASTIC SEDIMENTS IN THE RESEARCH LITERATURE

My research has concentrated on the origin of fine carbonate clasts that are present in cave sediments and in the manner in which the rock has to be altered, so that water is able to carry it away from the cave walls in the form of small particles. Autochthonous carbonate gravel and sand are created, when rock fragments are broken from the cave walls, carried away and rounded by flowing water. These rock fragments are mainly derived from fracture zones, from breakdown cones, from frost wedging and also from cave entrance areas (Gospodarič 1976, Kranjc 1989). Carbonate silt may be formed by the disintegration of already extant carbonate gravel and sand, which are created in the above-mentioned manner or, as we will see later by weathered material from cave walls being washed away.

I have noticed the high proportion of carbonate clasts of silt or clay size in cave alluvium in my previous research (Zupan Hajna 1995, 1997a, 1998a). Beside non-carbonate minerals in autochthonous sediments, which are brought into the cave by water streams, the presence of carbonate clasts was detected in recent sand and silt. Fine carbonate clasts occur: - in Velika ledenica in Paradana (Zupan & Mihevc 1988), in silt sediments in the springs in Malni (Zupan Hajna 1997a, 1998a), in some sand and clay samples from Brlog at Rimsko (Zupan Hajna 1998a) as well as in sediment flood clay in Martel's Chamber in Škocjanske jame and in cave Labodnica (Trebiciano) (Zupan Hajna 1995). Whether the carbonate clasts are calcite or dolomite, depends principally on whether the cave passages are being excavated in limestone or dolomite.

As autochthonous carbonate clastic sediments in the cave fluvial sediments I thus consider these particles that originate from cave passages walls themselves. Autochthonous carbonate clastic sediments in the describing cases do not have anything in common with the cement or flowstone crust, which are precipitated as autochthonous chemical sediments in unconsolidated cave sediments. The presence of small carbonate particles in unconsolidated cave sediments of silt or clay size, as well as the presence of carbonate colloids in subterranean streams are reported by several authors. I will discuss some of these reports later.

Zogović (1966) noticed that dolomite may dissolve incompletely and that are mineral grains left behind, which remain as silt. He found that fine dolomite sand, may accumulate in narrow passages and obstruct or slow down the flow of water.

During his water flow study in the Mendip Hills of England, Newson (1971a) detected a rise in the proportion of carbonate clasts and a fall in the proportion of quartz clasts in cave sediments between the entrance and the exit of the cave system. He studied the rise of the carbonate content in clastic sediments and their transport along the system. Simultaneously, he investigated the diminishing of the grain size in the sequence sand – silt – clay and the roundness of the quartz sand, that became more and more pronounced along the system. He tried to discover the reasons for the large quantities of carbonate materials in the nets, placed during high waters, in the abrasion processes on the cave walls. He emphasises the importance of abrasion for the cave development. Abrasion with quartz sand, which is carried by water as suspended load, seemed to him to be of special significance. He also detected the renewal of the erosion force with the introduction of fresh limestone material, added to the already present suspended charge, along the subterranean stream. To establish the ratio between corrosion and abrasion, he exposed limestone tablets to water current and measured the decrease in their weight. He came to the conclusion that in conditions of normal water flow dissolution prevails and that the abrasion becomes significant only near the outflow of the system, where the incline of the water stream locally increases. Abrasion is also more effective at high water flows, but only in the riverbed area. In his ensuing treatises Newson (1971b, 1972) concentrated his efforts mostly on the hydrological factors of the mechanical erosion in the subterranean environment. He did not concern himself in any detail however with the origin of carbonate particles (the same applies to Smith & Newson 1974).

Fine carbonate clasts in cave sediments are not mentioned by many authors and for that reason they appear all the more interesting. Ford & Williams (1989) stated the large quantity of autochthonous carbonate clasts in the suspended load originated in the weathered cave walls. Worthington (1991) noted that few authors had ever mentioned the presence of carbonate particles either in the suspended stream load or in cave alluvium. According to him, it is not surprising that less soluble particles are released during limestone dissolution and are later swept away by the stream and accumulated in the lower energy cave environments. Šušteršič & Mišič (1996) detected the formation of carbonate silt on the permanently wet dolomite wall of Pipar's Channel in Najdena jama, the movement of these particles by trickling water, and their transport and deposition by slightly stronger flowing water into smaller pools. After analysing colloids and particles of the karst water channel in the Swiss Jura, Atteia (1997) mentioned calcite and dolomite as their constituent parts, and their presence occurred to him quite intriguing.

As well as occurring in the suspended load of subterranean streams, the literature also mentions carbonate particles suspended in trickling percolation water. Kogovšek & Habič (1981) reported carbonate particles suspended in trickling water in Planinska Jama. They tried to determine the ratio between corrosion and erosion, depending on water quantity, quantity of chemically dissolved material and the quantity of the suspended matter in the sinking water. In their treatise they ascertained that erosion and corrosion prove to be equally effective during the precipitation, for in the same time period almost equal quantities of carbonates had been dissolved as were transported into the cave in the form of the suspension. The carbonate suspension in water trickles is mentioned also by Kogovšek & Zupan (1992) in cases from Planinska jama and Pivka jama. They attributed the suspended particles to carbonate rock weathering on the surface and the transport of the weathered rock particles through the open fissures into the cave. Kogovšek (1994) explained the presence of suspended carbonate particles in trickling water at Vilenica as resulting from contact between rock with the soil, where the dissolution is fastest followed by transport along the open fissures into the cave. Treatises on the suspended carbonate particles in sinking water generally regard as a part of the load the water is carrying away from the surface, through the open cracks, and into the cave.

The presence of carbonate clasts in clastic cave sediments is predominantly related to the freezing and thawing of ice. Glaciers and the water coming from under glaciers, as well as thawing ice mechanically erode carbonate rocks on the surface. Water then carries the eroded, finely grained carbonate particles into the cave and deposits them there. Audra (1995) associated the deposition of carbonate "varves" in the high-mountainous caves with large quantities of water, that flowed from under the surface glaciers, laden with silt, which were later deposited in the cave passages.

We should, however, not overlook the fact that in high-mountain caves there may also be formed such clay sediments, which are composed of carbonate clasts of different origin. What kind of origin this may be I will endeavour to describe later.

Let me emphasise the fact that in my work I have not concerned myself with: the mechanics of the carbonate clasts transport, with the mechanical and chemical properties of water which carries clastic sediments along caves, with the sedimentation of clastic sediments in cave passages, nor with the quantifying or granular analysis of clastic sediments. These entirely different domains have been already dealt with in all detail by numerous authors, focusing on processes along the surface streams (Pettijohn *et al.* 1972, Füchtbauer 1974, Allen 1985, Morris & Williams 1999, etc.), as well as along the cave passages (Newson 1971a, Gospodarič 1974 and 1984, Ford & Williams 1989, Kranjc 1989, Audra 1995, Kadlec 1999, etc.).

RESEARCH METHODS

INTRODUCTION

With the chosen topic I ventured into relatively uncharted territory, and was therefore, first of all, compelled to determine the most adequate research methods. These predominantly remained at the level of qualitative investigation, because the samples at my disposal lacked the statistical adequacy for quantitative studies. The emphasis of my research work was concentrated on the manner in which carbonate rock weathers and the impact of its lithological parameters on the manner and speed of weathering.

Field work was combined with different research methods, in the attempt to ascertain:

- how the carbonate rock texture influences dissolution; are there any differences in the manner of dissolution of micrite and sparite (also when they are of different ages)?
- which factors control the depth of the weathered zone in carbonate rock?
- are we witnessing carbonate rock weathering or just the precipitation of minerals?
- in which cases does the weathered rock remain on the channel wall and in which not?
- do microorganisms exert any influence on incomplete carbonate rock dissolution?
- what is the ratio between chemical and mechanical erosion in shaping the cave walls?

Different research methods were used to find out what is going on during the weathering of limestone and dolomite in the cave environment. At first the field work was done by mapping the passages where weathered cave walls occur. The appearance of carbonate rock weathered zones was recorded, their position in the cave passage ascertained, as well as the contact with sediments and the source of the rock moistening. Also the temperature was measured and in one case *in situ* pH of weathered limestone (in cave Pečina v Borštu). To define the pH of the weathered rock and sediment the direct method was used. Measurement was done with a pH-meter of the Testo 230 type, which has on its electrode a gel membrane Type 03pH.

In addition to field research, knowledge of the rocks mineral composition and texture proved to be of key significance for understanding the influence of rock's lithological properties on dissolution. To understand the differences between the weathered and the fresh part of the rock, samples were analysed applying various methods. Primarily, I intended to determine the mineral and chemical composition of the weathered rock, as well as the difference between the fresh and weathered part of the same rock sample.

With regard to the extent of the weathering, the weathered carbonate rocks were divided in three sub-samples (Fig.1):

- a - fresh rock; fresh colour,
- b - discoloured rock; faded colour; without porosity,

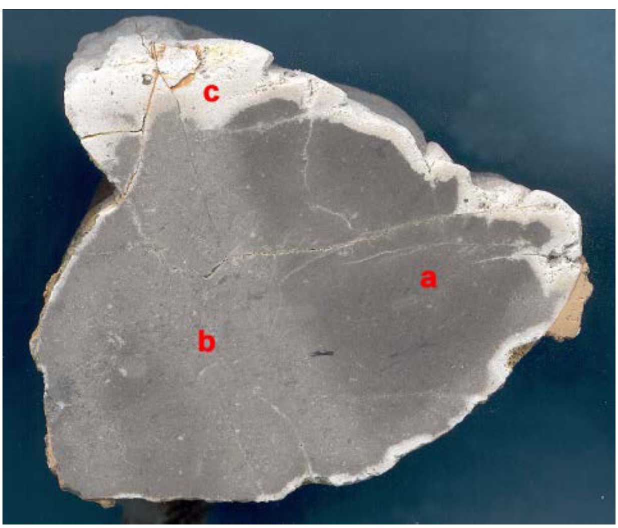


Figure 1: Cross-section (6,5 cm) of weathered limestone sample Pr1. Limestone is weathered in different degree; weathered zones were divided in three sub-samples: a - fresh rock, b - discoloured rock, c - weathered rock.

- c - weathered rock; entirely discoloured and strongly porous.

Samples were analysed by chemical methods such as complexometric method, EDS analysis on SEM and Ion Beam Analysis, then by X-ray Powder Diffraction Method, in thin-sections under transmitted light, in cross sections of the samples by computer scanner and under the SEM. Microbiological investigation of samples was also carried out. All analyses were of a qualitative kind, with the exception of semi-quantitative EDS analyses. With regard to the level of weathering, some of the SEM analyses samples were subdivided to sub-samples, whereas in some other analyses, especially those dealing with the surface and transitions, they were studied together. So the undertaken analyses are thus divided into four groups:

- optical analyses: macroscopic scanning of cross-sections, SEM of cross-sections surfaces and microscopy of thin sections;
- chemical analyses: the complete analyse of chemical composition, complexometric method, the analyse of organic carbon, EDS analyse on SEM, Ion Beam Analyse;
- mineralogical analyses: analyses with X-ray diffraction;
- microbiological analyses.

OPTICAL ANALYSES

The analyses of cross-sections by computer scanner

It was decided to undertake the analyses of weathered carbonate rock cross sections by computer scanner, because the transition from the unweathered into the weathered part is clearly visible. This approach represents a new, original method, which I opted for due to the simpler documentation and easier investigation of the details. Cross sectioned samples were firstly scanned and then processed on the computer, at which point I was able to magnify the areas of greater interest. The method proved to be highly suitable, especially for observation of the progress of weathering in the fresh rock. With the aid of macroscopic analyses of cross sections, I was able to determine the texture, the extent of fissure, the arrangement of calcite veins, the discoloration, planar distribution and the positioning of porous parts. More focused attention was centred on the transitions into areas of increased porosity, and the detection of the coloured clay as well as the presence of the flowstone crust. Colours of the fresh as well as the weathered part were identified by means of the Rock-colour chart (Goddard *et al.* 1970).

Microscopy

Samples were analysed using:

- the microscopy of thin sections under transmitted light and
- the microscopy of cross-sections under SEM.

CHEMICAL ANALYSES

Complete Chemical Analysis

Complete qualitative chemical analyses of four samples were carried out in the Actlabs laboratory in Canada (2000). The samples were analysed by methods included in the Package 4E uses ICP, INAA, ICP-Ms and XRF technologies to completely characterise samples. The following oxides and trace elements were looked for: $SiO_{2.}$ $Al_2O_{3.}$ $Fe_2O_{3.}$ MnO, MgO, CaO, Na_2O, K_2O, $TiO_{2.}$ $P_2O_{5.}$ Ba, Sr, Y, Zr, Be, V, Ag, Cd, Cu, Ni, Pb, Zn, Bi, LOI, Au, As, Br, Co, Cr, Cs, Hf, Ir, Mo, Rb, Sb, Sc, Se, Ta, Th, U, W, La, Ce, Nd, Sm, Eu, Tb and Yb. Samples from caves Martinska jama and Jama II na Prevali were submitted for these analyses.

Complexometric Analysis

Complexometric method uses titration to determine the percentage of carbonate present in the sample, as well as the ratio of CaO and MgO; and after further calculation also the ratios of calcite, dolomite and insoluble residue. Using this method the samples from Pečina v Borštu, Martinska jama, Jama II na Prevali, Krempljak, Turkova jama, Spodmol na Ždrolcah and Remergrund II cave were analysed.

EDS analyse on SEM

Using the special electron microscope JEOL JSM 5800 - SEM of the Micro-structural Analyses Laboratory of the Ceramics Section of the Institute Jožef Štefan and with the application of the EDS qualitative and semi-quantitative analyses, studies of two samples of weathered limestone from caves Martinska jama and Jama II na Prevali were undertaken (Samardžija 2000). Both samples were metalographically polished and dusted with graphite. In spite of all this, their surfaces were not entirely smooth, because of the great level of porosity in their weathered parts.

Ion Beam Analysis

In the laboratory for Ion Beam Analyses at the Section for the Physics of Low and Middle Energies of the Reactor Center Podgorica, Institute Jožef Štefan, point and linear microanalyses of trace elements of samples from Jama II na Prevali are carried out (Kavčič 2000).

Organic Carbon Analysis

Organic carbon analyses were done at Karst Research Institute ZRC SAZU using the Walkley-Black technique with potassium bichromate. First the samples were separated and then ground. Samples of the unweathered and weathered part of the Cretaceous limestone from Martinska jama and Krempljak were investigated, as well as the Paleocene limestone from Jama II na Prevali.

MINERALOGICAL ANALYSIS

The qualitative mineral composition of samples was determined by X-Ray Powder Diffraction at the Geological Institute of Faculty of Natural Sciences and Engineering (Dobnikar 2000), Ljubljana by Phillips diffractometer. The amount of minerals is given in respect to the height of the main reflection of a particular mineral in the X-ray record.

The conditions at the recording were: anode CuK_α, 40 KV, 30 mA and Ni filter. With regard to the extent of their weathering, the samples were subdivided into sub-samples. Amounts of individual minerals are expressed in diagrams relatively; amounts were calculated with the regard to the intensity of their main peak in the records. The investigated samples were gathered from caves Pečina v Borštu, Martinska jama, Jama II na Prevali, Krempljak, Turkova jama, Spodmol na Ždrolcah and Remergrund II.

In addition to analyses of the weathered rock, mineralogical analysis of samples of clastic sediments by X-ray diffraction was also undertaken. Its aim was to ascertain the ratio of carbonate clasts in those sediments is in direct contact with the weathering of cave walls. Being aware of their mineral composition, it was tried to determine the possibility of their chemical influence on the weathering of the bedrock and whether they, after all, contain also the insoluble residue.

MICROBIOLOGICAL ANALYSIS

There was interest in whether microorganisms are presented in the weathered rock or not and theirs relation to the dissolution of carbonate rocks. With this aim in view, analyses of the weathered rock from Pečina v Borštu were carried out. I was intrigued whether live organisms exert a direct influence on limestone dissolution or do they just passively inhabit the weathered limestone. Two samples from the weathered rock of the Končni rov were submitted to the micro-biological research, and for the purposes of comparison also a water sample from a smaller pool in the Končna dvorana, as well as some drops of condensed water from the cave's entrance area. Micro-biological analyses were undertaken at the Karst Research Institute ZRC SAZU and at the Biology Department of the Biotechnical Faculty, namely, in the laboratory for Molecular Genetics and Micro-Biology of the Ljubljana University (Mulec *et al.* 2001).

WEATHERING OF LIMESTONE AND DOLOMITE IN THE CAVE ENVIRONMENT – CASE STUDIES

INTRODUCTION

The selection of the caves, from which samples were collected, was designed to ascertain whether the weathering of carbonate rocks that differ with regard to their composition, texture or age is brought about in the same manner or not. On the basis of the analysed cases I endeavour to explain where and why the incomplete dissolution occurs and in what way may this occurrence is related to the location in the cave, to humidity level, to contact with sediment and to the type of the rock.

Parts of cave passages and rock samples from Pečina v Borštu, Martinska jama, Krempljak, and Jama II na Prevali, as well as individual samples from Turkova jama, Remergrund II and Spodmol na Ždroclah were investigated. Weathered and clastic rocks were subject to examination also from caves Velika ledena jama v Paradani, Črnelsko brezno, Čehi II and Renejevo brezno. The location of the researched caves (Fig. 2) differs according to the geographical position, the type of karst environment, speleogenesis and characteristics of limestones and dolomites, which may vary in their age and origin. Limestones and dolomites may range in age from Triassic to Paleocene. The major part of the analysed cases focuses on Cretaceous limestones, which are the predominant limestones in South Slovenia and in which a lot of caves are developed (Gospodarič 1986). Caves are from Alpine and Dinaric karst, from high mountain area to the area with Mediteranian climate. Caves are also different in their genesis and morphology.

The basic data of the caves are from Cave Register of Speleological Association of Slovenia and Karst Research Institute ZRC SAZU. Some parts of the individual caves were measured once again specially for the purposes of the present research (Fig.3).

For each of the selected caves, in addition to its speleomorphological characteristics and some basic geological facts, the survey of the incomplete dissolution residue of carbonate rocks is also presented, which were detected during field work, as well as results of analysis of samples taken from these caves.

The process of dissolution stopped before the rock dissolved entirely. For this reason, in the cases studied, the residue left over after the dissolution is not an insoluble admixture (addition), contained by limestones and dolomites, but the heavily weathered bedrock.

By the term "incomplete dissolution" is meant the phenomenon, by which the

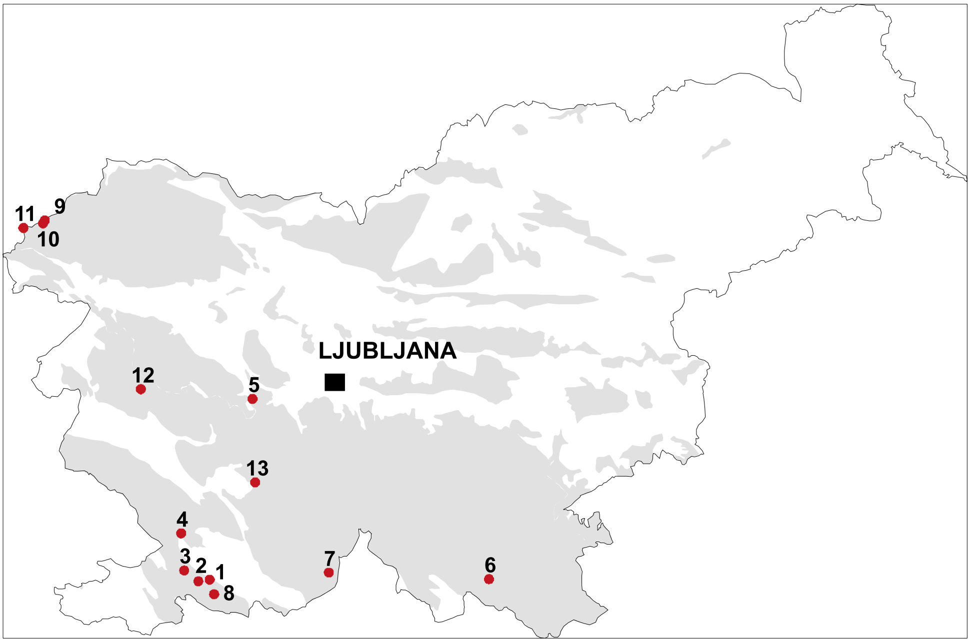


Figure 2: Location of the researched caves on Slovenia. 1-Pečina v Borštu, 2- Martinska jama, 3-Krempljak, 4-Jama II na Prevali, 5-Turkova jama, 6- Remergrund II, 7-Spodmol na Ždroclah, 8- Polina peč, 9- Črnelsko brezno, 10- Jama Čehi 2, 11- Renejevo brezno, 12- Velika ledena jama v Paradani, 13- Jama pod Pečno rebrijo.

Figure 3: Parts of the individual caves were measured once again for the research purposes. Weathered walls in Martinska jama

carbonate rock does not dissolve in its entirety, but remains on the cave passage walls as a heavily weathered fragment of the bedrock, which is very porous, discoloured and displays an appearance of chalk or carbonate silt.

In the work the insoluble residue of the weathering processes is deliberately neglected, mostly because both limestones and dolomites in all selected cases were exceptionally pure and its amount was very insignificant. The insoluble residue is fairly extensively studied, in Slovenia as well as worldwide, (Marić 1964, Gregorič 1969, Fitzpatrick 1984, Kočevar 1995, etc.), especially in relation to the soil formation on carbonate rocks.

The phenomenon of incomplete dissolution and partial weathering of carbonate rocks in caves occurs in the Slovenian karst areas, as well as in caves throughout the world. Some selected cases are presented later, for their interest, although I do not deal with them in detail.

In the eastern part of Skalarjevo brezno (Reg. no. 6000), at Kaninski podi in northwest Slovenia, the entrance area of which consists of Dachstein limestone, selectively weathered walls of entrance shafts may be detected. The limestone in the entrance shaft contains large Megalodontid molluscs, whose shells jut out of the walls, while in between them, the rock is heavily weathered and sandy to the touch. Pronounced boxwork, occurs on the shafts walls.

In Snežna jama (Reg. no. 1254), on Raduha mountain in northern Slovenia, coarse, heavily weathered rock is seen on the passage wall, where the cave entrance area with permanent ice ends. The passage wall is weathered (not flowstone moon-milk from the inner part of the cave) and its surface extremely rough. In this case we could ascribe the weathering to the effects of frost as well as to condensation corrosion, because in this area the cold air from the ice chamber and the warmer cave air mix together.

A good example of selective corrosion and the formation of a zone of weathered rock a few millimetres thick is also found in Koněpruske caves in the Czech karst area south of Prague. The main cave is formed (Bosak 1996) along the bedding plane in Lower-Devonian limestones. The cave ceiling follows the line of the bedding plane. In the upper part of the cave, the interchange of the cave air and air from the outside takes place. The cave ceiling is straight and to a great degree transformed by condensation corrosion. The limestone is selectively corroded and covered with calcite veins protruding out of its surface, and the formation of box-work is noticed.

The manner of bedrock weathering of in the deepest cave of the Bohemian karst, Arnoldka, which reaches a depth of 100 m is also of interest. The cave is of hydrothermal origin (Bosak & Kadlec 2000). Hydrothermal solutions, which were flowing through the rock along fissures, produced similar results as produced by weathering of the rock under sediments, by condensation corrosion or frost. The rock around the fissures is discoloured, porous and also softer. In these instances it is not the rock from the cave passage wall that is weathered, but the rock beside the fissures along which the hydrothermal solutions were percolating. Boundaries between weathering zones are sharply distinct and positioned across walls according to the location of fissures.

Incomplete dissolution of carbonate rocks is not typical only of the atmospheric conditions of regions governed by a moderate climate and perhaps of the Alpine climatic conditions. The phenomenon can be found also in the climatic conditions of the South China karst, where rocks in the caves and on the earth's surface are in contact with clastic sediments and soil are heavily weathered (Zupan Hajna 1998b, Slabe 1999). Selective dissolution of cement and washing away of the remaining grains also occurs and proves to be a decisive element in formation of caves in quartz sandstone in the region of Chapada Diamantina in eastern Brazil. In Lapăo cave north of Lençóis in the Brazil state of Bahia, passages were created along the contact areas of quartz conglomerate and sandstone (Karmann & Laureano 2001). In the active passages of that cave, dunes of quartz sand are present. The quartz grains in the dunes are the residue of quartz sandstone dissolution and are at present washed away and carried along the cave by water. It goes without saying that the dissolution of quartz sandstone is far slower than that of limestones and dolomites.

WEATHERING OF DOLOMITE IN SELECTED CAVES

TURKOVA JAMA, REG. NO. 41

Turkova jama at Zaplana was chosen as an example of a cave with an active flow of water, and which was formed and developed in the Upper Cretaceous dolomite, that is, in late diagenetic, spary dolomite. The passage walls are rough and mostly weathered for only few millimetres in depth; in some parts of the cave there are, however, also some thicker weathered zones to be found.

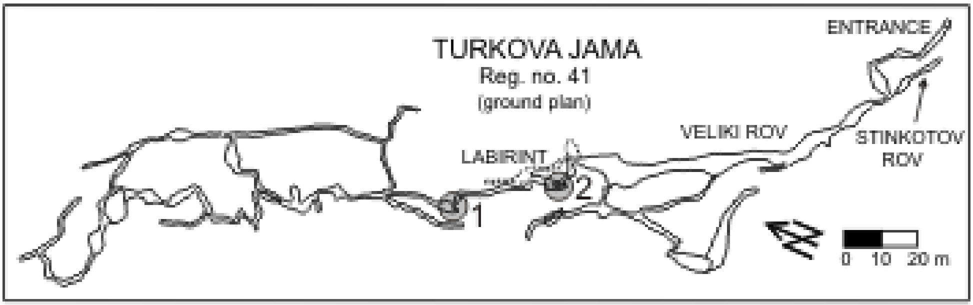
Cave location and geological setting

Turkova jama is located north-west of Zaplana, on the southern slope of Travni vrh, which is 685 m high; the cave's altitude above sea level is 640 m (y = 5439 450, x = 5092 000).

According to the Basic Geological Map, Sheet Postojna 1 : 100 000 (Buser *et al.* 1967) the cave is formed in Upper Triassic dolomite (T_3^{2+3}). The entrance in the cave lies in close vicinity of the overthrusting front of the Upper Triassic dolomite towards the Lower Triassic clastites with oolite limestones and dolomite with mica. The layers dip towards east at an angle of 25^0.

Speleomorphological characteristics of the cave

Plan of the cave is given on Fig. 4. The entrance into the cave is through an inclined shaft. The cave continues along an extremely steep, approximately 30 m deep passage. The total length of cave passages amounts to 900 m and the maximum depth is 80 m. At the spot where the entrance passage is level, a small rivulet flows into the cave through



(photo J. Žumer).

Stinkov rov. Afterwards, the cave expands into Veliki rov. In its incipient part the rivulet still flows along but soon afterwards it disappears into the lateral passages. This same rivulet was encountered again throughout the cave. The amount of the water flow in the rivulet depends on the rate of precipitation; in normal conditions it amounts to few l/s. The cave branches off in several directions. Various more recent pebbles of allochthonous origin lie on the floor of the active water channels; they consist predominantly of schisty siltstone, bauxite and sandstone.

Figure 4: Ground plan of the Turkova jama cave (Cave Register of IZRK ZRC SAZU).

The original phreatic shapes of passages are clearly visible in the uppermost, now non-active parts of the cave. These parts were probably never filled up with clastic sediments; whereas in the lower parts of the cave there are remnants of older sediments, i.e. various pebbles, sands and sandy silt, which at a certain period of the cave's development filled it up in its entirety. On the ceilings of some passages ceiling channels, anastomosis and also completely levelled parts are developed, which is typical of above sub-sedimental formations.

Passage walls throughout the cave are weathered to a depth of at least several millimetres. On those parts of walls, which are not in contact with permanent flowing water and where the disintegrated fragments are not being washed away as they form, there remains a thick weathered zone. The upper layer of the weathered late diagenetic dolomite displays the marked roughness of its surface. The surface of walls is less coarse in places where flowing water constantly washes the fragments away, i.e. under the percolating trickles of water and beside the constant water stream.

The thickest zones of the weathered dolomite are to be found in the part of the cave called the Labyrinth, where the main channel follows the fault plane with the incline of 95/80 degrees. Of considerable interest also is a smaller lateral passage, the entrance of which is situated few metres above the main channel's floor. At present this is a non-active part of the cave, the passage ceiling is levelled above the sediment and there is a ceiling channel carved in it (Fig.5). Across the passages walls and on its floor are the remains of fluvial sediments ranging from pebbles and sands to laminar sandy silt, the accumulation of which blocks the continuation of the passage.

The upper part of the Labyrinth contains abundant fluvial sediments of non-carbonate origin. These sediments contain pebbles and laminar silt and clay with sand. Where the passage wall is in direct contact with the sediment, it is weathered several centimetres deep. In the Labyrinth is situated also a smaller mud pool, which is supplied by a trickle of percolation water. The water from the trickle washes the walls of the narrow channel and the particles that have been washed away are accumulated as silt on the channel floor.

Samples of weathered, late diagenetic dolomite

Two large samples of late diagenetic dolomite removed from Turkova jama's walls were analysed. Sample *TJ1* is heavily weathered dolomite removed from the Labyrinth's main channel, whereas sample *TJ2* is weathered rock from the smaller lateral passage (Fig.6). The original location of both samples is indicated on the cave plan (Fig.4). The mineral composition of weathered dolomite from cave is given in Fig.7.

Sample *TJ1* is weathered to a considerable degree. On the weathered wall of the passage there are also some smaller layers of sandy red clay, which in some places fills

Figure 5: Weathered walls with remains of alluvial sediments in Turkova jama (photo A. Mihevc).

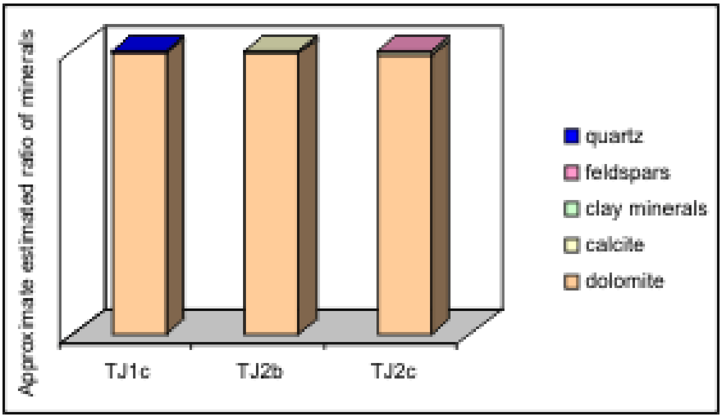


Figure 6: Dolomite sample TJ2 from small lateral passage of Turkova jama.

up the tiny hollows, which are dispersed across the same weathered wall. The inner part of the sample *TJ1* is still solid, yet discolored to extremely light grey (N8) whereas the sample's edges are completely discoloured (N9), as well as soft and very moist. Due to its high extent of weathering it was given the additional mark *TJ1c*. The sample consists almost entirely of dolomite with traces of clay minerals, feldspars and quartz.

Sample *TJ2* is a rock fragment from the lower part of the western wall of Stranski rov. This passage was completely packed with the fluvial sediments in the past. The projecting point of dolomite was jutting out into the passage so that it is heavily weathered on all its sides, with exception of the part that bound it to the passage wall. The sample hardly contains any fresh, unweathered dolomite, in its interior it is only slightly less weathered. The dolomite is dense, with tiny crystals and without any fossil remains. The surface of its cross-section is considerably fractured, and intersected with fissures extending in different directions, which are open or filled with calcite. Around some of these open fissures the dolomite is weathered to a larger extent. The least weathered part of the sample is of medium grey colour (N6). The sample is weathered most along its edges, where the dolomite is almost completely discoloured (N8) and very porous. The most porous parts are white (N9). The sample's surface is rough because the dolomite's individual grains are protruding out of its surface; it is also partly covered with a brownish coating. For the purposes of the research it was divided into two sub-samples: *TJ2b* – the discoloured part and *TJ2c* – entirely weathered part. The discoloured part – *TJ2b* – is composed almost entirely of dolomite, with traces of calcite. The weathered part *TJ2c*, as well consists of dolomite only, with traces of calcite and feldspars.

In X-ray records of the weathered dolomite the dolomite peaks are higher than in the less weathered sample. In case of dolomite the level of crystal lattice organisation was calculated. The level of organisation in the weathered dolomite *TJ2c* was 0.9, in *TJ2b* 0.8 while in *TJ2c* it amounted to 0.6. The level of crystal lattice organisation in the dolomite is thus the highest in the least weathered part of the sample. This indicates that in this instance the weathering brought about the destruction of the crystal lattice organisation.

Both sub-samples were submitted also to complexometric method, results are on Fig.129. The total amount of carbonate in the sample *TJ2b* was 90.79 % and in sample *TJ2c* 95.34 %. The amount of the insoluble residue was higher in the *TJ2c* sample of the weathered dolomite than in the sample of the discoloured part of the dolomite – *TJ2b*. The percentage of MgO, however, is higher in *TJ2b* than in *TJ2c*, which indicates that during the weathering Mg probably migrates out of the dolomite's lattice.

Samples of clastic deposits

Two samples of fluvial deposit: red clay sample *TJ0A*, which was stuck to the sample of the weathered dolomite *TJ1* and of the deposited laminar clay - sample *TJ0B*, were taken from virtually the same place as the previous samples. The red clay is at first sight different from the deposited laminar clay or sand. The mineral composition of samples taken from cave is shown in Fig.8.

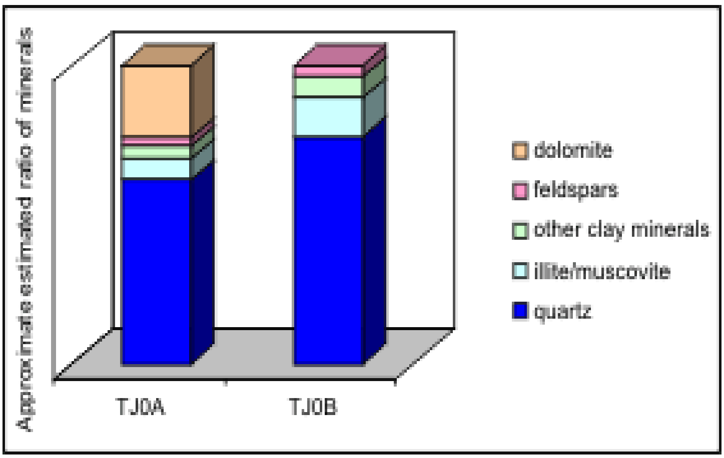


Figure 7: The mineral composition of weathered dolomite from Turkova jama.

Both samples differ in their mineral composition. The red clay- sample *TJ0A*, when in contact with the weathered dolomite (sample *TJ1*), consists mostly of quartz, dolomite, a small quantitie of mineral from illite/muscovite group and other clay minerals. Feldspars are present only in traces.

The brown laminar clay with the sand (sample *TJ0B*) contains predominantly quartz, some clay minerals and an insignificant amaunt of feldspars. The mineral composition is suggesting that the laminar clay originated from the weathering residue of Lower Triassic schist and sandstone, which are found in contact with the Upper Triassic dolomite outside the cave. The red clay, which is in direct contact with the weathered dolomite, contains, in addition to minerals of autochthonous origin, aabundant dolomite, which originates from the weathered passage walls.

Conclusion

Thicker zones of weathered dolomite appear only in places on the walls where water does not carry dissolved rock away immediately, as well as in places where there is at present or has been in the past, in contact with clastic sediments. In those parts of passages where water washes the rock away immediately, the thickness of the heavily weathered zone is only one to two millimetres. The wall surface is coarse due to dolomite grains jutting out from its surface. Slightly less roughened wall occurs where water a continuously washes the wall, that is, where it is exposed to incessant trickles of water and permanent water flow in the stream bed. Such a wall is smoother when touched by hand as water washes all the loosened grains away immediately.

REMERGRUND II, REG. NO. 2698

Cave location and geological setting

The entrance the cave is situated in the vicinity of the Knežja Lipa in the Kočevsko region at an altitude of 490 m (y = 5500 140, X = 5045 835). The cave is also a temporary ponor positioned on the contact boundary between Permian and Lower Triassic clastic rocks and the stratified Triassic dolomite (Novak & Rogelj 1993) according to the Basic Geological Map, Sheets Črnomelj (Bukovec *et al.* 1983) and Delnice (Savić & Dozet 1984). Cave passages are esccavated in the late diagenetic Triassic dolomite. In general, passages extend along one single bedding plane and other differently directed structures, mostly in direction north – south, as well as along the transverse Dinaric structures.

Sample of Late diagenetic dolomite

From this cave only one single sample was submitted for analysis and its surface was very rough. Sample *Rm* was taken from the wall of the Dragova pasaža in the eastern part of the cave. The location of the sample is indicated on the cave plan (Fig.9). Sample *Rm* is of massive, coarsely grained dolomite. Its interior is fairly fresh and of medium light grey (N6). Along its edges the sample is considerably weathered and decolourised (N8) and displays a very rough surface. The mineral composition of samples taken from cave is given in Fig.10. Sample *Rm* consists of dolomite; with clay minerals present only in traces. The crystal lattice organisation for this dolomite was calculated, is fairly high 0.8. Complexometric analysis indicated (Fig.129) 97.12 % carbonates, 95.44 % of which was dolomite and 1.68 % calcite. The percentage of insoluble residue in the sample is 2.88 %.

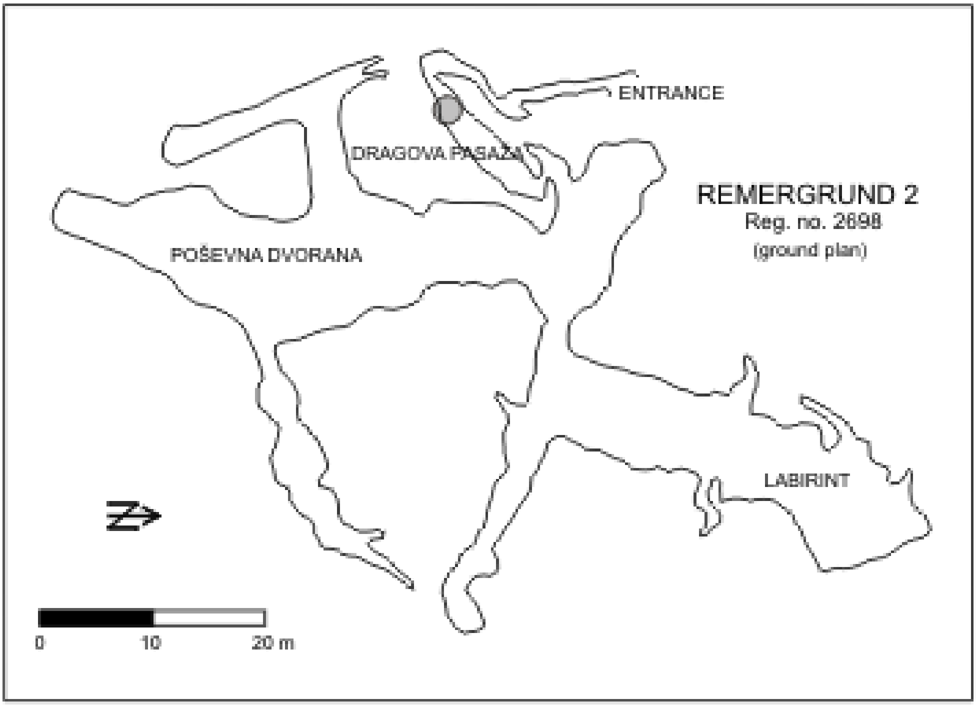


Figure 8: The mineral composition of clastic deposits from Turkova jama.

Figure 9: Ground plan of the Remergrund II cave (Cave Register of IZRK ZRC SAZU).

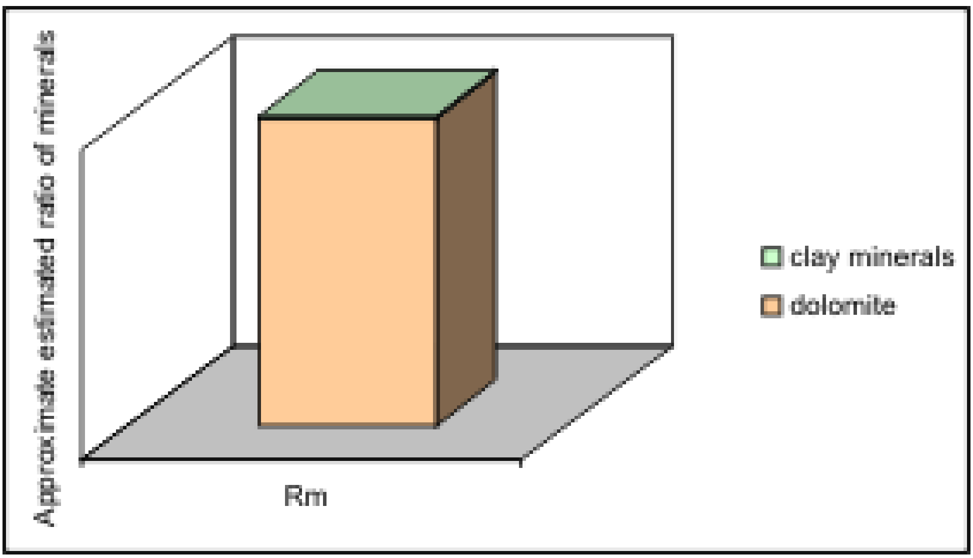


Figure 10: The mineral composition of dolomite sample from Remergrund II.

WEATHERING OF LIMESTONE IN SELECTED CAVES

In Slovenia the large number of known caves are developed in Cretaceous limestones; our longest caves are formed in limestone, like Postojnska jama cave system, Škocjanske jame, Predjama cave system etc. Weathered limestone zones occur in caves, formed in limestones ranging in age from Upper Triassic to Palaeocene with different genesis. Limestone weathering in the caves Polina peč, Krempljak, Martinska jama, Spodmol na Ždroclah, Pečina v Borštu and Jama II na Prevali, is described below.

POLINA PEČ, REG. NO. 938

Polina peč cave is located at Matarsko podolje (Fig.11) south of Obrov, near Poljane at Podgrad, in SW Slovenia, at an altitude of 570 m asl. (y = 5429 610, x = 5041 990). According to the Basic Geological Map (Šikić *et al.* 1972) the cave is developed in Lower Cretaceous carbonate rocks, which consist of bedded massive limestone and dolomite

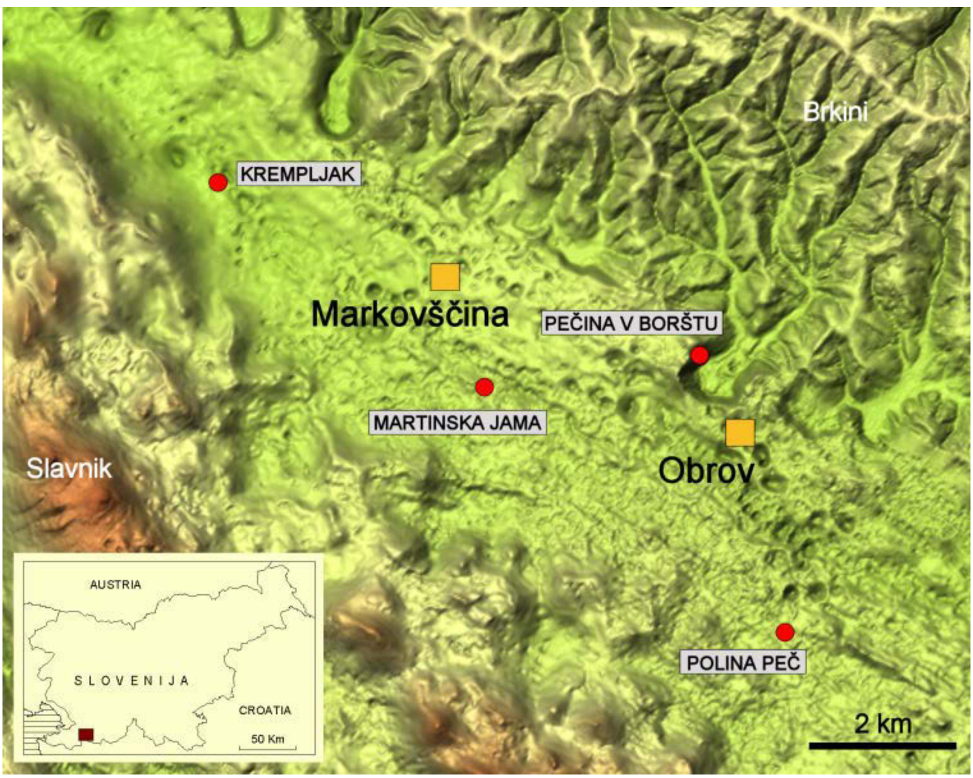


Figure 11: Position of the caves Polina peč, Krempljak, Martinska jama and Pečina v Borštu in Matarsko podolje.

with limestone breccia. Beds dip NE at an angle of 20 to 30^0.

The entrance of the cave is a fairly large rock shelter at the base of doline, which extends through a passageway into a larger chamber. Along the limestone bedding planes in the chamber slippage along beds has occurred. Slippage along bed is also indicated by slip of upper part of small phreatic passage along bedding plane. The chamber and the entire upper part of the cave are full of collapsed blocks covered with flowstone. Speleothems and walls are considerably fractured, which indicates an intensive tectonic event. Passages below the chamber are at first similar to the upper part of the cave, then the morphology of the passage changes because this part of the cave has formed in sedimentary breccia.

The upper part of the cave, which was also transformed by breakdown, is covered to a large extent with flowstone, and fluvial sediments also occure there. In these sediments are layers of pebbles, sand and clay, and at some points they are also covered with the flowstone crust. The clastic sediments are in the direct contact with the passage walls. The walls are weathered across larger surfaces. Limestone is discoloured and extremely porous. The weathered walls are dry at their contact with the clastic sediments. These circumstances led to the assumption that inflow of percolation water, which trickled along the wall, had already stopped. The sediment in contact with the passage walls also remained dry and for that reason weathering has also ceased. In recent times these weathered walls were subjected just to mechanical removal of the weathered rock particles by dormice which are excavating the wall.

KREMPLJAK, REG. NO. 2718

Krempljak cave is significant because in the ceiling of Stranski rov weathered limestone occurs in a form strongly reminiscent of wafers. The heavily weathered rock is divided into several thin layers separated by thin laminae of secondary calcite, which was precipitated along micro-bedding planes in limestone.

Cave location and geological setting

Krempljak is a cave in Matarsko podolje, Southwest of Materija near the village of Polžane (Fig.11). The cave entrance lies at an altitude of 492 m asl. (y = 5421 955, x = 5048 080).

According to the Basic Geological Map 1 : 100 000. Trst and Ilirska Bistrica Sheets (Pleničar *et al.* 1969, Šikić *et al.* 1972) this cave is formed in transitional beds between the Lower and Upper Cretaceous ($K_{1,2}$) with a succession of dolomite, breccia and to a minor extt limestone. Bedding dips towards the NE at an angle of 20 to 30^0.

Speleomorphological characteristics

The cave is 290 m long and 47 m deep (Fig.12). The entrance to the cave passes through a widening along a fault. The entrance is 3 m deep and the cave subsequently continues as a steep slope, which ends with the 3 m deep shaft. At the base of the entrance chamber the main passage ecstends toward the west across a flowstone mass. Over it we come to chamber where breakdown of ceiling is presented. From that part of the cave Stranski rov turns towards the east and the main passage continues towards the west. After approx. 50 m the main passage turns in a NW direction and steeply descends over scree, which is partly covered by flowstone crust (Fig.13). The scree consists of finely grained cryoclastic rubble, which flows into passage below the ceiling, which shows on closeness of the surface. Across the scree, several up to 25 cm high stalagmites have grown up. All over the scree smaller as well as more sizeable rock blocks are scattered, which were broken off the ceiling.

Walls in this part of cave are transformed by breakdown along fractures. Passage walls break along the bedding planes and fissures, as if the rock were stitched. Fissures in the walls are of tectonic or stress release origin; so that the rock is ejected from walls due to the tension in the limestone beds. Rock fragments from the brokendown are 10 to 15 cm across. In this part of the cave no fluvial sediments could be found, nor any residue of them on the passage walls.

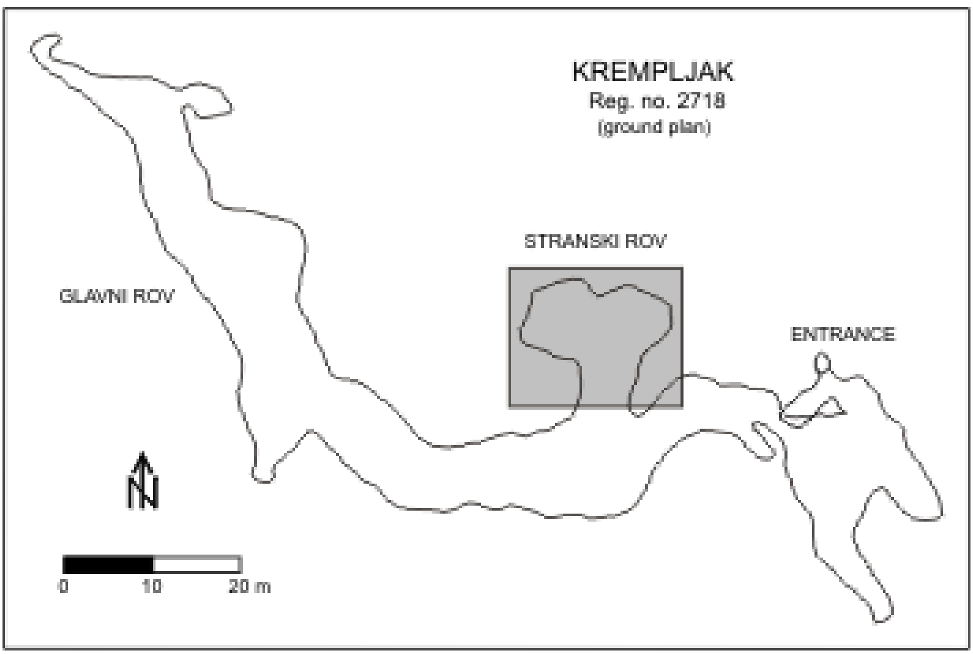


Figure 12: Ground plan of the Krempljak cave (Cave Register of IZRK ZRC SAZU).

As a result of breakdown processes, which have transformed the original cave passages, the cave is now close to the surface. There is no evidence about its previous development. Šušteršič (1999b) related the genesis of Krempljak to that of the cave Svidretova pečina (Reg. no. 3643), which is situated in the vicinity of the Matarski dol. He also found out that without more detailed investigation of the caves in the area, he could not ascertain whether they were formed by influence of Brkini's sinking streams or they were a remnant of older hydrogeological conditions. Brkini are Eocene flysch hills in the contact with limestone of Matarsko podolje.

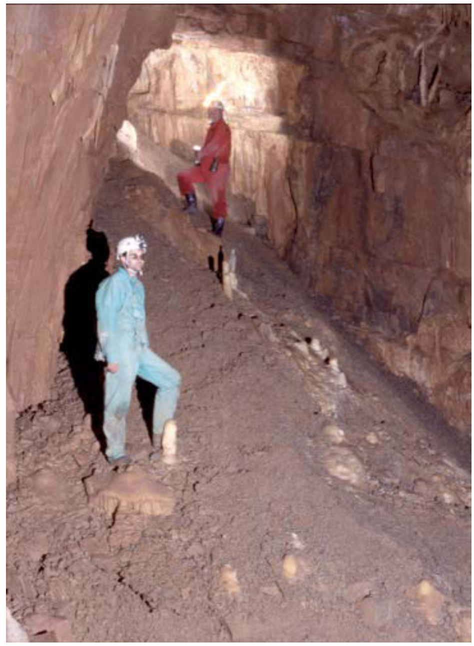


Figure 13: Cryoclastic scree flows into main passage of Krempljak cave (photo J. Hajna).

Stranski rov

In the collapse chamber the Stranski rov passage descends toward the north; its walls are weathered except where the ceiling has recently broken off (Fig.14). The passage contains aboundant flowstone; typical forms are columns and coral-like flowstone. The temperature in this part of the cave ranges from 8.8^{0}C to 9^{0}C. Cave pools in the central part of the passage are repeatedly filled up with the trickling water. For exploration purposes the passage has recently been measured and mapped (Fig.15).

The ceiling of the passage runs along one single bed, the lower part of which forms the ceiling itself. The bed dips at an angle of 20^0 to the NE (the dip 45/20). Where ceiling is cuteed by fissures, water seeps in and the flowstone is being precipitated. The flowstone appears in form of a crust, which is filling up fissures and attains the thickness of up to 10 cm; it may occur also as a column, which follows the fissures along the entire passage.

The cave ceiling is failing due to the incessant breaking off of the thin sheets of bedrock breaking off along parallel microstratification. Breaking proceeds along the thickness of the layer at every 0.5 cm or less. Laminarity of bedrock is caused by limestone's sedimentary properties or/and by tectonic deformations or/and stress releases, as well growing of the calcite crystals in the micro- bedding plane. The water trickles among the laminae, is partitioning them in a planar manner, so that the lower lamina is pushed down, which subsequently causes the continual breaking off of the thin lower layers from the ceiling. The extension among laminae, due to the growing of crystals, additionally increases the instability within the limestone, which consequentially would not break. On the cave floor large amounts of flowstone and crusts with stalactites, which were torn off the ceiling together with the thin limestone lamina, are presented.

The southwest passage wall is a tectonic plane, which dips towards SW at the angle 80^0 (the dip 210/80). After few metres, due to the breakdown, which at this point spills its material into the passage, it turns to the north. The northern wall of the Stranski rov's initial part ends already after few metres. Variously thick layers are fairly illustratively displayed across this wall; they are intersected by strongly fissured zone in direction NE – SW. From this point on the passage proceeds toward north, yet simultaneously extends also to the east.

In this area the wall is built of thin layers of dark grey limestone, which are across their surface heavily weathered (Fig.16). Walls and ceiling in this part of the passage are weathered up to 2 cm deep but the wall feels firm and solid. Out of these layers sample *Kr1* was taken (Fig.17). The outer edge is white and subsequently passes over several light grey shades into the dark, fresh rock. Some bedds have, due to more recent fractures caused by stratification and fissures zone in NE – SW direction, grey colour. At places where the wall remained unbroken, the soft weathered material is presented under the crust of the reddish-grey flowstone.

In the eastern extension of the passage plenty of speleothem and flowstone are

Figure 14: In Stranski rov all the walls are weathered with exception of ceiling, recently broken off (photo J. Hajna).

abundant, but some parts of the wall still remained uncovered. In a small chamber behind speleothem there is an unusual example of weathered limestone, which is unlike that found in any other cave in the area. The ceiling of the passage runs parallel to the main bedding plane. In between sheets of calcite, which were secondarily precipitated from between the micro-bedding planes (the thickness of laminae is up to 0.5 cm), there are some entirely weathered limestone laminae. At certain places the sheets of secondary

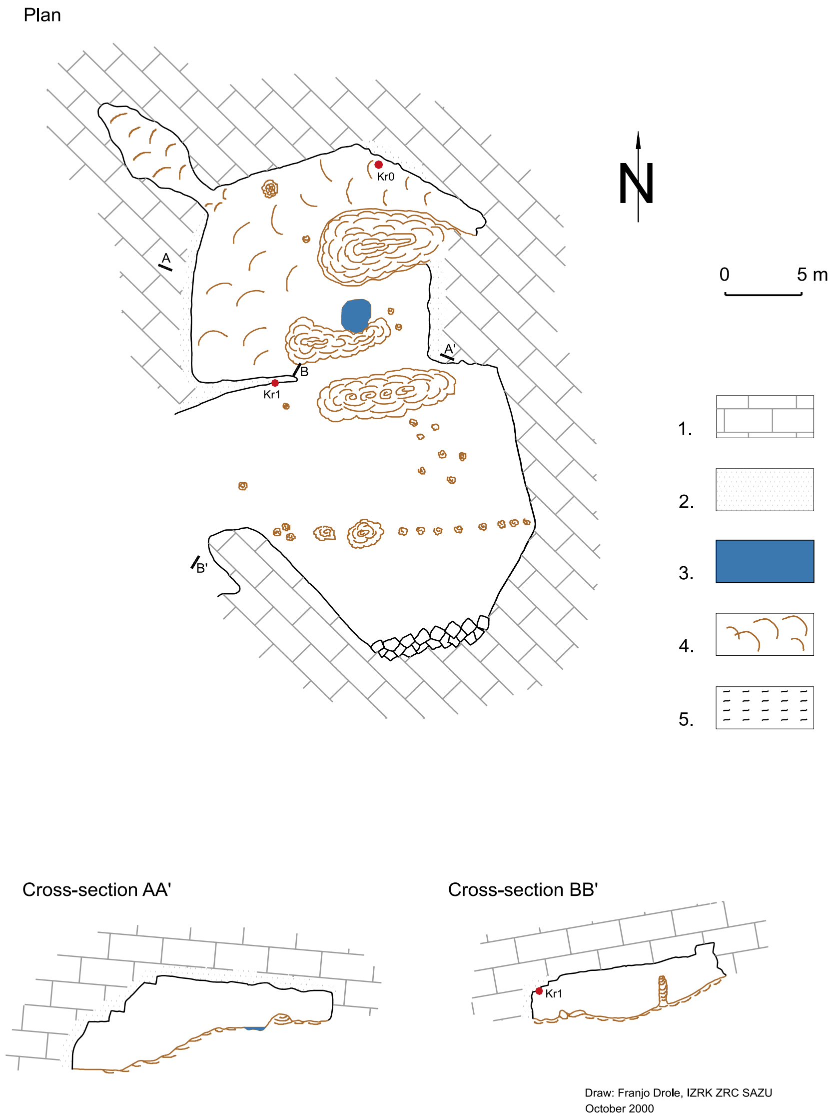


Figure 15: Plan of Stranski rov and cross sections in NW-SE and NE-SW directions with position of the samples. Legend: 1 – limestone, 2 – weathered limestone, 3 – flowstone, 4 – alluvial deposits.

Figure 16: Weathered walls of Stranski rov are covered by red flowstone crust. New precipitated flowstone crust is light grey (photo J. Hajna).

Figure 17: Position of sample Kr1 on the Stranski rov wall (photo J. Hajna).

calcite hinder the further progress of the weathering into the depth. Limestone laminae in the ceiling are weathered to different degrees (Fig.18). Large crystals of secondary calcite are for the most part not weathered and obstruct further dissolution. However, where the secondary calcite sheets fell off or were dissolved, or at least initially etched, the limestone situated beneath it is, due to the increased inflow of the aggressive water, initially or even heavily weathered. The weathered rock on the ceiling is soft and in places, where the weathered rock is being carried away by trickling water, covered with parallel flutes. The weathered matter is more or less dry on the surface, whereas the weathered limestone laminae that are positioned deeper may be fairly damp. The weathered limestone laminae and secondary calcite sheets are thus following one after the other as the slices in wafers into the depth of the rock's mass. Completely weathered limestone laminae are succeeded by discoloured ones and subsequently by fresh and unweathered.

In certain parts of the same small chamber the weathered rock has been cemented anew. It is solid to the feel and from its surface large crystal planes of the secondary calcite are shining, which has been growing in the pores of the weathered limestone. At some points soda straws are growing from the cemented parts of the ceiling. For this reason, incoming percolation water at these points is capable of forming flowstone.

From the chamber at the end of the Stranski rov a smaller passage descends toward Northwest and subsequently rises to Northeast into the small chamber beneath the ceiling. This small chamber has a weathered ceiling. Across the ceiling there is a conspicuous network of deep fissures, which were widened by corrosion. All over the small chamber speleothems and crusts are growing. Part of the reddish crust as well as some stalactites,

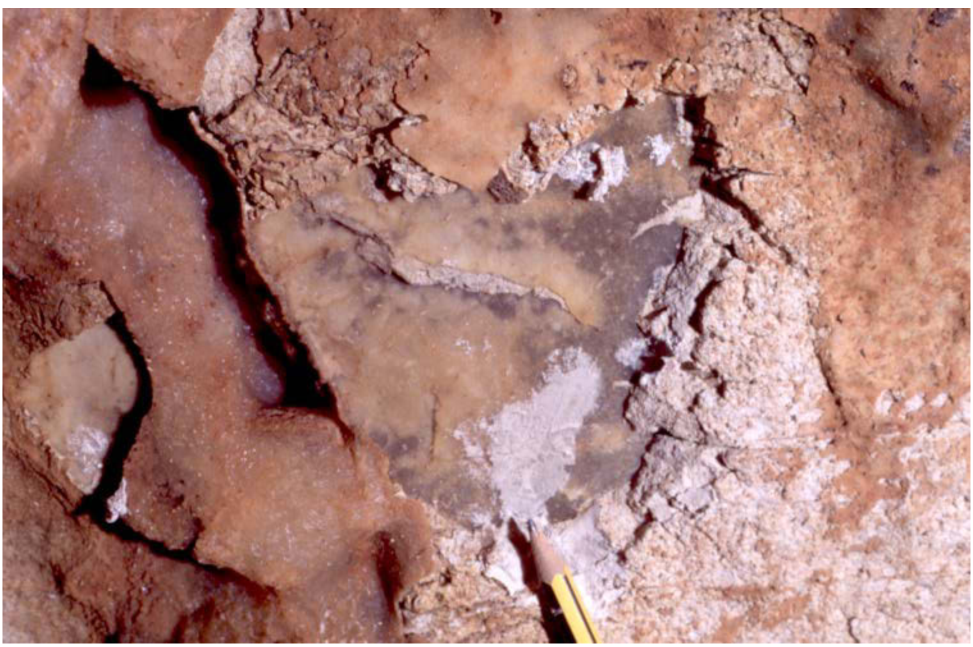


Figure 18: Limestone laminaes in the ceiling are weathered to different degrees.

are heavily corroded, as if they were incised by aggressive water. The floor of the small chamber is covered with laminated loam, which not found in other parts of the passage. The part of the loam is coated with flowstone and for that reason it has not been carried away. The limestone layers, on which the sediment lies, are weathered as well. Their surface at the contact points with the sediments is smooth and covered with a crust of flowstone.

Limestone sample

Sample *Kr1* was brought from Stranski rov and is part of the weathered layer from the wall at the beginning of the passage (Fig.17). The wall, adjacent to the sample's location, as well as the sample itself, are coated with a thin flowstone crust, which is in some places corroded to such an extent that the weathered surface may be noticed. The limestone's mineral composition was determined by X-ray diffraction. The sample was divided into two sub-samples according to the degree of weathering, the fresh part *Kr1a* and the weathered part *Kr1c*. The mineral composition of the sample is shown in Fig.19. Sample *Kr1a* consists almost entirely of calcite; clay minerals and quartz are present only in traces. In sample *Kr1c* the calcite peak is even higher, while clay minerals and quartz occure only in traces.

Within the weathered part the calcite, peaks are higher than in the fresh one, whereas insoluble minerals are more abundant in the fresh part than in the weathered one. The amount of the accessory minerals is lower in the weathered part with respect to the assumption that the crystallinity of these minerals proves to be identical in both parts of the sample, whereas their main peaks are lower. Why there is more insoluble residue in the fresh part of the limestone than in the weathered one I am not able to clarify, since the amount of the insoluble residue should actually rise proportionately with the weathering. I presume that during the weathering, clay minerals were washed away from its texture in the ionic or more likely in the colloid form.

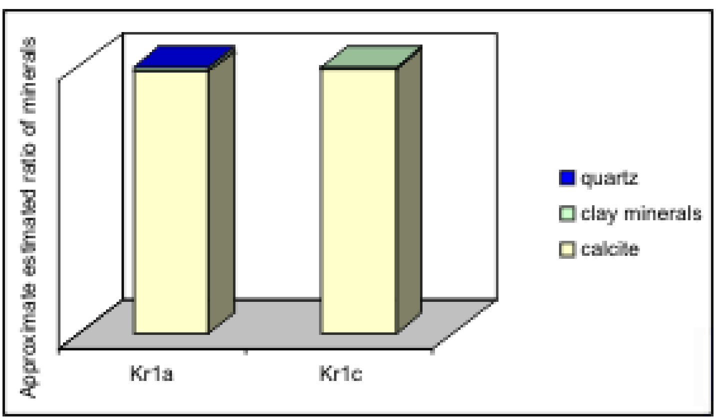


Figure 19: The mineral composition of the limestone sample from Krempljak cave.

Both parts of the sample *Kr1* were analysed by the complexometric method. The resulting values are presented in the Fig.129. The carbonate ratio in the samples from this cave is lower when compared with the samples from other caves, i.e. from 94.53 % to 95.18 %. In the fresh limestone sample *Kr1a* the percentage of the MgO is higher than in the sample of the weathered limestone.

- The amount of the insoluble residue in the fresh parts of the limestone is greater than in the weathered part of the sample, which is consistent with the results of the X-ray analysis.

The organic carbon content was also determined (Fig.130). In the fresh a part of the sample *Kr1a* the ratio of the organic carbon amounts to only 0.69 %, whereas in the weathered part to 1.17 %.

Sample of clastic deposits

In order to compare the mineral composition of the weathered bedrock and the clastic sediments a sample of the stratified, already slightly bound alluvial sediment (*Kr0*) from the small chamber at the end of the Stranski rov was selected. In this sediment there is a succession of layers of clay and finely grained sand. Sample *Kr0* consists almost entirely of quartz, with a small amount of clay minerals, whereas claystones are present in traces (Fig.20). Loam was according to its mineral composition transported into the cave from the flysch recharge area.

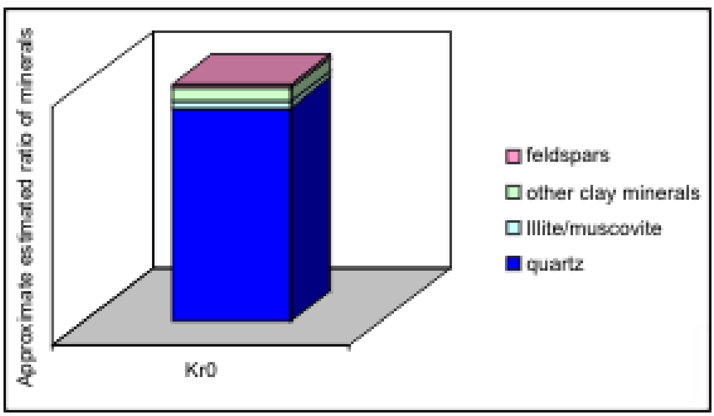


Figure 20: The mineral composition of clastic deposit sample from Krempljak cave.

Concution

Cretaceous limestone in Krempljak is most weathered in Stranski rov, where the crushing processes are considerably less pronounced than in the main passage. In the main passage the ceiling and walls are constantly crumbling and leaving behind in some places fresh, unweathered rock. In Stranski rov, percolating water deposits flowstone, and calcite is precipitated between the open laminae, which are formed by micro-lamination. Calcite crystal precipitation causes the formation of the layer along this lamination, as well as the continuous breaking off of fragments from the cave ceiling. Seaping moisture persists in these "micro bedding planes and causes weathering. Although there atre fluvial sediments at the end of Stranski rov there is no evidence that they completely filled the passage in the past or that they significants is fluenced limestone weathering. Condensation corrosion also does not appear to be a factor in the weathering processes in Stranski rov.

MARTINSKA JAMA, REG. NO. 2883

Cave location and geological setting

Martinska jama is significant because almost all the walls of its lateral passages are heavily weathered. For this reason Boeganov rov was investigated in greater detail.

Martinska jama lies within Matarsko podolje (Fig.11) south of Markovščina on the slopes of Veliki Mavrovec 565 m above see level (y = 5425 555, x = 5045 305).

According to the Basic Geological Map, Sheet Ilirska Bistrica (Šikić *et al.* 1972) the cave is formed in transitional layers between the Lower and Upper Cretaceous ($K_{1,2}$). Transition stratas represent limestone and dolomite beds, which generaly dip towards N – NE at angle of 20 to 30^0.

Speleomorphological characteristics

The main cave entrance is a small collapse doline at northern slope of the hill. There are also two vertical entrances that lead into the cave. The total length of cave passages is 1004 m, and the depth is 120 m. The plan of the cave is on Fig.21. From the collapse onward the cave expands in two directions. The western part ends after several tens of metres. The main extension to the east continues in direction N – S. The main passage subsequently turns in direction NW – SE, whereas the final part of the cave extends in direction E – W. Almost all passages follow fault zones and fissures in the Dinaric direction, i.e. NW – SE. Collapse chambers with large blocks at their floors are formed along them. Phreatic shapes may be detected but at other places were in wiped away by breakdown processes and the growth of flowstone.

As well as in Boeganov rov weathered limestone is located on the walls just before the cave's largest shaft. Limestone in this part is considerably weathered, but is almost entirely coated with a thin crust of reddish flowstone, which at some points is corroded. In the lower part of the wall white micro-crystal "spray" and white calcite crystals are precipitated on top of the reddish flowstone. The limestone on the walls of the lateral passage, which leads in direction E – W towards the vertical entrance into the cave, is also

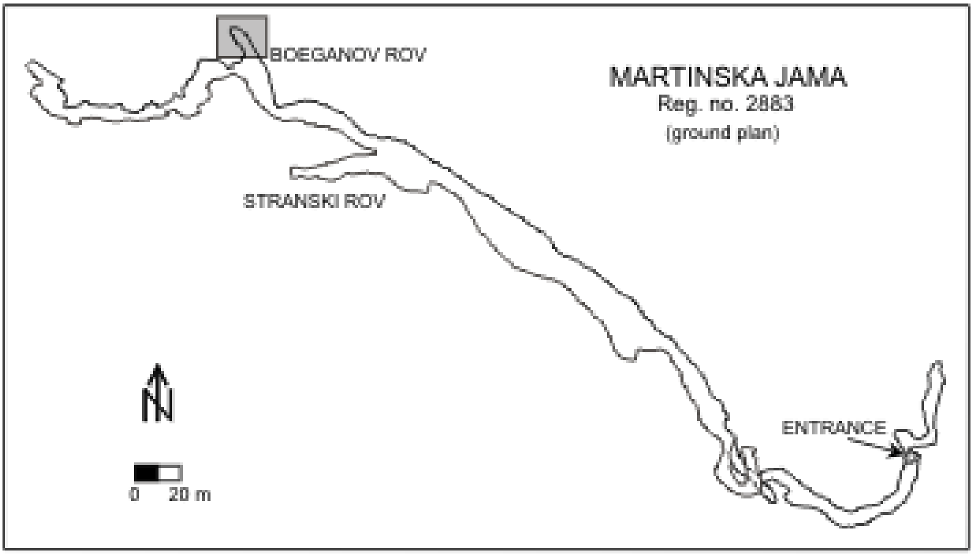


Figure 21: Ground plan of the Martinska jama cave (Cave Register of IZRK ZRC SAZU).

weathered. Limestone is discoloured up to few cm deep, yet it is, however, not porous. The passage was in the certain period of the cave's formation filled with sediments, since their remnants may be found on the rocky shelfs. A narrow ceiling channel meanders along the entire ceiling of the lateral passage and tiny anastomosis, which were carved by water as it flowed along the contact between sediments and the ceiling are developed.

Boeganov rov

Boeganov rov lies approx. 100 m before the end of the cave (Fig.21) and is slightly elevated above the main passage floor. Its walls are totally weathered (Fig.22). For the purposes of the present research the passage was measured anew, its map and profile were completed as well (Fig.23). The entrance into the passage is narrow and contains a considerabl amount of flowstone; at its end a small chamber is developed.

Annual temperatures in the passage range from 8.7^{0}C to 9.0^{0}C. The passage is closed and isolated; there is no draught to be sensed in it. At its conclusion the ceiling significantly declines and it ends filled up with sediments. Remnants of the sediments at the passage's bottom and on the wall shelves along the bedding planes we may infer that the passage was in certain period filled up with the sand sediments, which were subsequently removed. Sediments on the passage's floor are covered with crusts of flowstone, whereas in the middle of the passage, within the sediment, a larger collapse may be found.

Limestone beds in Boeganov rov dip toward NE at 20^0 (the dip 30/20). Within the beds stylolites are present, which occure mostly in upper parts of the passage and across

Figure 22: Weathered walls of Boeganov rov in Martinska jama (photo J.Hajna).

the ceiling and the walls of the passage's end section. Flowstone is precipitated across walls, particularly from water that flows in along the bedding plane, which may be observed along the entire passage. The bedding plane is strongly expresed in the western wall, where parallel to it, a thick red coloured seam runs along its course. The prominence of the bedding plane and the presence of the red clay beside it, indicate that it has been tectonised. Due to the weathered walls across the entire passage, this cannot be confirmed. The limestone layer adjacent to the bedding plane is heavily weathered on all sides. Under the bedding plane the prevailing amount of the flowstone is precipitated in the form of the crust and speleothems; through this bedding plane large water seepage is evident.

At the end of the passage weathered rock above the bedding plane is grey in colour (Fig.22), because it is more wetted than the surrounding. At some places the weathered rock is already cemented; the calcite cement was precipitated in pores from saturated trickling and seeping water. When the inflow of the saturated solution on the ceiling increases, tiny soda straw stalactites start to grow from the weathered walls (Fig.24). Their growth is dispersed, since it is not bound to any definite open fissure, but it depends on the water flow along the open pores of the weathered limestone.

Where it is not covered with crust, stylolites and calcite veins protrude from the weathered surface for several millimetres (Fig.25). The network texture of the protruding stylolites and calcite veins creates incipient "boxwork". Weathered passage walls are also in places covered with flowstone.

During the precipitation the weathered wall in the passage is wetter than in periods without precipitation. In order to determine quantity of moisture, contained in the wet

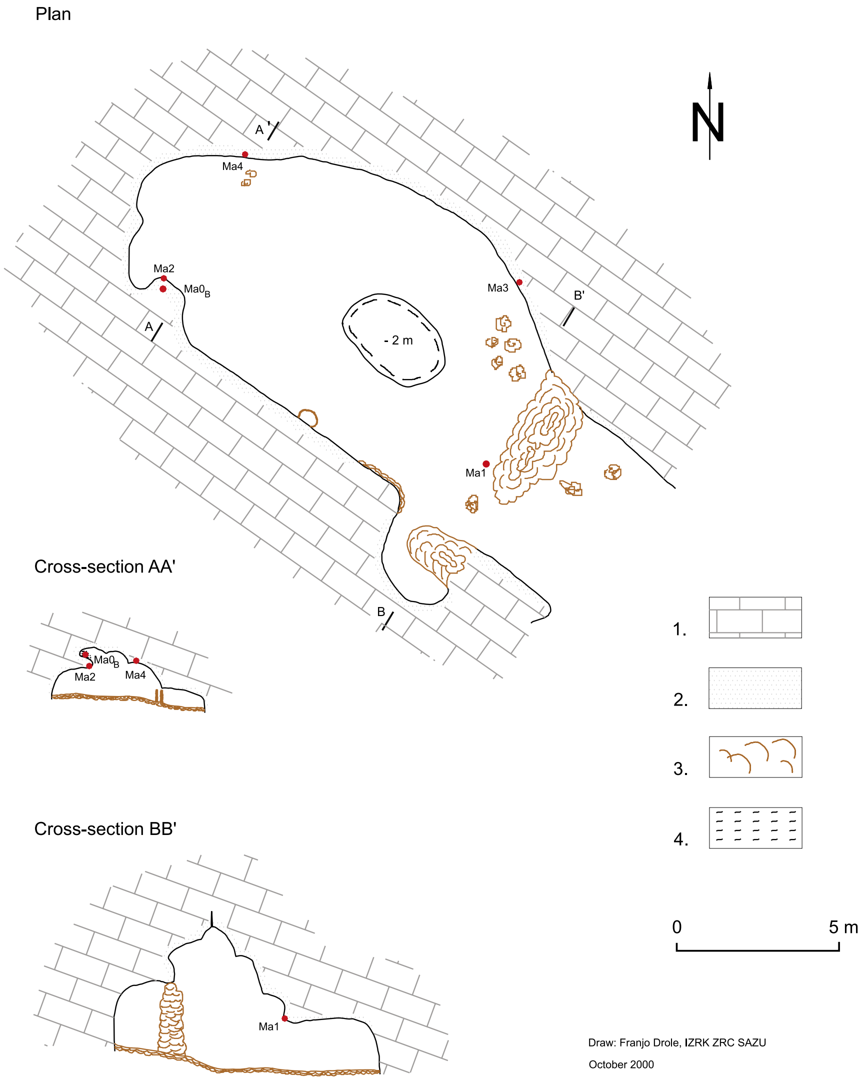


Figure 23: Plan of Boeganov rov and cross section in NW-SE direction with position of the samples. Legend: 1 – limestone, 2 – weathered limestone, 3 – flowstone, 4 – alluvial deposits.

weathered matter, a sample of the weathered limestone *Ma4* was taken from the NE wall of the passage. It was weighed in its wet state and after drying for 7 days at room temperature. The difference, which represents the moisture within the rock, was to 39.8 % (Fig.26). The moisture content of the porous rock depends on the momentary wettness of the cave wall, which is related to the amount of the precipitation on the surface, the incline of the cave wall and the evaporation rate.

Figure 24: When the inflow of the saturated solution on the ceiling increases, the porous weathered limestone is cemented and tiny soda straw stalactites start to grow if inflow still increases.

Figure 25: Network of the protruding calcite veins creates incipient "boxwork" on the weathered wall (photo J. Žumer).

Sample Ma4	Sample weight (g)	%
Wet	24,3712	100
Air dry (7 days)	14,6948	60,21
Difference	9,6764	39,79

Figure 26: Moisture rate in the weathered limestone from Martinska jama is high. Sample Ma4 after 7 days of drying lost about 40 % of its weight.

During the sample taking it was discovered that the limestone is not weathered equally deep at different locations within the passage. For that reason the depth of the weathered and just initially weathered zone was measured by drilling along the circumference of passage. Drilling was carried using an electric boring machine, with a drill's diameter of 6 mm, which stopped when reaching the fresh rock (Fig.27). To testing the method,

Figure 27: Weathered zone was measured by drilling with an electric boring machine, drilling stopped when the fresh rock was reached.

the weathered limestone was drilled at the locality where sample *Ma1* was collected. The weathered edge of the sample was from 30 to 44 mm wide. During drilling the drill stopped at the depth of 31 mm. The drilled depth corresponded with actual depth of the weathered zone and confirmed the utility of the drilling. Several holes were drilled along the profile BB' shown in Fig.23. Results (Fig.28) indicated that the thickness of the weathered zone is relatively constant. The weathered zone is very thin only at the point where a piece of wall was broken off.

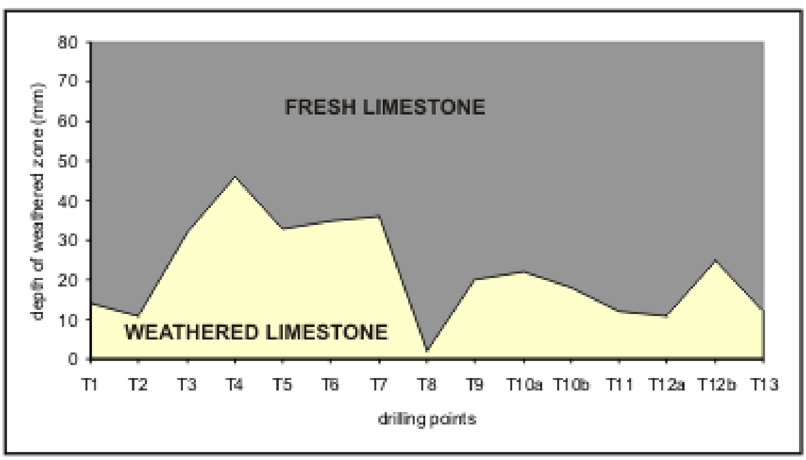


Figure 28: Results of weathered zone thickness, measured in profile BB' of Boeganov rov in Martinska jama.

Limestone samples

Figure 29: Sample Ma1 is a rock projecting from the eastern wall at a height of 1.8 m in Boeganov rov (photo J. Žumer).

Four larger samples were taken from the walls of Boeganov rov. Locations of samples are shown on Fig.23. Sample *Ma1* is a rocky projecting from the eastern wall at a height of 1.8 m, which is weathered on all sides (Fig.29). Along the weathered edge a net of holes, approx. 0.5 cm in diameter and up to 2 cm deep, are presented (Fig.30). Sample *Ma2* (Fig.31) is part of the limestone bed (rocky shelf) from the end of the passage, where, limited with strongly expressed stylolite, it comes in contact with the cave sediments. It is weathered at all its sides, except at the contact point with the passage wall (Fig. 32). Sample *Ma3* is weathered rock, removed from the NE wall near sample *Ma1*, whereas sample *Ma4* is weathered matter from the NE passage wall.

The mineral composition of the limestone was determined by X-ray diffraction and is shown in Fig.33. For the purpose of X-ray analysis sample *Ma1* was separated into the discoloured part *Ma1b* and the weathered part *Ma1c*. Sample *Ma1b* consists almost entirely of calcite, while clay minerals (montmorillonite) are present only in traces.

Figure 30: Base of the weathered sample Ma1 from Boeganov rov; along the weathered edge a net of holes, approx. 0.5 cm in diameter and up to 2 cm deep, are presented.

- The X-ray analysis of samples demonstrated that the calcite peaks are higher in the weathered part of the limestone than in the fresh part. In weathered parts of the sample there is slightly less clay minerals.

Figure 31: Sample Ma2 was taken from limestone bed covered by alluvial deposit at the end of Boeganov rov.

Figure 32: Sample Ma2 is weathered at all its sides, except at the contact with the passage wall.

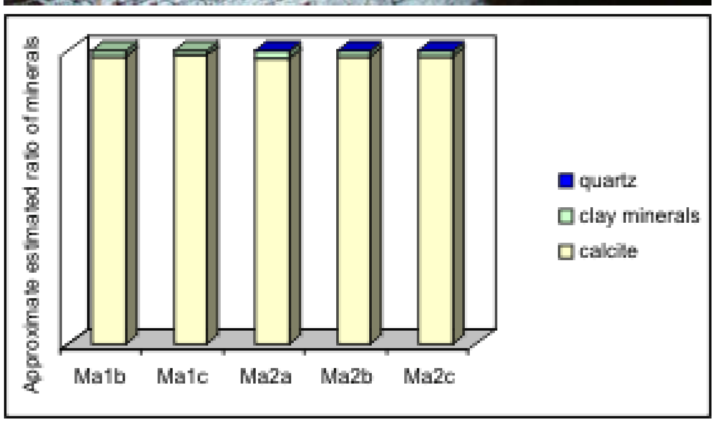


Figure 33: The mineral composition of the limestone samples from Martinska jama cave.

Sample *Ma1* from Martinska jama was also for complete chemical analysis divided into the fresh and the weathered part. Chemical analysis results (Fig.128) indicate that the amounts of titanium oxide, beryllium, cadmium, nickel, lead, zinc, bismuth, arsenic, cobalt, cesium, hafnium, iridium, molybdenum, rubidium, selenium, tantalum, thorium, tungsten, cerium, neodymium, europium, terbium, ytterbium and lutetium were in both parts of the sample below the detection limit.

In the weathered part of the sample *Ma1c,* the quantity of MgO, SiO_2, Al_2O_3 in Na_2O was reduced, while K_2O significantly increased. In the weathered part of the sample the quantities of strontium, zirconium, vanadium, aurum, antimony and uranium also decreased, while that of yttrium, argentum, chromium, scandium, lanthanum and samarium was higher. The loss on ignition (LOI) is larger in the fresh part of the limestone: oxides make up 99.81 % of the fresh limestone and 99.56 % of the weathered one.

Comparing the chemical composition of the fresh and weathered part of the rock in the sample *Ma1* in the weathered part:

- SiO_2, Al_2O_3, MgO, Na_2O, LOI (loss on ignition), strontium, zirconium, vanadium, gold, antimony and uranium decrease;
- CaO, K_2O, yttrium, silver, chromium, scandium, lanthanum and samarium increase;
- $Fe_2O_{3.}$ MnO, $P_2O_{5.}$ barium, copper and bromine remains unchanged.

5 samples from Martinska jama were analysed by the complexometric method; two from the fresh part of the limestone and three from the weathered part. Values obtained results are shown in Fig.129. The concentration of carbonates in samples from this cave is extremely high, with values from 99.84 % to 100 %. The only exception is sample *Ma3c* where it is 97.87 %, and contains more insoluble residue. The presence of the insoluble residue was not detected in samples of the fresh (a) limestone, whereas in the weathered limestone (c) it is absent only in one sample, while in other two its ratio proves to be of different value.

- In fresh limestone samples *Ma1a* and *Ma2a* the percentage of the MgO is the highest, whereas in samples of the weathered parts of the limestone it is lower, which points to the loss of the Mg ions during the weathering.

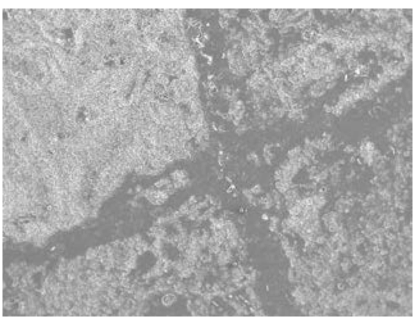


Figure 34: In the weathered part of sample Ma2, dark micrite belts remained unweathered (width of the photo 1,65 mm).

Sample *Ma2* was analysed by EDS on the SEM. In this sample the boundary between the fresh and the weathered part is not distinct, the transition between them forms continuous wide zone. In the weathered part, dark micrite belts of still unweathered limestone can be seen (Fig.34).

Qualitative analysis of the fresh micrite part of the sample and its weathered surroundings were done, using window size of 50 x 50 µm. In the unweathered part, qualitative analysis detected the presence of C, O, Ca, Mg, S, Sr and Fe, as well as Ni in traces; Fe and Ni are just at the EDS detection threshold. In the weathered part the

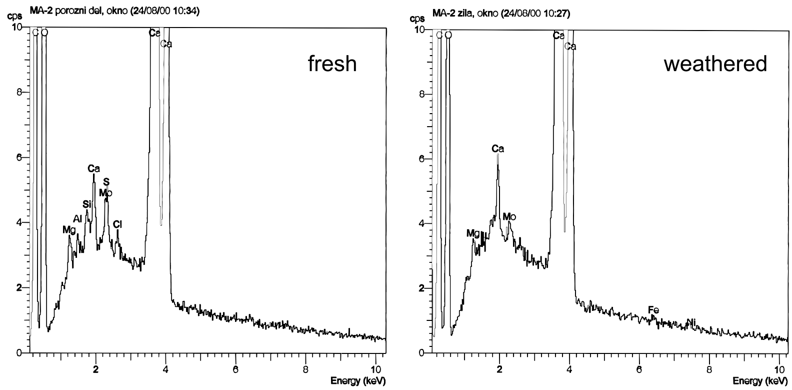


Figure 35: Measured spectrum from the fresh and the weathered part of sample Ma2, from the window 100 x 100 μm. Analyses of the weathered and unweathered parts demonstrate that the fresh part of the limestone is purer than the weathered part.

presence of C, O, Ca, Mg, Al, S, Si and Cl was detected. The presence of Mo is questionable, more likely only S may be present. Analyses of the weathered and unweathered parts demonstrate that in the fresh part of the limestone is purer, while the weathered part also contains Al, Si and Cl. It is not known whether Al, Si and Cl were brought into the weathered part with the sediments or they are insoluble residues. Qualitative analysis of sample *Ma2* was also carried out in the window 100 x 100 μm for the fresh and the weathered part. In the fresh part C, O, Ca, Mg, S and Sr were detected, whereas in the weathered one C, O, Ca, Mg, Al, S and Si were detected. Results are shown in Fig.35.

Organic carbon analysis revealed that of the organic carbon content in the fresh part of *Ma2* was 1.94 %, whereas in the weathered part to 1.55 % (Fig.130).

Mineral composition of the sediments

In order to compare the mineral composition of the weathered cave wall and the sediments cave sediment, two samples of the sediments were taken from the cave. The first one, $Ma0_A$ is the alluvium (fluvial deposit) from the lateral passage under the vertical entrance into the cave. It is sand, which was preserved in the upper parts of the passage wall. The second is alluvium sample $Ma0_B$ taken from the small shelf above the rock sample *Ma2* in Boeganov rov (Fig.36). The sediment that lay on this shelf was in direct contact with heavily weathered limestone. A third sample, *Ma0c*, is clay from the bedding plane adjacent to sample *Ma2* which was chosen to determine, if it is insoluble residue of limestone or the insertion of some other rock, or even infiltrated sediment. The mineral compositions of samples are given in Fig.37.

Sediments sample $Ma0_A$ from the lateral passage contained predominantly quartz, with clay minerals and a mineral of illite/muscovite group present in small quantities and

Figure 36: Alluvium sample $Ma0_B$ from the small shelf at the end of Boeganov rov.

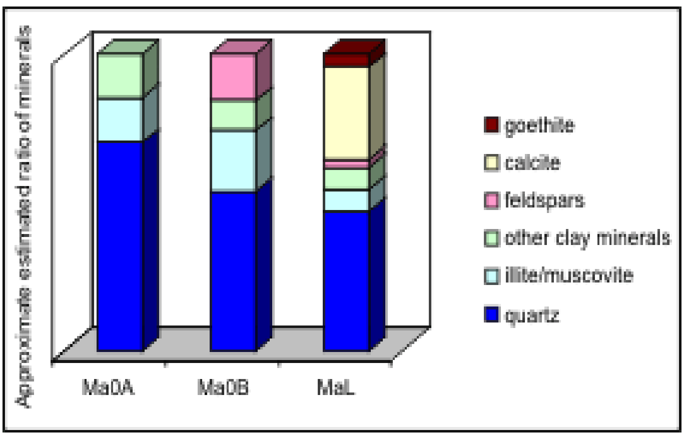


Figure 37: The mineral composition of clastic deposits from Martinska jama cave.

traces of goethite. In the sediment sample from the Boeganov rov $Ma0_B$ quartz prevails, with the mineral of illite/muscovite group and plagioclase in small quantities and few other clay minerals, as well. Red clay from the bedding plane $Ma0_L$ consists mostly of quartz with abudant of calcite, whereas the mineral of illite/muscovite group and other clay minerals are present in a lesser quantities; and insignificant amounts of goethite and plagioclase. Hematite is present only in traces.

The mineral composition indicates that the sandy sediments originated from the flysch, most probably from Brkini. The red clay from the bedding plane, however, is a mixture of limestone insoluble residue and infiltrated loam.

Conclusion

Boeganov rov's passages are soaked with percolating and not condensed water. Condensed water is trickling down the walls and dissolves them. In some places flowstone is being precipitated. The inflow of larger quantities of water is reflected in grey, water drenche stains and in the flowstone precipitation in the form of small pipes and palettes, as well as in the cemented parts of the weathered rock. In these cemented parts of the weathered rock the porosity of the weathered area, due to secondary precipitated calcite, significantly decreases.

With regard to the occurance of both alluvial sediments in Boeganov rov and thick layers of the weathered limestone, it can be interred that the alluvium and the weathered limestone are closely related. This relation is made more credible because the moisture persists in the rock under the sediment rather than because of chemical activities of the alluvium. Moisture that sinks through the ceiling and from the most prominent bedding plane in the passage soaks the walls and dissolves them. The rock is weathered also in the interior, along the predominant bedding plane and under and above the clay that lies in the bedding plane. The microclimate conditions in this passage exclude condensation corrosion as a possible mechanism for weathering. When water in pores becomes supersaturated flowstone begin to be precipitated; most extensively under the main bedding plane.

SPODMOL NA ŽDROCLAH

Cave location and geological setting

Ždrocle are deep karst depressions with steep, precipice walls. These depressions are typical of the plateau Southeast of the mount Snežnik at an altitude between 1300 and 1400 m asl.. According to Basic Geological Map, Sheet Ilirska Bistrica (Šikić *et al.* 1972) they are developed in Lower Cretaceous limestone with dolomite breccia. Precipice walls are controlled by fissured zones striking N – S and by faults striking in the Dinaric direction NE – SW (Zupan Hajna 1997b). Snow may sometimes be preserved throughout the whole year at the Ždrocle's bottom and may consequently transform the floor.

A rock shelter (Reg. no. 4263) is developed at the NE side of Ždrocle 3, at an altitude of 1389 m asl. (y = 5459 060, x = 5047 550). Here strata dip towards NE (70/20). A few metres Southwest of the rock shelter the limestone is intersect by a strong fault in Dinaric direction, along which the rock is crushed. The rock shelter was formed along a bedding plane, where the rock falls apart in a more intense manner and is consequentially slightly more marl-like and of a greenish colour. The weathered rock along the bedding plane is very wet, because the bedding plane conducts precipitation water; however, the rock also simultaneously and intensely disintegrates since it is exposed to frost. Not only does the rock crack due to temperature fluctuations, but mechanical disintegration is also accelerated by water freezing in cracks and pores of the weathered rock along the bedding plane. Two samples of weathered rock were taken from the rock shelter.

Limestone samples

Two samples of weathered limestone from Spodmol pri Ždrocli 3 have been analysed by X-ray diffraction. Sample *Žd1* is weathered limestone from the layer above the main bedding plane, whereas *Žd2* is weathered matter from the bedding plane. Their mineral composition is shown in Fig.38.

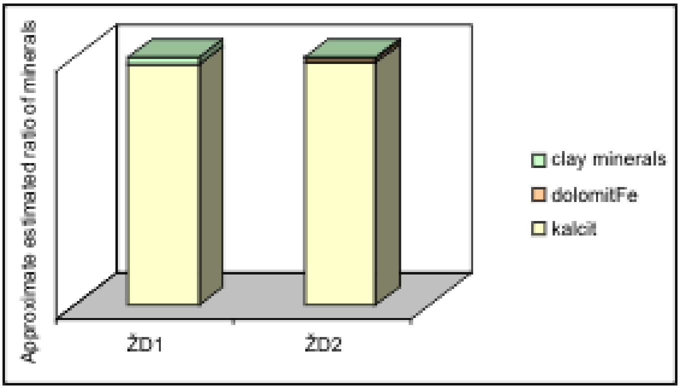


Figure 38: The mineral composition of the samples from rock shelter Spodmol pri Ždrocli.

The initially disintegrated limestone *Žd1* almost entirely consists of calcite, while clay minerals are only present in traces. The weathered, slate-like layer from the bedding plane *Žd2* is also mostly composed of calcite, while the dolomite has a considerable amount of Fe, with traces of clay minerals. The main dolomite peak is shifted towards the ankerite peak, indicating that Mg in the dolomite was replaced with Fe.

Two samples from Spodmol pri Ždrocli 3 have been analysed by the complexometric method. The results are shown in Fig.129. The carbonate composition of both samples ranges from 92.02 % to 97.1 %. There are also substantial amounts of insoluble residue present in both samples with a larger quantity in the marl-like limestone *Žd2*. The percentage of MgO is higher in sample *Žd2* than in *Žd1*.

PEČINA V BORŠTU, REG. NO. 935

Pečina v Borštu was chosen as a representative sample cave, due to its easy access and because it contains large quantities of heavily weathered limestone in its furthest part (Fig.39). Walls in other parts of the cave are weathered as well, however, they are, mostly covered by flowstone.

Figure 39: Weathered walls in Končni rov of Pečina v Borštu cave are covered by red flowstone crust. Alluvial deposit lies at the bottom of the wall (photo J. Hajna).

Cave location and geological setting

Pečina v Borštu cave lies on the western slope of Jezerina, a blind valley in Matarsko podolje (Fig.11) at an altitude of 566 m (y = 5428 460, x = 5045 715). The blind valley was formed at the contact between Cretaceous and Palaeocene limestones and flysch (Mihevc 1994). Two rivulets, which flow in from Brkini, sink underground at the valley bottom. In the beds of both streams several swallow-holes may occur, their activity depends on the water level. Ponikve v Jezerini, cave is located at the valley bottom. It is also a temporary swallow-hole of one of the rivulets and its lower parts are flooded several times a year (Slabe 1992).

Pečina v Borštu, however, is situated around 100 m above the floor of the blind valley. Mitjetova jama is located on the western slope of the blind valley, slightly lower than Pečina v Borštu. The beginning of the speleothem growth on breakdown in its interior was dated by the U/Th method at well over 16 000 years (Mihevc 2001).

According to the Basic Geological Map 1: 100 000, Sheet Ilirska Bistrica, (Šikić *et al*. 1972) Pečina v Borštu cave formed in well stratified Turonian limestones (K_2^2). At their contacts with the flysch the Upper Cretaceous limestones dip steeply towards the NE.

Spelomorphological characteristics

The cave entrance is situated below the top of the western slope of Jezerina pod Bukovjem. Its opening was caused by a 5 m deep collapse, measuring 10 × 15 m. The plan of the cave is on Fig.40. The cave is approx. 250 m long and is oriented in a N-S direction following a fissured zone. Limestone beds dip towards the NE.

The passage walls are extensively covered with flowstone; individual features of the cave passages indicate their foramtion in phreatic conditions. At specific places within the cave there are remains of alluvial deposits, which indicate a phase of intensive cave filling in the past. Subsequently water washed most of the sediment away.

The cave is of phreatic origin; however initial phreatic features are only visible in a small chamber beside the eastern wall of the chamber in front of the passageway, where flowstone is not so abundant. Elsewhere almost all of the passage walls are coated with a thin layer of reddish brown flowstone, while the entire cave contains much flowstone. The considerable age of the cave was confirmed by U/Th dating. Mihevc (2001) dated speleothem from the small chamber beyond the passage to an age of more than 200 000 years.

There are several generations of flowstone in the cave. The speleothems are of various forms; some are broken, other inclined, some stopped growing, whereas the cracks

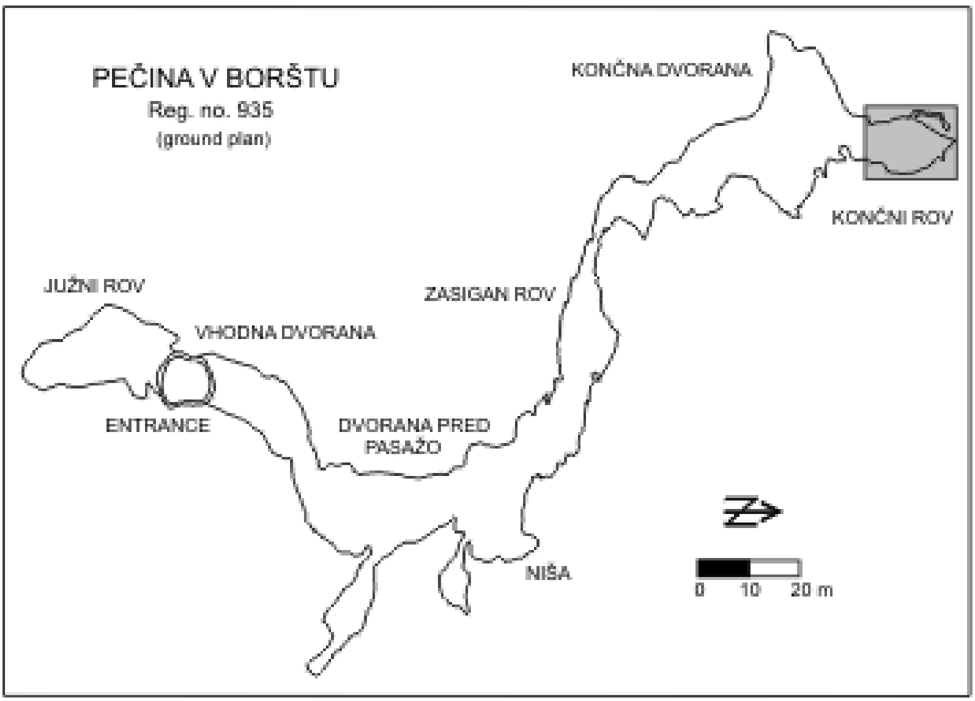


Figure 40: Ground plan of Pečina v Borštu cave (Cave Register of IZRK ZRC SAZU).

in others were filled up by younger flowstone. Flowstone is only absent from part of the ceiling and walls of the small chamber on the eastern wall of Dvorana pred pasažo, which I named Niša, and from part of Končni rov, and from some small sections of Končna dvorana and Zasigani rov. In places where the rock is not covered by flowstone, it shows signs of weathering. The surface of the wall has initial weathering and in some sections "boxwork" a few millimetres deep has formed. In some places "boxwork" is visible through the thin layer of flowstone that covers the walls.

There is no flowing water in the cave, only percolating water that accumulates in pools after rainfall. The cave is generally dry; after rainfall, however, in some parts of Zasigani rov it may get quite wet. The temperature in the entrance area fluctuates with the exterior temperature. During winter, the effect of surface air on the cave temperature may be felt in the cave all the way up to Pasaža. For example: at the end of December the temperature just beneath the ceiling of Vhodna dvorana was 3.9^{0}C, in Dvorana pred pasažo it was 9.6^{0}C, while in Končna dvorana it was 10.4^{0}C and in Končni rov 10.4^{0}C. During summer, different conditions reign in the entrance area, since in Dvorana pred pasažo it was much colder. Temperatures measured at the end of December 1999 and in the beginning of July 2000 are given in table (Fig.41). The measured temperatures demonstrated that the air within Dvorana pred pasažo is warmer in winter than during summer. This chamber is warmed up in winter by air from the cave, while in summer the temperature is lower due to cave air circulation. The temperature in Niša, on the eastern wall of Dvorana pred pasažo was only 7^{0}C July. Pasaža, itself, however, has relatively constant temperatures, ranging from 10.3 to 10.6^{0}C.

Condensation corrosion occurs when cold air enters the cave. An abundance of condensed water drops was observed during winter in Dvorana pred pasažo. In summer

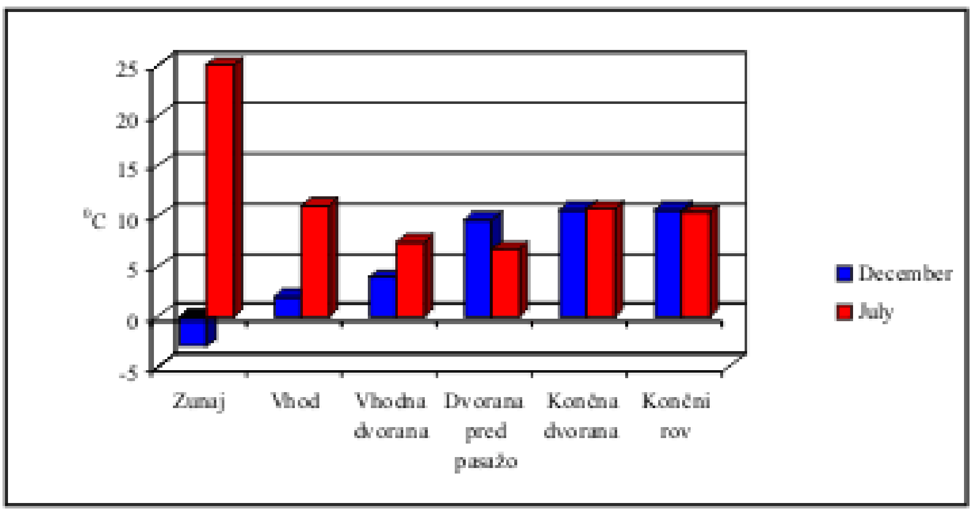


Figure 41: Temperatures measured in Pečina v Borštu cave in December 1999 and in July 2000.

the condensed water drops in Dvorana pred pasažo are not so plentiful. Condensation does not appear in other parts of the cave. In Končna dvorana the temperature is constant throughout the year. Moisture on the ceiling and walls of Končni rov cannot be ascribed to condensation but is a consequence of percolating water seeping through the walls. In Končna dvorana the walls are wet only after the more extensive precipitation outside the cave; at such times water trickles from soda straw stalactites and fills up the cave pools.

Končni rov

Končni rov is, the most interesting part of the cave as far as the weathering of cave walls is concerned. There are large amounts of intensely weathered limestone on the passage walls. The weathered zone is up to several cm thick. For this project the passage was resurveyed and a new plan and profiles were drawn (Fig.42).

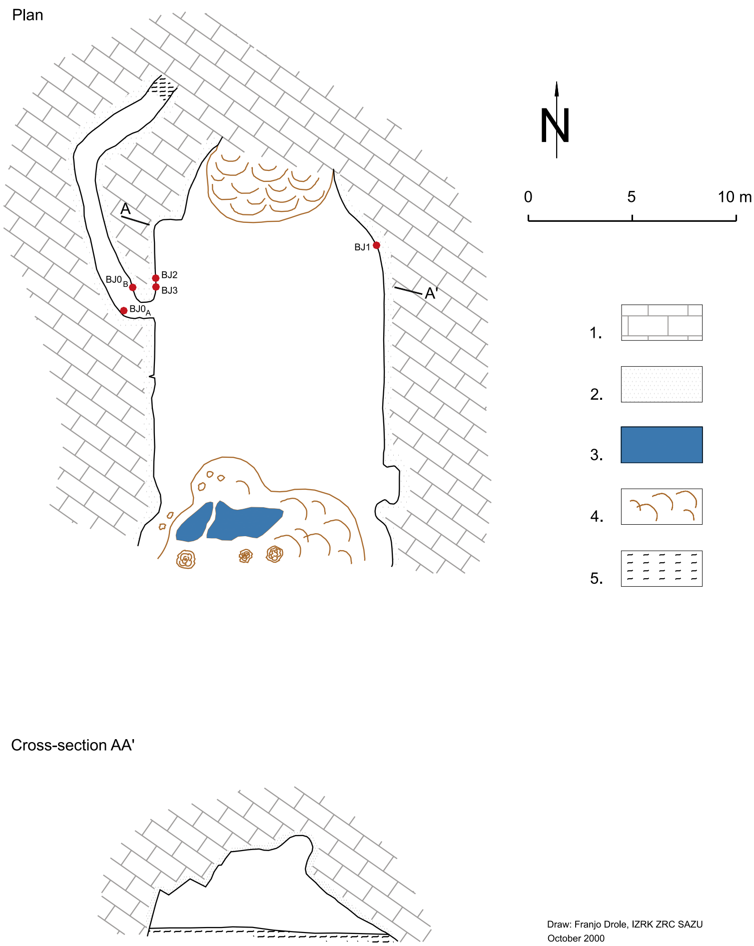


Figure 42: Plan of Končni rov, with cross-section (AA') in NW-SE direction and position of the samples. Legend: 1 – limestone, 2 – weathered limestone, 3 – water, 4 – flowstone, 5 – alluvial deposits.

Bedding in the limestone in the cave walls dips towards the NE. As does a distinctive bed containing broken rudist shells and a bed with stromatolites on the western wall of the passage. Prominent fissures oriented N–S is exposed in the ceiling and walls of Končni rov.

In some places the walls of Končni rov are covered with a reddish brown crust several millimetres thick. In the small part of the passage ceiling, grey soda straws are growing from percolating water (Fig.43). All walls and the ceiling have extensive flowstone and not a single fresh rock could be detected on the wall's surface. On one of the walls there is a layer of Rudists shells protruding out of the wall. The layer is weathered to depth of several cm and the shells are also weathered and soft, while their original shape has remained unchanged (Fig.44)

The rock is not only of a different colour due to weathering, but also its outer layer has become substantially porous and is very soft to the feel, while in the lower parts of the passage it is also rather wet. At some places the soft part of the weathered rock is up to 10 cm deep. It is succeeded by few cm of solid, noticeably discoloured and porous rocks, becomes less decolourised and less porous with depth. It was not possible to sample completely fresh and non-decolourised rock in Končni rov, because passage walls are so even that collecting might have damaged the wall's surface.

Fluvial clastic sediments may be found across the floor of Končni rov and in Odkopani rov, which is entirely filled up with them. In some places the shape of the flowstone indicates that it was deposited on top of the clastic sediments, which were later removed.

In the course digging to find an extension of Odkopani rov, cavers removed large amound of sandy sediment. Because deposits were in direct contact with the passage walls, a question arose if the thickness of the weathered zone increases as a result of contact between limestone and sediments. If limestone weathering is caused by contact with sediment, then the passage wall should be weathered only up to the level of the top of the alluvial deposit.

Figure 43: Wet part of the weathered passage ceiling is grey in colour; from the percolating water small soda straw stalactites are growing.

Figure 44: Weathered Rudists shells in the Končni rov wall of Pečina v Borštu cave.

For this reason the depth of the weathered zone in Končni rov was measured on the western and eastern passage walls. The cave wall was drilled using an electric boring machine; with a 6 mm diameter drill. Drilling stopped when the bit struck fresh rock and the depth of penetration was measured. The thickness of the weathered zone on the wall was not even. On the western wall of Končni rov the thickness of the weathered limestone ranged from 4 to 52 mm, while on the eastern wall of Končni rov it was from 8 to 71 mm.

The weathered part of the limestone was fairly wet, and wettest in the lower part of the wall, which is still in contact with the sediment. The moisture level is higher after more extensive precipitation during autumn or winter, while in summer there is considerably less moisture in the weathered zone, except after the intense rainfall. High moisture levels persist throughout the year only at the foot of the passage walls and at contacts with the sediment.

In order to determine the moisture content of the weathered limestone a wet sample *BJ3* was weighed and then dried at room temperature. The moment it was exposed to room conditions it started to dry rapidly, so that its weight was visibly falling. After 7 days of drying the sample's weight had dropped by almost Ľ. The difference between the two weights represented the actual amount of moisture in the rock. The ratio of moisture in the wet sample was fairly high, since it amounted to 23.97 % of the sample's entire mass (Fig.45). This indicated that the rock was very porous to be able to absorb large quantities of water.

Figure 45: Moisture rate in the weathered limestone from Pečina v Borštu. Sample BJ3 after 7 days of drying lost about 23.97% of its weight.

Sample BJ3	Sample weight (g)	%
Wet	25,2305	100
Air dry (7 days)	19,1824	76,03
Difference	6,0481	23,97

Measurements of pH in the weathered matter, water and fluvial sediment

Measurements were carried out by the pH-meter Testo 230, which has a gel membrane (type 03 pH) on its electrode. The instrument was utilised for the direct measurement

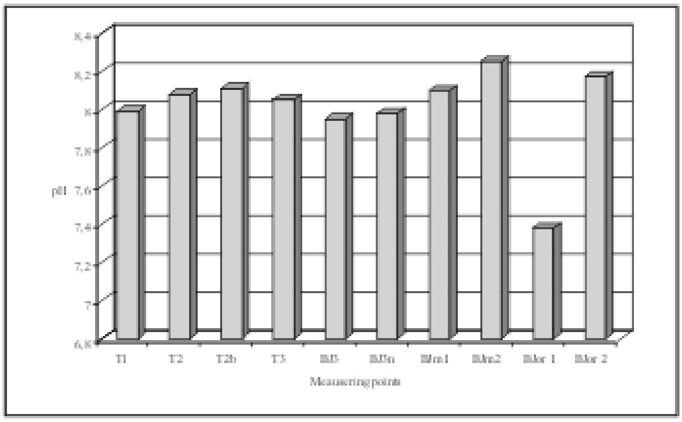


Figure 46: Results of pH measurements in weathered limestone in Pečina v Borštu.

of the active pH in the weathered wet rock and in the wet sand sediment, which is in direct contact with the weathered passage wall and in the flowstone-generating water. Measurements of the pH within the cave were carried out in the middle of July at T=10.6^{0}C, a few days after the rainfall. Weathered walls of Končni rov were wet, yet less than in January. Results for weathered limestone are given in Fig.46, for sediment in Fig.47 and for water in Fig.48.

Four measurements in Končni rov were made within the wells, where the depth of the limestone weathered zone was also quantified: two measurements at the original place of sample *BJ3,* and measurements of pH at both points, from where for the purposes of the microbiological research the samples *BJm1* and *BJm2* were taken. The pH in Odkopani rov was measured in the weathered matter immediately after the passage's entrance and at the direct contact point between the rock and the sand sediments.

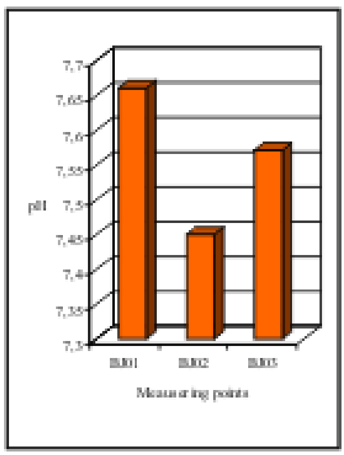


Figure 47: Results of pH measurements in alluvial deposits in Pečina v Borštu.

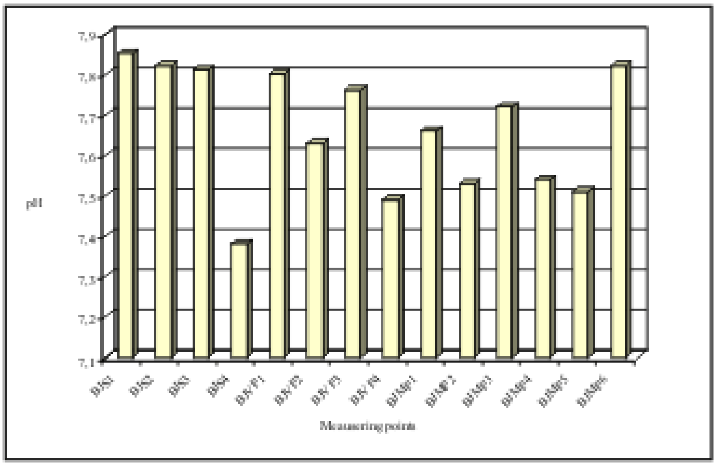


Figure 48: Results of water pH measurements in Pečina v Borštu. Legend: water from: Š – soda straws, VP – Velika ponvica (Large pool), MP – Mala ponvica (Small pool).

pH values in the weathered limestone generally ranged around 8; in the wet weathered matter the lowest pH value was 7.38. The sample intended for the repeated microbiological research, *BJm2*, had at the sample preparation a pH of 8.25. During measurement in the field the value was 7.95, whereas at the renewed measurement after precipitation when the sample was wetter the pH was 7.5. pH measurements were undertaken in Odkopani rov, where the fluvial sediment it is still present *in situ* and is in direct contact with the weathered passage wall. The sediment (at point *BJ01*) in contact with the weathered limestone (at the point *BJOR1*) had a pH value of 7.66. The sediment (at point *BJ02*) in contact with the weathered limestone (at point *BJOR2*) had a pH value 7.45. The pH value of the alluvial sediment (at point *BJ03*) positioned between both previous samples and located under them was equal to 7.57.

For comparison the pH of the percolating water from soda straws and cave pools in Končna dvorana, which are filled up with water after extensive rainfall, has been measured as well. In water drops at the end of soda straw it amounted to 7.8; only in one single case was the value lower than 7.38.

Water in pools dries up quite fast. It remains for longest in Mala ponvica and on its surface float thin calcite rafts (Fig.49). Rafts are precipitated at the water's surface owing to the change in the partial pressure of CO_2 (Hill & Forti 1997). The largest of them get coated with tiny crystals on its lower side and due to the increased weight they subsequently sinks. When water in pools dries out completely, all the rafts sink to the bottom. In Velika and Mala ponvica we measured pH on the surface, where the calcite rafts were floating, as well as in pools where they were absent and at the bottom of the same pools. Two measurements were carried out at the edge of Mala ponvica, where those too heavy calcite plates had already sunk to the bottom. Measurements yielded different values within the both pools and in the same pool. In Velika ponvica the following pH values were measured: the surface with rafts 7.8; the bottom with rafts 7.63; surface without rafts 7.76 and the bottom without rafts 7.49. In Mala ponvica, in contrast, the following pH values were measured: the surface with rafts 7.66; surface without rafts 7.72 the bottom with rafts 7.53; the bottom without rafts 7.54 the water at the bottom and the calcite plates 7.51 and the wet rafts 7.82.

Different pH values within the same pool and at such short distances point to the precipitation of calcite in the upper part of the water and to slight dissolution at the bottom. Within cave pools no mixing of water occurred; layers with different concentrations of H^+ ions, however, got established in them, i.e. the water got stratified. This in turn signifies that the diffusion is negligible and that layers with different concentrations of dissolved ions do not mix together.

Figure 49: Calcite rafts in the bottom of Mala ponvica in Končna dvorana of Pečina v Borštu.

Comparison between all resultes of pH meauserements from Pečina v Borštu is shown in Fig.50. pH measurements indicated that moisture in the weathered part of the rock is supersaturated with calcite, since pH values in the weathered rock, with the exception of one single sample, did not exceed the value pH = 8.0. The pH values of the flowstone-generating water in the same part of the cave ranged around 7.8. In view of these facts, I assume that limestone dissolution in the weathered zone was not taking place at the time of our measurements. The only exception was the part of Odkopani rov where the surface of weathered limestone in contact with the sand sediment had a pH value of 7.38.

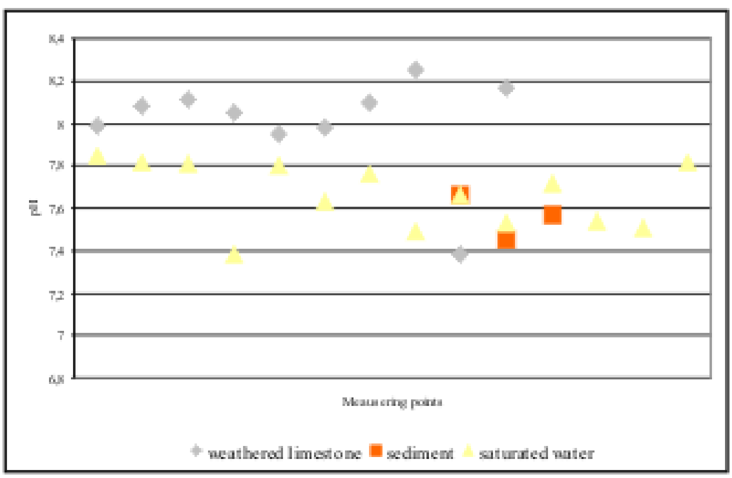


Figure 50: Comparison of all pH measurements in Pečina v Borštu.

Samples were collected from three points in the walls of Končni rov. Sample *BJ1* is part of the rocky horn, which protruded from the lower part of Končni rov's eastern wall. Sample *BJ2* is part of the soft weathered matter from the wall situated above the entrance into Odkopani rov and sample *BJ3* is a piece of very wet and soft weathered matter from the wall to the left of Odkopani rov's entrance.

The mineral composition of the limestone was determined by X-ray diffraction and is shown in Fig.51. I separated the sample *BJ1*, i.e. the weathered rocky horn from Končni rov's eastern wall, into a discoloured part *BJ1b* and a weathered part *BJ1c*, which is soft and very porous. *BJ1b* consists almost entirely of calcite; feldspars and clay minerals (probably montmorillonite and a mineral from the illite/muscovite group) are present in traces. *BJ1c* is composed of calcite, whereas clay minerals (probably montmorillonite) are present in traces. Sample *BJ2* is soft weathered matter from the wall above Odkopani rov's entrance and consists almost entirely of calcite, feldspars and quartz can be detected only in traces. In the weathered limestone samples calcite peaks were higher than in the discoloured sample. The ratio of insoluble minerals is higher in the discoloured rock than in the weathered rock.

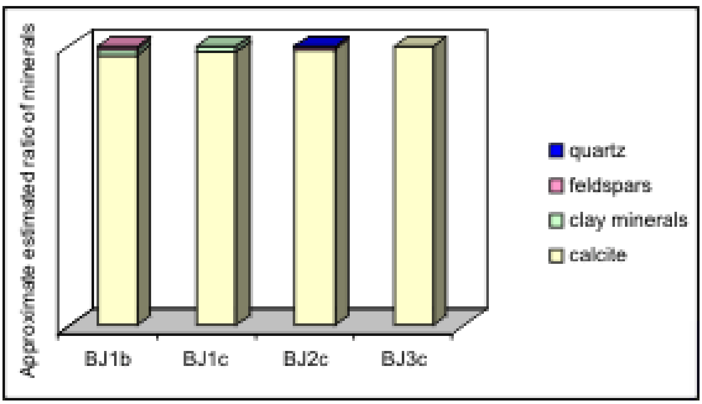


Figure 51: The mineral composition of the limestone samples from Pečina v Borštu cave.

Sample *BJ3* is very soft weathered matter, which was in contact with the sand, collected from the wall beside Odkopani rov's entrance. It consists entirely of calcite. The wet sample is of slightly grey orange colour (10 YR 8/2), while the dry one is white (N9). Due to the intense humidity I was able to measure the sample's pH directly using pH paper with a result of 7.5.

Four samples of fresh limestone and three of the weathered limestone were analysed by the complexometric method. Results are shown in Fig.129. The concentration of carbonate in the samples is extremely high, from 99.5 to 100 %. There is slightly less in *BJ3c*, only 93.8 %. In this sample, however, a stylolite was present so the sample contained more insoluble residue. Particularly large amounts of insoluble residue were found in the extremely weathered sample *BJ3c*. This may be due to infiltration from the surface or to flooding, which might have deposited material into the porous rock or on the other hand to mere coincidental presence of some stylolites consist insoluble minerals in this part of the cave.

- The percentage of MgO is highest in the sample of the fresh limestone *BJ1a*, while it is always lower in samples of weathered limestone. This indicates that the Mg ion probably migrated out of the calcite crystal lattice in the course of the limestone weathering.

Sediments samples

To compare the mineral composition of the weathered cave wall with that of the fluvial cave sediments two sediment samples were taken.

The first one, *BJ0A*, is fluvial sand from the beginning of Odkopani rov (Fig.52), while the second, *BJ0B* is a lump of sand removed from the niche in the heavily weathered wall of Odkopani rov. The mineral composition of samples is shown in Fig.53.

Figure 52: Alluvial deposits from Odkopani rov passage (photo J. Hajna).

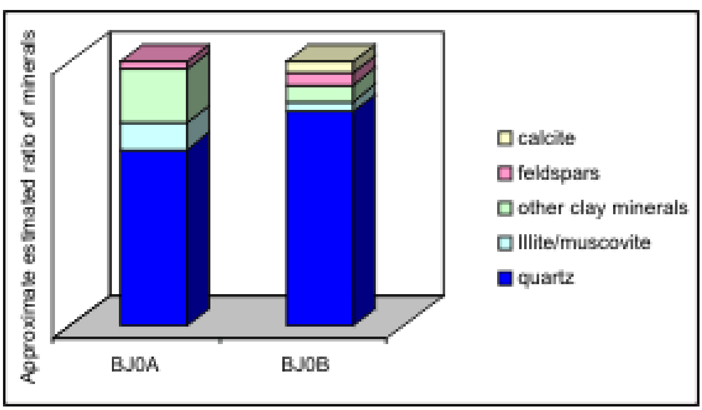


Figure 53: The mineral composition of clastic deposits from Pečina v Borštu cave.

Sand from the beginning of Odkopani rov, *BJ0A* contains predominantly quartz, with an insignificant quantity of a mineral from the illite/muscovite group and other clays. The lump of sand removed from the heavily weathered wall (*BJ0B*) consists mostly of quartz, with small amounts of feldspars, calcite and a mineral from the illite/muscovite group. The mineral composition suggests that the sand is derived from the flysch rocks of Brkini, where water flows into the Jezerina blind valley. No calcite was found in the sediments from the passage. The loam from the hollow in the weathered wall contains only a little calcite. Its mineral composition is similar to that of the sand sediments at the passage bottom. The calcite in the sand consists of limestone grains derived from the weathered cave wall, which is in direct contact with the sediments.

Microbiological analyses

Two samples, *BJm1* and *BJm2*, were removed from walls of Končni rov (Mulec *et al.* 2001) for microbiological research. Microbiological analysis indicated that microorganisms are abundant on the weathered rock. Cultures from the weathered rock differ from those from the cave pools (Fig.49) and luminescent water drops (Fig.54). At this stage of research, however, it is not possible to confirm a relationship between the presence of microorganisms and the dissolution of limestones on walls of Pečina v Borštu. Results are shown in Fig.55.

Figure 54: Luminescent water drops were taken for micro-biological analyses in the entrance part of Pečina v Borštu.

Another sample for microbiological research was taken from Martinska jama. Results, however, were not positive, which is most likely due to the inadequate culture medium. For that reason a new sample was taken later, principally with an aim of determining the presence and number of microorganisms. The research up to now suggests that microorganisms are present in the weathered matter, it is still not clear what type they are, although we however it is fairly certain that they are not sulphur bacteria.

	HABITAT (microniche)		
	SILVER FLASHING DROPLETS	POND	WEATHERED LIMESTONE
BACTERIAL COUNT	COLONY FORMING UNITS (CFU) / ml		
King B	ND	$2{,}5\times10^4$	$4{,}0\times10^4$
Prep medium	ND	$1{,}0\times10^4$	$1{,}1\times10^6$
BACTERIAL GROUPS	NUMBER OF ISOLATED STRAINS		
FLUORESCENT PSEUDOMONADS	1	6	5
GRAM NEGATIVE NONFERMENTATIVES		6	2
GRAM NEGATIVE FERMENTATIVES (violet pigmented)		2	
GRAM POSITIVE COCCI		4	4
GRAM POSITIVE IRREGULAR RODS (*Actinomycetes* like)			

Figure 55: Micro-biological results (from Mulec et al. *2001)*

Conclusion

Throughout the cave, where the walls are not covered by flowstone, the walls are visibly weathered. At some places only the surface has been affected, while at others the weathered zone may be several centimetres deep. The walls and ceiling of the Končni rov are particularly intensely weathered. The outer layer of the weathered limestone has also lost its primary hardness and is currently quite soft. Deeper in, where the weathering has just started, rock is discoloured but there is no increase in porosity. The rock still remains solid after its discoloration. More intensely weathered, porous, parts of the wall are frequently soaked with water that trickles down the walls and remains caught in the pores. The soft, weathered zone in contact with the flysch alluvium on the passage floor is frequently very wet. Following extensive rainfall outside the cave all weathered parts of the wall become soaked with water. Where the crust of flowstone or alluvium does not cover the walls the weathered parts dry up and little holes with diameters of up to 1 cm emerge on their surfaces.

The surface of the weathered Cretaceous limestone in the walls of Končni rov displays depositional textures, for example, a layer with dried up pores or a layer containing fragments of rudist shells. The textures are not just weathered superficially but also deep into the rock. This indicates that the surface texture is due to limestone weathering, rather than to mineral deposition on the wall's surface.

Weathering is further indicated by the gradual, continuous transition between the weathered and fresh part of the rock. In case of mineral precipitation from condensed moisture or from water present in pores, the contact would be sharp, the secundary calcite crystals would be discharged directly to the smoothly corroded and solid cave wall.

During measurements of the pH in the weathered rock some differences in results occurred. The mechanisms of dissolution and precipitation in caves are constantly interchanging in the border pH conditions and saturation. The pH values of streams in karst are usually slightly above 8. In case when the solution is supersaturated with regard to $CaCO_3$, its pH decreases. The differences between measured pH values at the same location probably arise because during the summertime the saturated water was stagnating in the pores of the weathered rock. More extensive precipitation may squeeze this water out of the pores, so that fresh, more aggressive water may flow in them and continue the dissolution. This is also the reason why the wintertime pH drops after the lengthy autumnal rainfall by almost one unit. When fresh water squeezes the saturated water out of the pores, the release of CO_2 from the solution causes the deposition of flowstone on walls. The amount of moisture and the saturation of the weathered rock at a given part of the passage wall depend on: -

- micro-local factors,
- the nature of the rock's contact with water,
- the time period of this contact,
- the manner and velocity of the water flow
- the water's aggressiveness and saturation.

No increase in the aggressiveness of the water that flows between the fine-grained sediment and the rock was detected. The minutely grained sediment apparently holds the moisture in rock, because the area close to the floor, where the weathered rock is in contact with the alluvium, is much wetter than the upper parts of the wall. Where the rock is in contact with sediment it is also intensely weathered and has a smooth surface. Flowstone was not deposited at the contact points between the rock and the alluvium.

The limestone weathering in Pečina v Borštu cannot be attributed to condensation corrosion. It forms the shapes of cave passages walls only where circulation of cold and warm air is present. At some places, at least in cave entrance areas, this type of dissolution is efected by condensed water. In the case of Končni rov, however, condensation corrosion is impossible because there is no connection with the earth's surface. The temperatures in the cave are constant throughout the year, and the mixing of cold and warm air was not detected.

The water that drips from the ceiling, trickles down the walls and soaks into the weathered rock is percolating water. In this case percolating water is of the greatest significance for the humidity of and weathering of the walls. The volume of percolating water permeating the walls is proportional to the rainfall. The wall becomes soaked and then dries out in numerous cycles during the year. In Končni rov, increased water dripping, as well as increased cave wall humidity has been observed after abundant rainfall.

JAMA II NA PREVALI, REG. NO. 1095

In Jama II na Prevali, weathered limestone occurs only on walls of a small-sized lateral passage. The weathered surface is thickly criss-crossed with probably dormice tracks.

Cave location and geological setting

Jama II na Prevali is well known as an archaeological site and is also called Mušja jama. The entrance lies at Preval, south of Sokolak dol near Škocjanske jame, at an altitude of 467 m asl. (y = 5421 155, x = 5057 590).

According to the geological map of the southern part of the Trst-Komen plateau (Jurkovšk *et al.* 1996) the area is developed in Slivje limestone and Alveolinid-nummulitid limestone. According to Gospodarič (1983) and the Basic Geological Map, Sheet Trst (Pleničar *et al.* 1969), the cave is formed in Palaeocene limestones. These are thick massive, while its surface layers dip toward the SW (223/30).

Speleomorphological characteristics

The cave entrance is located on the boundary between Pc_1 and Pc_2 limestone, while the cave itself is predominantly formed in Pc_2 limestones (Gospodarič 1983). Small vertical entrance leads in a large chamber which is 45 m high. Its' floor is covered by pieces of limestone, which are corroded below the soil surface (Mihevc 1998). Beyond the entrance chamber, the cave continues as a passage oriented E – W, and subsequently broadens into Glavna dvorana, large chamber with N – S orientation. The floor of Glavna dvorana is covered with breakdown blocks mixed with alluvial sediment and flowstone. From this chamber several smaller passages continue in various directions. In the southern part of the cave, the entrance into the short Južni rov opens just beside a fault striking transverse to the Dinaric direction. The entire length of passages amounts to 200 m, and the depth to 90 m. Plan of the cave is in Fig.56.

Južni rov

Južni rov begins alongside the fault plane striking transverse to the Dinaric direction but then continues in N – S direction. After first high part along the fault plane, the passage

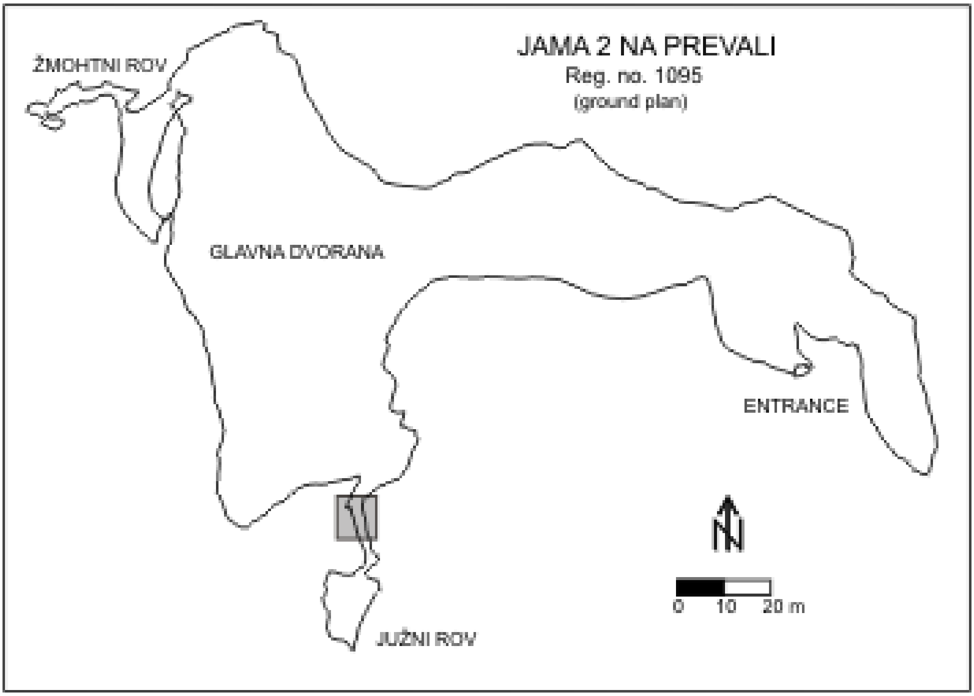


Figure 56: Ground plan of the cave Jama II na Prevali (Cave Register of IZRK ZRC SAZU).

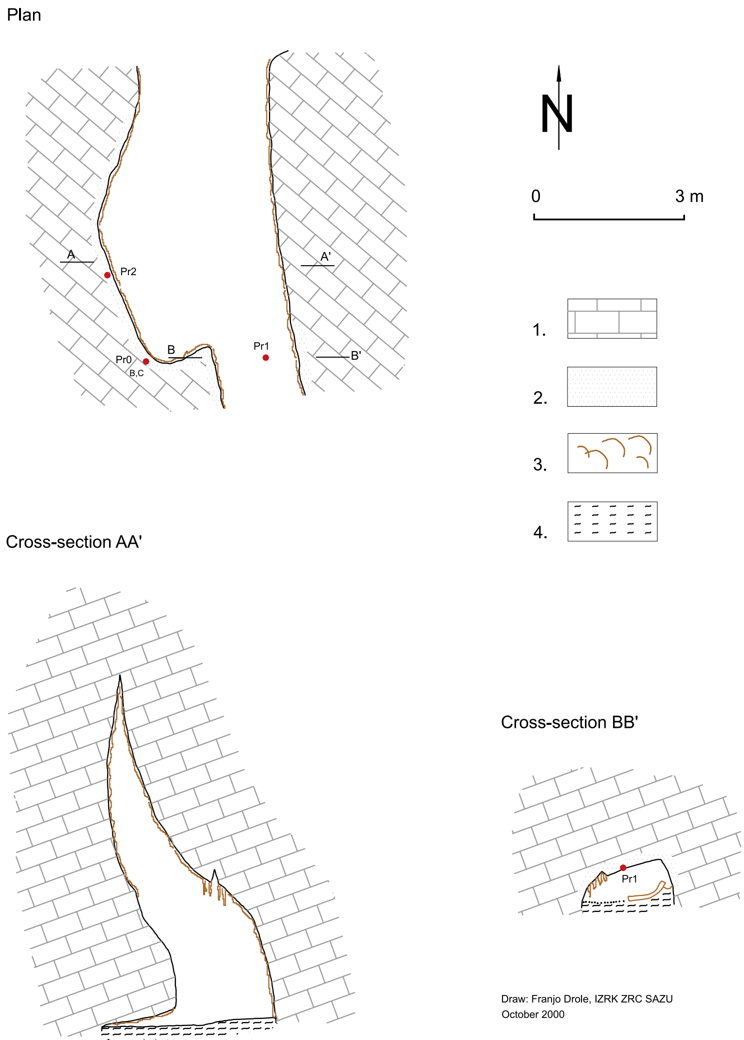
extends through a narrow section and ends in a smaller chamber. The chamber floor is covered with rubble. In the middle of the rubble mound there is a small depression in the rubble, which was dissolved by trickling formed by percolation water. We resurveyed the entrance to Južni rov, drawing a plan and profile (Fig.57). Limestone in this part of the cave appears in massive blocks; they dip at 20 degrees towards 220.

The eastern wall in the entrance area of Južni rov is covered with red brown flowstone with tiny transparent calcite crystals on its' surface and thickly precipitated white spray. The floor of this part of the passage is covered with coral-like flowstone. This kind of flowstone is typical of the entire cave; it is formed from trickling and dispersed water and requires considerable humidity of the cave air for its' growth.

At the beginning of Južni rov the western wall and the first part of the low passage are heavily weathered (Fig.58). The weathered limestone is white in colour and mostly fairly soft. A part of the wall is covered with a layer of reddish brown flowstone, among which there are some incised surfaces, which were carved by the bites of animal teeth or claws. Their location indicate that they were excavated in different time periods (Fig.59). Those closer to the surface are already drier and of the yellowish hue. Others, which are deeper, give an impression of being fresher and younger due to their white colour.

Mihevc (1996c) interpreted the white parts of the wall with traces of animal gnawing as resulting from dissolution by condensation corrosion, which incised the surface of the Palaeocene limestones and covered them with a patina. Incision of the rocky surface by

Figure 57: Plan of the entrance part of Južni rov and 2 cross sections in E-W direction (AA' and BB') with position of the samples. Legend: 1 – limestone, 2 – weathered limestone, 3 – flowstone, 4 – alluvial deposits.



condensation corrosion modifies the shape of the rock's surface by removing the binding matter between individual grains. As a consequence the rock loses some of its mechanical strength. Mihevc (1996c) was primarily interested in the shape and origin of the incision of marks on the rock surface. Within the small hollows in the passage wall, parallel flutes occur, which are undoubtedly the traces of small mammals' teeth. Mihevc could not find any remnants of the rock on the cave floor. For that reason he assumed that the animals actually swallowed the rock. On the basis of similar indentations in the rock surface at Kevdrc pod Raskovcem (Reg. no. 654) and Dolarjeva jama at Kališe (Reg. no. 201) Mihevc considered that the rock was most likely nibbled by dormice. The reason for the occurrence of the indented patches in the rock should consequently not lie in the differences in rock's sedimentary characteristics, although he did not undertake any more detailed

Figure 58: Weathered walls at the entrance to Južni rov, cave Jama na Prevali II (photo J. Hajna).

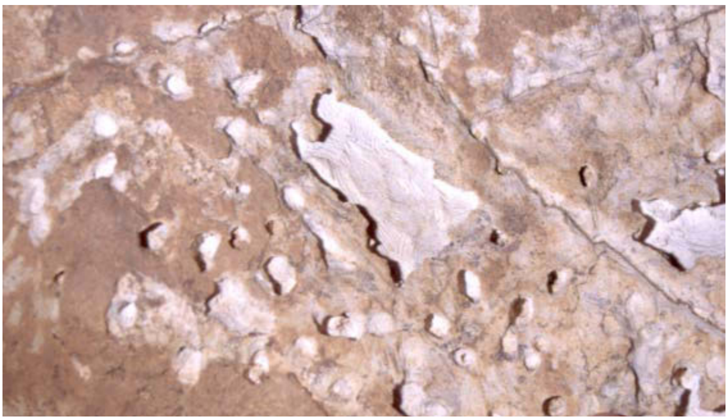


Figure 59: The weathered surface is criss-crossed with probably dormice tracks. It is possible to distinguish different generations of them.

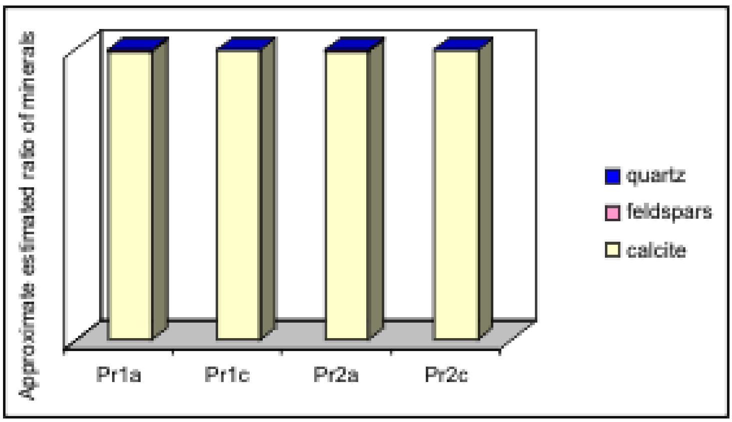
analysis to back up such an assumption. He tried to find the causes for the formation of softer parts in condensation corrosion, in precipitation of salts on the rock's surface and in the activities of microorganisms. These should, due to the favourable microclimatic conditions, have some convenient culture mediums in parts of the cave wall. Mihevc (1996c) noted that Valvasor (1689) who reported that dormice in a certain cave had been licking the rock stone plates had already investigated this phenomenon. Valvasor thought that the dormice licked the rock to obtain a substance similar to saltpetre from the rock.

In some parts of the western wall of Južni rov finely grained clastic sediments occur in direct contact with the weathered rock, indicating that this part of the cave was probably at one time filled with fluvial sediments. Under the sediments the weathered wall is smooth, without any hollows or traces of tooth marks. This suggests that animals started to gnaw the weathered rock only after the sediment had already been removed. Weathered walls along the pathway are not indented, their surface, however, is densely criss-crossed with calcite veins that protrude from the surface. The walls are weathered and soft. Many small hollows to 0.5 cm deep and to 0.5 cm in diameter are developed in them.

Limestone samples

Two samples of weathered limestone from Jama II na Prevali were analysed by X-ray diffraction. The mineral composition of the samples is presented in Fig.60. The sample *Pr1*, weathered limestone from the ceiling of the pathway in the southern passage, was further divided into a fresh part, *Pr1a*, and a weathered part, *Pr1c*. The fresh part of the limestone *Pr1a* consists almost entirely of calcite, with feldspars and traces of quartz; the weathered part of the limestone *Pr1c* only contains calcite, with some traces of quartz. Sample *Pr2*, part of the weathered and indented wall in front of the entrance into the southern passage, was divided into a fresh part *Pr2a* and a weathered part *Pr2c*. The fresh part of the limestone *Pr2a* consists almost entirely of calcite, with traces of feldspars and quartz; the weathered part of the limestone *Pr2c* contains only calcite with some traces of quartz.

Figure 60: The mineral composition of the limestone samples from cave Jama II na Prevali.



In both samples the fresh limestone also contains feldspars. In the weathered part, however, feldspars are not present even in traces, which indicates that they were removed in the weathering process. Where they have been transported to and in what form is hard to say. Most likely they were washed away in colloidal form; the quartz, however, remained within the rock. The main calcite peak in *Pr1* higher than in the weathered part, while in *Pr2* it is higher in the fresh one, which indicates that there is no connection between the weathering and the arrangement of the calcite crystal lattice.

Sample *Pr1,* limestone from Jama II na Prevali, was analysed by Ion Beam, point and line, in order to determine its elemental composition. Point analysis of the *Pr1* (Fig.61) was carried out at a proton energy of E_p = 2.5 MeV. In *Pr1* the concentrations (mass ratios in %) of trace elements Ti, V, Cr, Mn, Fe, Ni, Zn, Sr, Y Zr and Pb were measured. The results for 4 selected points are presented in Fig.62. Figure 63 shows typical spectrum from sample *Pr1* at point 2. Peaks that correspond to individual elements are indicated.

Comparisons between the trace element contents at individual points indicated that the difference in composition between points in the sample's fresh part and those in

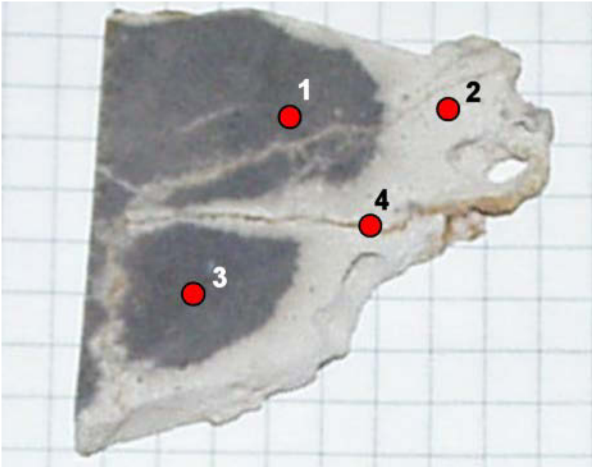


Figure 61: Cross-section of sample Pr1, Jama II na Prevali, with marked points where the concentracions of trace elements were meausered by Ion Beam Analyse.

Element	Point 1 [%]	Point 2 [%]	Point 3 [%]	Point 4 [%]
Ti	/	5,3 x 10^{-3}	1,1 x 10^{-3}	1,5 x 10^{-3}
V	2,2 x 10^{-3}	2,1 x 10^{-3}	2,0 x 10^{-3}	1,9 x 10^{-3}
Cr	2,4 x 10^{-3}	1,4 x 10^{-3}	2,4 x 10^{-3}	1,9 x 10^{-3}
Mn	2,1 x 10^{-3}	2,4 x 10^{-3}	2,2 x 10^{-3}	4,8 x 10^{-3}
Fe	9,0 x 10^{-3}	1,1 x 10^{-1}	1,0 x 10^{-2}	6,1 x 10^{-2}
Ni	3,8 x 10^{-3}	4,0 x 10^{-3}	3,6 x 10^{-3}	3,8 x 10^{-3}
Zn	1,4 x 10^{-3}	2,4 x 10^{-3}	1,9 x 10^{-3}	1,2 x 10^{-3}
Sr	7,0 x 10^{-2}	5,0 x 10^{-2}	7,0 x 10^{-2}	6,4 x 10^{-2}
Y	2,3 x 10^{-4}	1,4 x 10^{-3}	2,1 x 10^{-4}	4,7 x 10^{-4}
Zr	/	4,0 x 10^{-4}	1,2 x 10^{-3}	8,2 x 10^{-4}
Pb	/	8,4 x 10^{-4}	/	/

Figure 62: Concentrations of elements (mass ratios in %) in 4 points of sample Pr1.

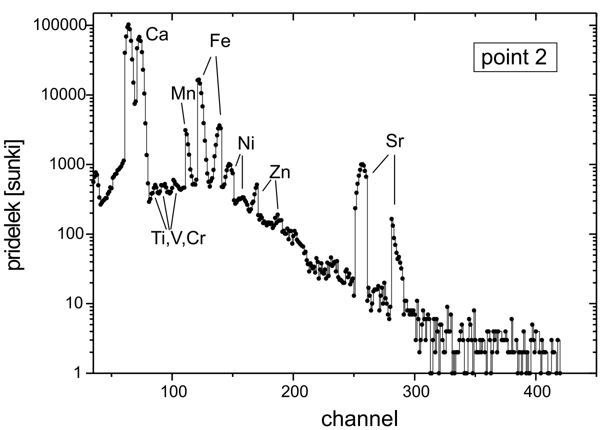


Figure 63: Meausered spectrum of the elements in point 2 of the sample Pr1.

the weathered part were smaller than the difference between points within the fresh or weathered part of sample (Fig.64 and Fig.65).

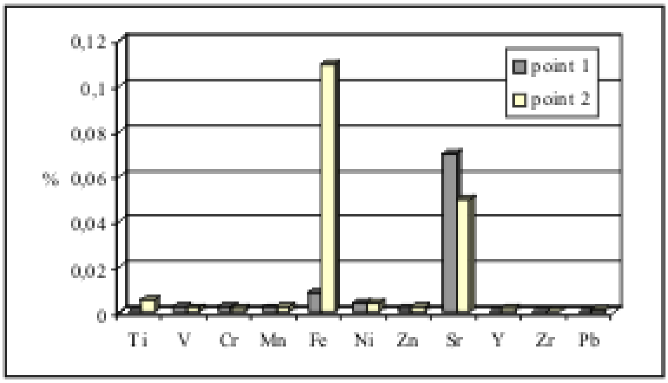


Figure 64: Comparison between concentrations of elements of points 1 and 2. Point 1 is from fresh part and point 2 is from weathered part of limestone.

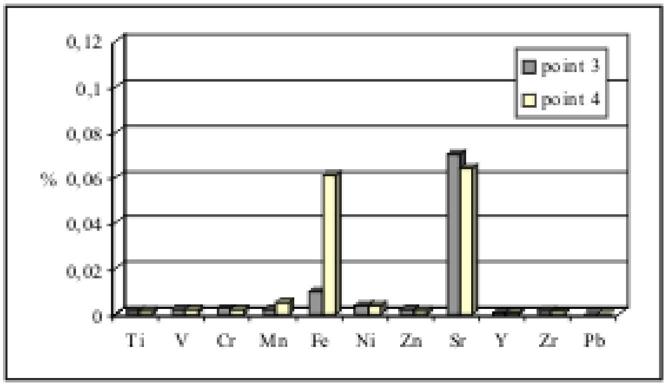


Figure 65: Comparison between concentrations of elements of points 3 and 4. Point 3 is from fresh part and point 4 is from weathered part of limestone.

Line analysis of sample *Pr1* was carried out along a straight line with the trace element ratios measured transversely to the boundary between the solid and the weathered part of the sample (Fig.66). The proton energy was - E_p = 3.5 MeV. The results show the

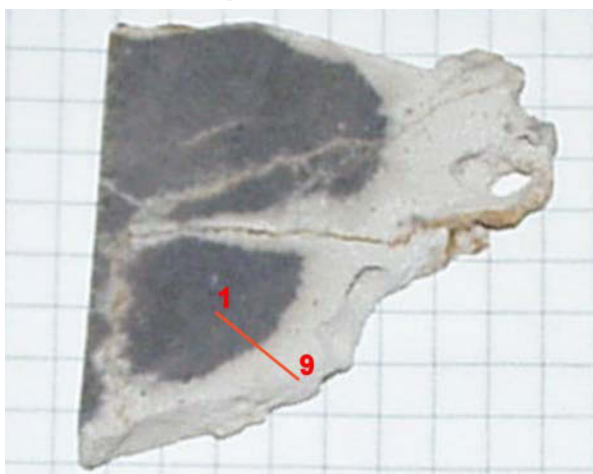


Figure 66: Line analyse of sample Pr1 by Ion Beam Analyse. Meausered were elements in 9 points along the line, distance between points was 0,5 mm.

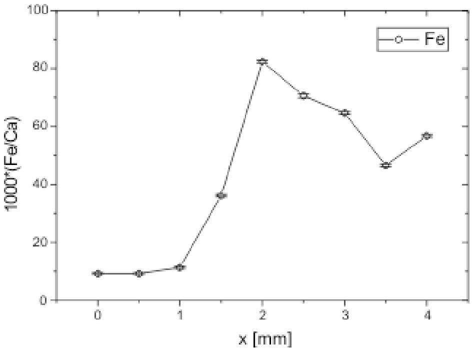


Figure 67: Concentrations of Fe along the line in sample Pr1. There is increase of it between fresh and weathered part.

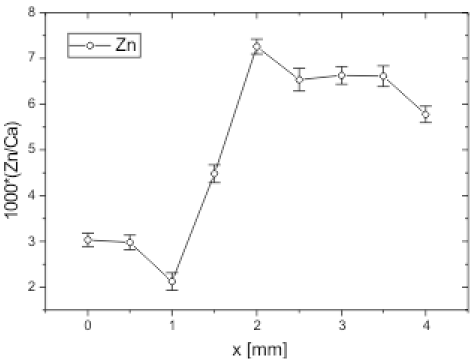


Figure 68: Concentrations of Zn along the line in sample Pr1. There is increase of it between fresh and weathered part.

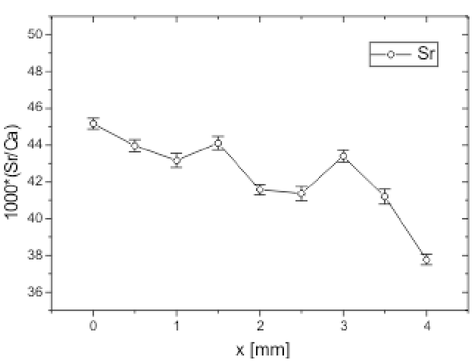


Figure 69: Concentrations of Fe along the line in sample Pr1. There is gentle decrease of it between fresh and weathered part.

measured increments of the characteristic spectra and not the concentration. Along the marked red line the distance between adjacent points of measurement was 0.5 mm and the increments of elements were measured in 9 points. Results for elements, which increased substantially in relation to Ca, are shown in following figures. There was considerable increase in concentration of Fe (Fig.67) at the transition between the fresh and the weathered part of the sample. The increase in the Zn (Fig.68) ratio was sizeable as well; in general, however, there was less Sr (Fig.69) in the weathered part of the sample.

A complete chemical analysis of sample *Pr2* was also undertaken. Results of the analysis indicated that the concentrations of titanium oxide, beryllium, lead, zinc, bismuth, arsenic, cobalt, cesium, hafnium, iridium, molybdenum, rubidium, selenium, tantalum, thorium, tungsten, cerium, neodymium, europium, terbium and lutetium were below the detection threshold (Fig.128).

The MgO and CaO content in the weathered part of sample *Pr2c* decreased, while the SiO_2, Al_2O_3, Fe_2O_3 and Na_2O content rose. The strontium, silver, gold, chromium, and uranium concentration fell, while the barium, yttrium, zirconium, vanadium, cadmium, copper, nickel, scandium, lanthanum, samarium and ytterbium concentration increased. The loss on ignition (LOI) was lower in the fresh part of limestone. Oxides made up 98.50 % of the fresh limestone and 99.14 % of the weathered part of the same limestone.

Comparison between the chemical compositions of the fresh and weathered parts of limestone in sample *Pr2* reveals that: - MgO, CaO, strontium, silver, gold, chromium, and uranium dropped; while: - SiO_2, Al_2O_3, Fe_2O_3, Na_2O, LOI (a loss on ignition), barium, yttrium, zirconium, vanadium, cadmium, copper, nickel, scandium, lanthanum, samarium and ytterbium rose. MnO, K_2O, P_2O_5 and antimony remained constant.

Two sub-samples, one from the fresh and the other from the weathered part of limestone of *Pr2* were analysed by the complexometric method. The results obtained are shown in Fig.129. The concentration of carbonates in samples from this cave is very high, from 99.3 to 100 %. In the sample of the fresh part of the limestone insoluble residue is completely absent, while in the weathered part it is below 1 %. In the sample of the fresh part of the limestone *Pr2,* the percentage of MgO is higher than in the sample of the weathered limestone, *Pr2c*.

The same sample was also analysed by EDS analysis on the SEM. Qualitative analysis the fresh and weathered parts of the sample, at the 150 × magnification, in windows of 100 x 100 μm, revealed the presence of following elements: - C, O, Ca, Mg as well as traces of Mo and Sr (Fig.70). The difference between both parts is in the magnesium content.

Semi-quantitative analysis of fresh and weathered limestone was carried out in

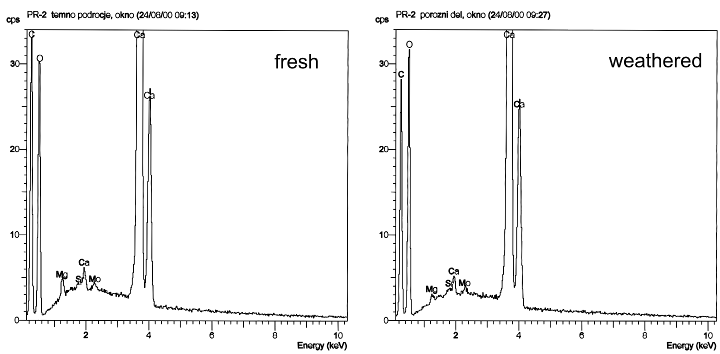


Figure 70: Measured spectrum from the fresh and the weathered part of sample Pr2, from the window 100 x 100 μm. The main difference between both parts is in the magnesium content.

windows dimensioned at 100 x 100 μm. Contents of Ca, Mg, Mo in Sr were measured as well; results are shown in Fig.71.

Comparing the analyses of the fresh and weathered parts of the limestone showed that they differ primarily in Mg content, in the weathered part it is 0.2 % lower, while the Sr content is also slightly decreased, on average by 0.03 %. The difference between average values of Ca, Mg, Mo and Sr from all three windows of the fresh and weathered part of limestone *Pr2* is given in the Fig.72. Differences in determining the surface arrangement of Mg in the fresh and weathered parts of the sample are too minute to be actually perceived (the absolute difference in weight % should amount to at least 5 % to be detected). In the weathered part of *Pr2* the Ca content is on average 0.26 % larger than in the unweathered part.

In *Pr2* sample the ratio of the organic carbon in the fresh and weathered parts was also measured (Fig.130). In the fresh part there is little organic carbon present, only 0.53 %, while in the weathered part its concentration is 1.01 %. The organic carbon content is higher in the weathered part of the limestone.

Pr2a	**net**	**net**	**net**	**net**		**total %**	**total %**	**total %**	**total %**
window	**MgK**	**SrL**	**MoL**	**CaK**		**MgK**	**SrL**	**MoL**	**CaK**
1.	1114	164	847	215847		0,5	0,1	0,4	99
2.	1284	413	799	218802		0,6	0,2	0,4	98,9
3.	1033	195	920	219441		0,5	0,1	0,4	99
Average Pr2a	**1143,67**	**257,333**	**855,333**	**218030**		**0,53333**	**0,13333**	**0,4**	**98,9667**
Pr2c	**net**	**net**	**net**	**net**		**total %**	**total %**	**total %**	**total %**
window	**MgK**	**SrL**	**MoL**	**CaK**		**MgK**	**SrL**	**MoL**	**CaK**
1.	571	153	886	210499		0,3	0,1	0,4	99,2
2.	769	135	779	213343		0,4	0,1	0,4	99,2
3.	652	144	746	210380		0,3	0,1	0,4	99,3
Average Pr2c	**664**	**144**	**803,667**	**211407**		**0,33333**	**0,1**	**0,4**	**99,2333**

Figure 71: Semi-quantitative analyse of four elements in three windows 100 x 100 μm of fresh (a) and weathered part (c) of sample Pr2 from Jama II na Prevali.

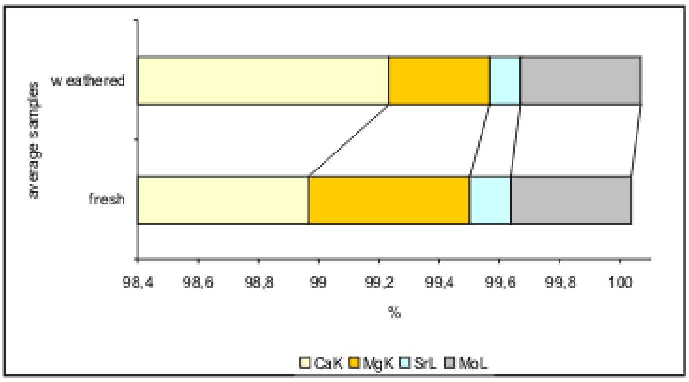


Figure 72: Difference between average concentrations of meausered elements by semi-quantitative analyse from fresh (a) and weathered (c) part of sample Pr2.

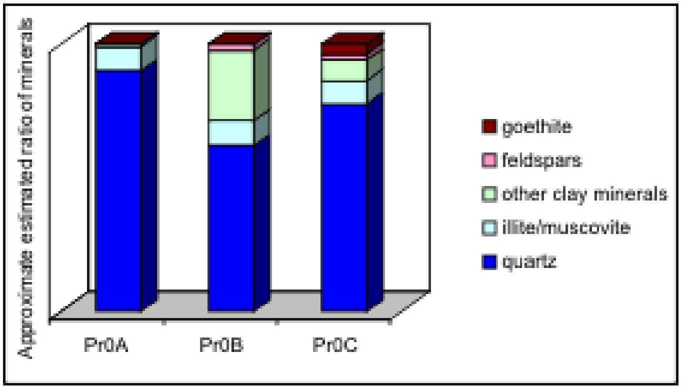
Sediment samples

In order to compare the mineral composition of the weathered cave wall and the fluvial cave sediment, three samples of the loam were analysed by X-ray diffraction. Resultes are givenin Fig.73. The first sample *Pr0A* is sediment from Žmohtni rov, while *Pr0B* is a sample of the loam that was stuck to the weathered and indented wall near limestone sample *Pr2*. Sample *Pr0C* is a black part of sample *Pr0B*.

Sample *Pr0A*, loam from Žmohtni rov, contains large quantities of quartz, smaller amounts of an illite/muscovite group mineral and traces of kaolinite, feldspars and goethite (Zupan Hajna 1995). Sample *Pr0B*, loam stuck to the weathered wall, contains abundant quartz, little of the illite/muscovite group mineral, plenty of other minerals (montmorillonite), and traces of feldspars and goethite. The black part of the stuck sediments, *Pr0C*, contains abundant quartz, insignificant amounts of illite/muscovite group mineral and other clay minerals, very little goethite, and feldspars only in traces.

The mineral composition suggests that the sand from the Žmohtni rov originated

Figure 73: The mineral composition of clastic deposits from cave Jama II na Prevali.



from flysch rocks. The sediment stuck to the wall has the same mineral composition as the sand, but it contains more clay minerals. These are by not, however, the insoluble residue of limestone; they are of allochthonous origin. The contact between the Palaeocene limestones and the Eocene flysch is located near the cave. The weathered flysch could easily be transported into the cave by a small sinking stream. Sands may also represent remnants of deposits by the larger stream of water that formed Škocjanske jame.

Conclusion

In the entrance passage area of Južni rov, Paleocene limestone has been weathered at the contact between the limestone and the sediment remnants. The field relationships and the mineral composition suggest that the sediment only influences weathering by its humidity and/or its capacity to retain moisture. The water it traps in the rock it affects the dissolution of limestone. There is no evidence that certain minerals from the sediments chemically react with limestone.

There was no indication that water was condensing in this part of the cave. However, the cave's micro-climatic conditions are not sufficiently known to entirely exclude the possibility of condensation corrosion occurring there.

JAMA POD PEČNO REBRIJO, REG. NO. 1577

An example where corroded cave wall surface is coated by secondary calcite

This cave was selected because its walls are covered by white substance, which on the first sight looks like weathered limestone (Fig.74) in desribed examples.

The cave is situated NE of Postojna, at an altitude of 650 m (y = 5440 160, x = 5070 620). According to Basic Geological Map, Sheet Postojna (Buser *et al.* 1967), the cave is formed in Upper Cretaceous limestones. It was formed along two bedding planes. The

Figure 74: White walls of cave Jama pod Pečno rebrijo (photo J. Hajna).

northern passage displays obvious phreatic origin characteristics. Cave plane is shown in Fig.75.

The shape of the wall surface in the northern passage suggests that incomplete dissolution of the limestone has occurred, with a residue of the original bedrock remaining on the wall. A more thorough survey of the sample revealed a thin layer of white microcrystalline crust on the wall surface its surface. This indicates that the wall was reshaped by condensation corrosion. The southern passage is shorter, while walls in the entrance area are coated with a thin layer of spar.

A strong circulation of air is present in both passages and consequently considerable quantities of condensed water are deposited on the passage walls. On individual parts of the wall finely formed features brought about by selective corrosion occur. Rudist shells, calcite veins and stylolites protrude from the surface. During the dry

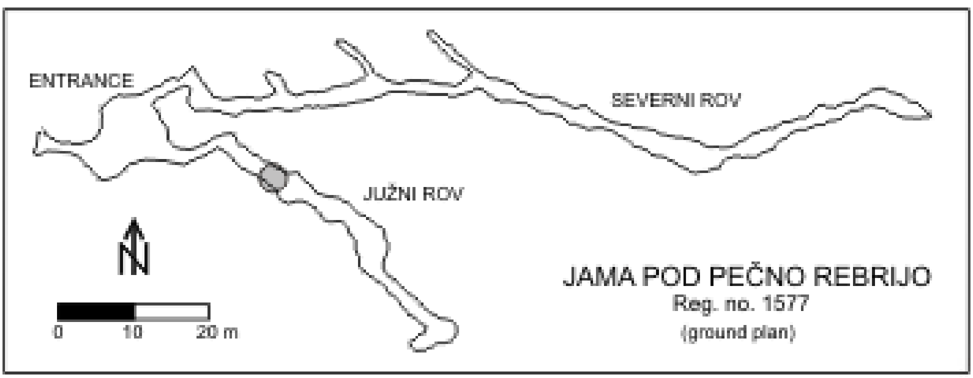


Figure 75: Ground plan of the cave Jama pod Pečno rebrijo (Cave Register of IZRK ZRC SAZU).

periods calcite spar was precipitated from the condensation on the corroded wall. Slabe (1988) described the same phenomenon occurring in Komarjev rov in Dimnice. The boundary between the rock and the coating is sharp and conspicuously delineated (Fig.76).

Figure 76: Grey limestone with corroded surface is covered by thin calcite coating.

CROSS-SECTIONS OF THE SAMPLES

Sections of the weathered limestone and dolomite were examined microscopically. Thin-sections were made from some of them. The progress of dissolution and the advancement of moisture into the weathered limestone were examined under the electronic microscope.

Initial samples from the cave were quite sizeable so it was possible to obtain several cross-sections out of them and also to separate them, into sub-samples for mineralogical and chemical analyses. Differences in results obtained by different methods occurred, because the chemical or mineral composition of samples may change according to the micro-location of the analysis.

LIMESTONE CROSS-SECTIONS

Laminated limestone

Sample *Kr1* is laminated limestone from Krempljak cave limestone taken from the transitional strata between Lower and Upper Cretaceous ($K_{1,2}$). The surface of the sample is weathered, slightly granular and white. The sample itself is a dark limestone, with a white (N9) - coloured intensely weathered edge that is very porous and ranges in width from 0.5 cm to 2 cm. The weathered edge of the limestone is dry and solid.

Cross-section of the sample Kr1 is given in Fig. 77. In the sample's interior, zones of different weathering stages succeed each other; each zone is a different shade of grey ranging from N7 and N6 (most weathered) to N4 (fresh limestone). In cross-section, the fresh part is not homogeneous. In its lower part it is firstly light grey (N4) and homogeneous, then it subsequently passes into the breccia with parallel oriented lighter clasts (light grey N7). The upper part of the cross-section is compact, homogeneous and medium grey in colour (N6); it is weathered. The transition between the porous partand the discoloured yet non-porous part is fairly sharp, very light grey (N8), except that at places where they are separated by fissures, light grey (N7) areas may occur. The extreme outer edge and the area beside the fault are of white colour (N9) and are very porous.

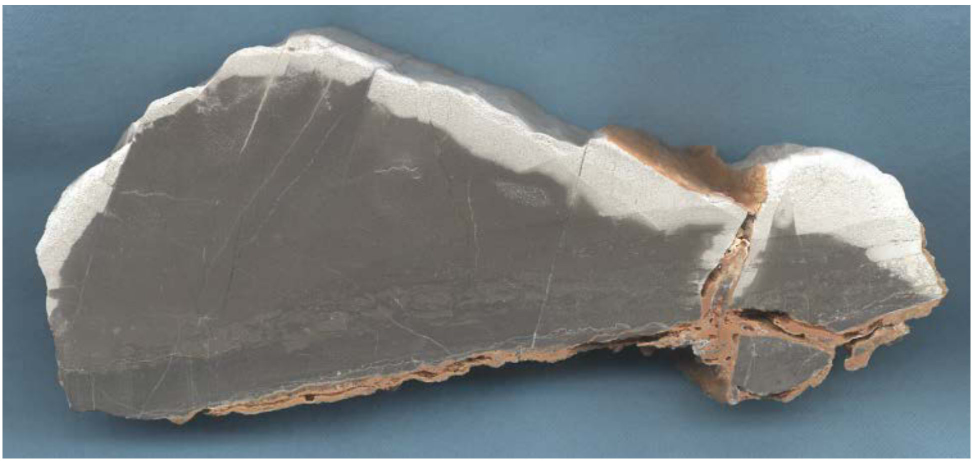


Figure 77: Cross-section (16 cm) of sample Kr1. Limestone is weathered in different degree.

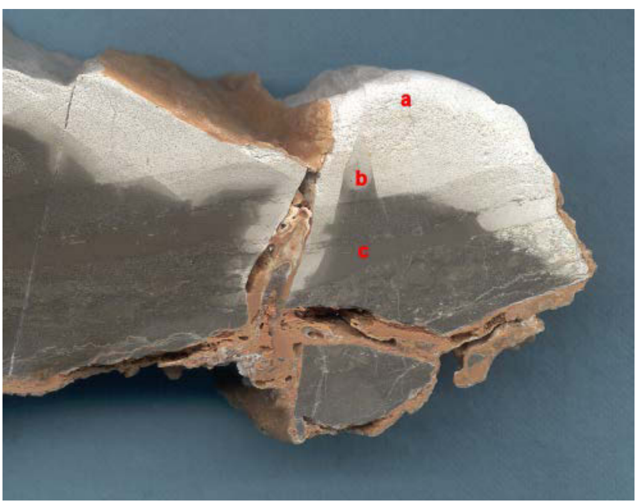


Figure 78: Detail of sample Kr1 cross-section (6 cm). Displacement of weathering zones along open fissure indicates that fissures are younger then weathering. Legend: a – weathered zone, b – discoloroued zone, c – fresh limestone.

The sample is intersected with numerous fissures; some of them are open, others filled with calcite. Alongside some open fissures an intensified weathering processes may be noticed. The sample is fractured and in the resulting crack brown sediment has infiltrated. In this mud secondary, strongly porous calcite has crystallised. Near the same crack textures in the limestone are displaced by 5 mm (Fig.78). The weathered zones are similarly displaced, indicating that the rock had been weathered before it broke apart.

Limestone breccia

Two samples of the fine limestone breccia, *Ma1* and *Ma2* and a sample of homogeneous limestone, *Ma3*, which was already completely weathered, were collected from Martinska jama. The limestone originates from the transitional beds between Lower and Upper Cretaceous ($K_{1,2}$).

Sample *Ma1* is a piece of limestone with a 30 to 45 mm thick weathered edge (Fig 29). The sample's surface is soft, very porous and partly covered by brownish crust and black coating and a net of tiny holes are developed (Fig. 30).

Figure 79: Cross-section (11 cm) of sample Ma1. Weathered limestone is brecciated, it contains fragments of fossiles and intraclasts.

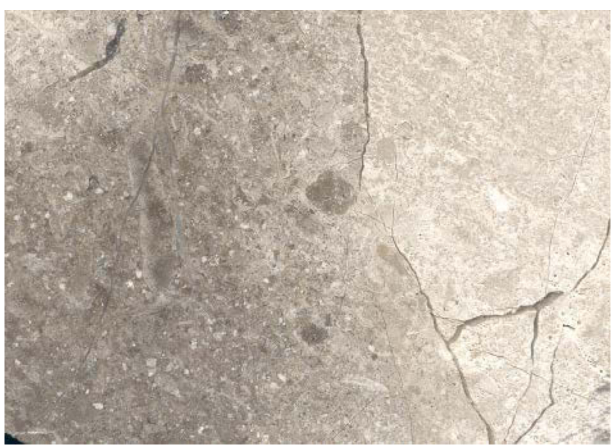


Figure 80: Detail (2 cm) of sample Ma1. Weathered limestone is brecciated, it contains fragments of fossiles and intraclasts.

The limestone is variegated in colour, very finely brecciated and contains broken fragments of fossils and intraclasts. There is no entirely fresh limestone in this cross-section (Fig.79). In the middle of the sample, the less weathered part is separated from the rest by a calcite vein (Fig.80). Towards its edge the sample becomes more light-coloured and porous. The fresh part of the limestone that remained on the wall is medium grey (N5). The surface of the cross-section passes from the limestone of medium grey colour N5 into the pink grey colour 5YR 8/1 towards its edges. The sample is criss-crossed by numerous calcitised fissures and a few holes also occur in the weathered part.

In the central part of the sample *Ma1* the limestone is less weathered, and contains broken fragments of fossils and differently coloured lithoclasts. Close to both calcite veins the limestone is more intensively discoloured, while from veins toward the edges even greater discoloration and an increase in porosity is distinctly exhibited. In the outer, weathered part of the sample some points are less weathered and of darker colour. These points belong to intraclasts, which weather in a different way to the other parts of the limestone.

In thin-section there are large intraclasts are observed, which display signs of previous dissolution. Limestone contains intraclasts, fossil remains of algae, fragments of rudist shells and of Orbitoids. There are also some pellets and reddish coloured micrite. The sample is criss-crossed by calcite veins. The micrite base is predominantly re-crystallised, while in the dissolved micrite base sparite grains are growing. Sample *Ma1* can be described as a biointrepelmicrite (grainstone).

Sample *Ma2* is non-homogeneous limestone with weathered edges from the western wall of Boeganov rov, from below the most prominent bedding plane in the passage (Fig.31). Above the bedding plane there is a rocky shelf, on which the residue of the fluvial sand deposit is lying.

The sample's surface is smooth, weathered and white and without flowstone; its

Figure 81: Cross-section (11 cm) of a weathered limestone sample Ma2. The edges are completely weathered, sample is crossed by calcite veins.

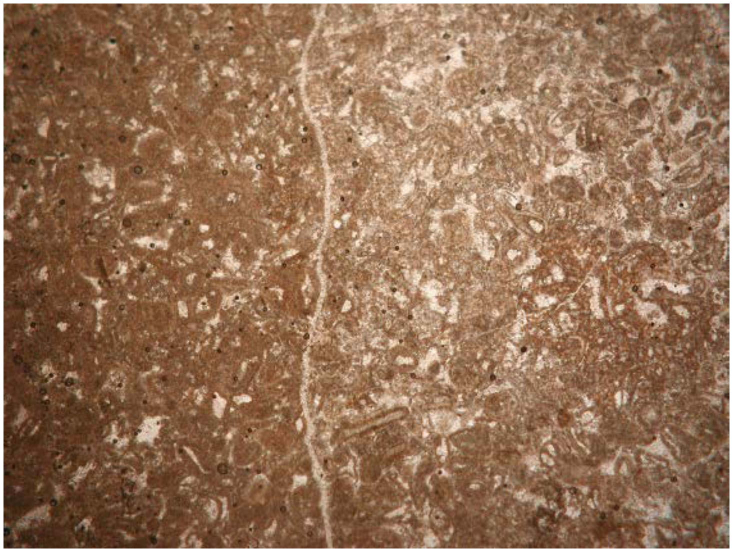


Figure 82: Thin-section of sample Ma2. Less and more weathered sides are divided by calcite vein. More weathered part is discoloured, more porous and some pores are filled by calcite cement.

Figure 83: Cross-section of weathered limestone sample Ma3 (5 cm). Sample is wholly weathered, with some dissolutional holes in it. Connected holes of different diameters may act like the first channels in karst development.

upper part was in direct contact with the sediments. At the side, where it has been in contact with the passage wall it is a reddish brown colour (7.5YR 6/8) due to the sediments infiltrated along the fissure (Fig.32). The soft part of the sample is from 8 to 80 mm thick, while its interior is discoloured. Sample Ma2 is shown in Fig.81. The fresh part of the rock is medium grey in colour (N5), while the discoloured part is very light grey (N8) and the weathered part is white with a pink grey hue (5YR 8/1). Limestone cross-section is crossed by calcite veins; three of them are particularly expressive. The boundary between the dark central part and the upper discoloured, and in this case also more porous, is sharp. The sample's edges are thoroughly weathered, very porous, soft and white (N9).

The thin-section reveals that the interior of the limestone contains many bioclasts, pellets and intraclasts. Calcite veins intersect the limestone, while part of the micrite is re-crystallised. The outer part of the limestone is extensively weathered, as is another part in the middle of the sample. Brown micrite is abundant in the porous part of the sample. The weathered limestone in the sample is partly re-crystallised biointrapelmicrite. On Fig.82 the transition between more and less weathered part is expressed.

Sample *Ma3* was collected t from the lower part of the NE wall of Boeganov rov, where the limestone is heavily weathered. A cross-section of the sample is shown in Fig.83. In the lower part of the sample there is a smaller dark patch of medium grey colour, N6, which is compact. Otherwise the sample is heavily weathered, discoloured and porous. The weathered part ranges from pink grey (5YR 8/1) to white (N9) in colour. In the cross-section some open fissures are seen, along which the limestone is more intensively weathered. This is reflected in an overall greater porosity. Holess formed by corrosion can be detected along fissures in the sample.

Homogeneous micrite limestone

Sample *BJ1* is micritic limestone from Pečina v Borštu cave. The limestone dates from the early Cretaceous (K_2^2). In sample *BJ1,* the limestone passes from solid rock to soft, that is, from the less porous to very porous limestone. Tiny holes from 2 mm to 8 mm in diameter and up to 10 mm deep are dispersed all over the sample's surface. Part of the sample is coated with a thin, brown layer of flowstone.

The limestone in the sample is fairly homogeneous; the discoloration is more or less even, some darker patches with irregular shapes only occur close to the centre of the sample. At room temperature the dried sample is light pink-grey (5YR 8/1) in colour. Initially disintegrated, partly discoloured rock is a light grey colour (N7), while fresh rock from Končna dvorana is light grey (N6). The porosity is greater in the more intensely discoloured parts of the sample.

Two cross-sections of the sample were examined. The surface of the first section (Fig.84) is evenly coloured and fossil fragments are not apparent. The sample is criss-crossed by open fissures, adjacent to which there are some larger hollows. Most of the fissures are completely or partly filled with milky white calcite. The surface of the entire cross-section is very weathered. The extent of the discoloration varies from partial in the lower part of the sample (light grey N7) to pronounced (very light grey N8) or almost complete (pink grey 5YR 8/1) in the strongly porous part of the cross-section. Along its edges the sample is noticeably porous, to the extent that individual granules fall off. A very distinct gradual transition from partly discoloured rock into entirely discoloured and strongly porous rock is clearly visible.

The second cross-section is more homogeneous (Fig.85); gradual discoloration and there is a conspicuous increase in porosity from the centre of the cross-section toward its edges. In thin section the limestone is thoroughly recrystallised and weathered. Broken fragments of fossils (which are likewise weathered) and numerous calcite veins are visible, as well as a pronounced inter-granular porosity. The limestone is a heavily weathered recrystallised biomicrite.

Figure 84: First cross-section (11 cm) of weathered limestone sample BJ1. Sample is discoloured, strongly porous along the edges, along the fissures and on the surface there are some holes

Figure 85: Second cross-section (6 cm) of weathered limestone sample BJ1. Different degree of discoloration is visible in cross-section.

Recrystallised biomicrite limestone

Two samples of recrystallised biomicrite limestone from Jama II na Prevali, *Pr1* and *Pr2* were examined. The limestone is early Palaeocene (Pc_2) in age.

Sample *Pr1* is from a rocky horn, which protruded into the pathway. The limestone in this part of the wall is weathered to a depth of several centimetres. The weathered part of the rock is very wet and soft. Calcite veins, among which a web-like pattern of tiny hollows is arranged, stand out from the sample's surface. The calcite veins are heavily weathered and soft to the feel as well as wet. The surface of sample *Pr1* is weathered and covered by the brownish microcrystalline spar and a crust of the brown flowstone. In the cross-section the tiny holes were not seen. Two cross-sections of this sample were examined.

The surface of the first cross-section is unevenly coloured (Fig.1). It changes from dark to medium grey (N5) and subsequently from slightly lighter grey to light grey (N7). One section the sample, that contains perceptible fossil remains and differently coloured lithoclasts, stands out from the rest. The sample is criss-crossed by open fissures, along which the rock is more intensely weathered. Alongside the fissures tiny hollows occur, which were formed by dissolution. Some fissures contain infiltrated sediments. The transition from grey, compact limestone to porous and discoloured limestone is very distinct. The intensely weathered edge of the sample varies from very light grey (N8) to white colour (N9) and is also soft due to porosity.

The second cross-section is more homogeneous (Fig.86); its centre is dark, medium grey (N5) and compact; individual foraminifera may be discerned within it. The transition from fresh limestone to porous and completely discoloured limestone is sharply delineated. The weathered edge of the sample is white (N9) in colour. Its porosity ranges from limited to strong. The cross-section is crossed by open fissures, along which the rock is more intensively weathered towards its interior. A brown flowstone crust coats the sample's surface, which is thicker in its lower part.

Figure 86: Second cross-section (7 cm) of a weathered limestone sample Pr1.

Figure 87: Cross-section (7cm) of a weathered limestone sample Pr2. Open fissures help water to penetrate deeper into the sample.

In thin-section the limestone is seen to contain foraminifera, Miliolida - caracteristic for Thanetian, and algae. Besides fossils the limestone also contains intraclasts and pellets. Individual clasts are oriented and sin-sedimentary fillings may also occur. The micrite base is largely recrystallised into microsparite (grainstone). The limestone is recrystallised intrabiopelmicrite.

Sample *Pr2* is a piece of rock, with a weathered edge up to 2.5 cm wide, which was removed from the western wall of the passage. Its surface is covered with a network of tiny hollows approximately 0.5 cm or more in diameter in which there tooth marks in form of 5 tiny parallel flutes. The surface of sample *Pr2* is weathered, indented, and coated with a deposit of brownish spar. The sample's cross-section is illustrated in figure. The surface of the cross-section is unevenly coloured; the transition from compact dark, medium grey (N5) limestone to lighter, light grey (N7) limestone is clearly visible. In the compact part of the cross-section fossil remnants and individual bright points can be seen. Sample cross-section (Fig.87) is crossed by open fissures, some of them are filled with calcite.

Fissures for the most part accelerate the progress of dissolution; a single one, however, obstructs its advancement into the compact part of the rock (Fig.88). The transition from grey compact limestone to porous, discoloured limestone is sharp, but wavy.

In thin-section the limestone is seen to contain fragments of recrystallised crinoids and foraminifera. Intraclasts and pellets are also present. The sample is criss-crossed by calcite veins. The micrite base (matrix) is largely recrystallised into microsparite. The limestone is a recrystallised intrabiopelmicrite. The outer part of the limestone is so intensely weathered that its textures are hardly detectable.

Figure 88: Detail (2,5 cm) of sample Pr2 cross-section. Penetrating of weathering is well expressed, calcite vein stops its progressing.

Secondary calcite on the corroded wall surface

A sample of Upper Cretaceous limestone, from Jama na Pečni rebri, was examined to determine the difference between weathered rock and spar-covered rock in cross-section. Sample *Jp1* is limestone from the southern passage of Jama na Pečni rebri. It is incised by condensation corrosion and covered by white calcite crust and coating. In cross-section the fresh limestone is white (N7) in colour (Fig.89). The sample is intersected by several calcite veins and does not show any signs of weathering. The limestone is solid and compact, evenly coloured and with evenly arranged bioclasts, particularly fragments of rudist shells. Calcite coating covers selectively - corroded surface of the sample. It is obvious that the limestone is not weathered but that its corroded surface is coated by secondary calcite.

Figure 89: Sample Jp1 cross-section (5 cm). Fresh limestone surface is corroded, fossils are jutting out, and covered with calcite crust.

SEM OBSERVATIONS ON THE TRANSITION FROM FRESH INTO THE WEATHERED ZONE OF LIMESTONE

The transition of from fresh to weathered part was distinctly visible in thin-sections examined by SEM. This can be best seen in sample *Ma2* from Martinska jama and sample *Pr2* from Jama II na Prevali.

Sample Ma2

Images of the surface of sample *Ma2* were taken with secondary electrons at magnifications of 80 ×, 1000 ×, and 2000 ×. The weathered parts of this limestone are not evenly distributed; consequently there are large unweathered areas, which appear as dark patches and belts. Two dark belts of unweathered limestone, shown in the image, are between 120 and 140 μm wide (Fig.34).

Small and larger-sized pores (from 0.5 to 10 μm) occur in the fresh part of the micritic limestone (Fig.90). In the weathered part (Fig.91) the matrix consists of calcite grains, approximately 1 ěm in diameter on average. There are also some larger grains up to 20 μm in diameter interspersed within it.

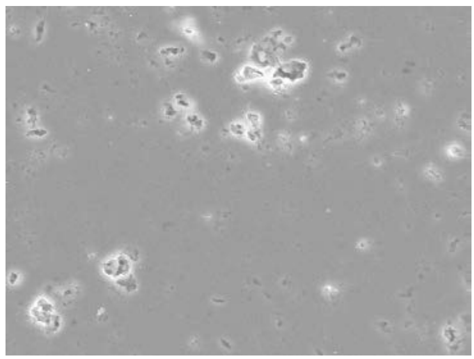


Figure 90: There are some pores presented in fresh part of micrite limestone in sample Ma2 (width of the photo suits to 132 μm).

Sample Pr2

Images were taken of two thin-sections of sample *Pr2* to show the transition from the compact fresh limestone to the porous weathered zone. In these sections the transition is distinctly delineated.

Images of the polished surface of sample *Pr2* were taken with secondary electrons at magnifications of 80× and 1000×. In sample *Pr2*, the boundary between the weathered and unweathered zone is conspicuous and the transition between them is rapid. The fresh part of the sample is dark-coloured, and little porosity is visible. The weathered zone is light-coloured and highly porous.

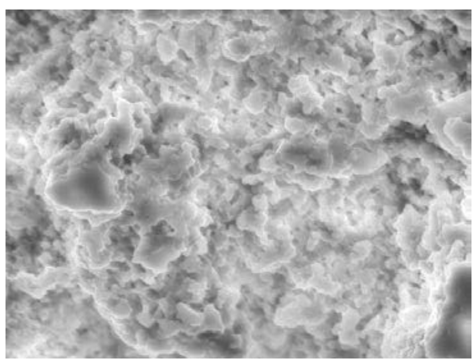


Figure 91: Weathered part of micrite limestone in sample Ma2 (width of the photo suits to 132 μm).

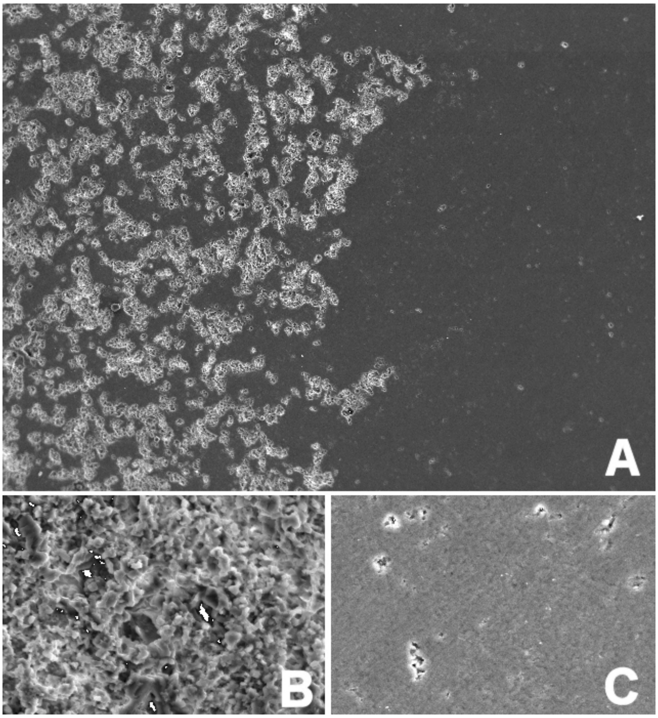


Figure 92: Transition between fresh and weathered part of limestone sample Pr2 is represented in part A (width of the photo suits to 1,65 mm), weathered limestone is in part B (width of the photo suits to 132 μm), and non-weathered in part C (width of the photo suits to 132 μm).

An uneven yet rapid transition from fresh limestone to the weathered zone is fairly well seen in this thin-section (Fig.92). The darker part of the image is fresh limestone, while the light part is the weathered zone. In the fresh limestone, the grains are arranged in a compact manner with individual pores measuring from 0.5 to 3 μm. In the areas at contact between fresh and weathered limestone, the porosity is much greater. In the porous part of the limestone the calcite grains are generally 1 μm in diameter, with some individual grains up to 8 μm. In the weathered zone of sample *Pr2* the edges of calcite grains are also dissolved. As the strangeness a microtexture following contacts between granins can be discerned, becoming visible at a magnification of 1000 ×. In sample *Ma2*, the same microtexture was only visible at a magnification of 3000 ×, indicating *Ma2* is a micrite, while *Pr2* it is almost entirely recrystallised into microsparite.

DOLOMITE CROSS-SECTIONS

Early diagenetic dolomite

Sample *LP1* is Lower Jurassic (J_1), dolomitised limestone from Mala ledena dvorana in Velika ledena jama in Paradana. The limestone has dry pores filled up with calcite crystals. The outer part of the sample is a completely weathered in a few millimetres thick zone (Fig.93).

Figure 93: Dolomitised laminated limestone sample LP1 (9 cm) from Velika ledenica v Paradani; the surface of the sample is weathered and rough.

Late diagenetic dolomite

Sample *TJ2* (Fig.94) is the Upper Triassic (T_3^{2+3}), dolomite from Turkova jama. A transition from compact dark, medium grey (N5) dolomite to the brighter light grey (N7) dolomite can be seen in the sample. The darker, less weathered part of the sample is light grey (N7) in colour while towards the outer, more weathered zone the colour becomes very light grey (N8).

Figure 94: Weathered late diagenetic dolomite TJ2 (4,5 cm) from Turkova jama is crossed by many fissures.

Sample *Rm* (Fig.95) is Upper Triassic (T_3^{2+3}), dolomite from Remergrund II cave. Its surface is weathered and rough, with individual dolomite grains protruding out from it. The dolomite's colour is evenly distributed, weathering being most intense at the outer edge of the sample. The unweathered part of the sample is dense dolomite with

Figure 95: Weathered late diagenetic dolomite Rm (4 cm) from Remergrund II; edge of this sample is entirely weathered.

a medium light grey (N6) colour. The weathered edge is very porous and white (N9). This sample is a late diagenetic dolomite (dolosparite) with detectable intragranular porosity that has been intensely weathered along its edges. Dissolution progressed into the rock along contacts between grains, which are intensely weathered, and along open fissures.

Figure 96: Weathered late diagenetic dolomite LP6 (5 cm) from Velika ledenica v Paradani edge of the sample is entirely weathered.

Samples of Lower Jurassic dolomite (J_1) were collected from Velika ledena jama in Paradana. Sample *LP6* (Fig.96) is grey dolomite from Glista. The outer part of the dolomite in this sample is heavily weathered and porous. Its surface is very rough and completely discoloured with individual rhomboid-shaped grains protruding from it.

Figure 97: Weathered late diagenetic dolomite LP7 (5 cm) from Velika ledenica v Paradani is completely weathered.

Sample *LP7* (Fig.97) is coarse-grained dolomite collected from under the first shaft in Glista; it also has a very rough surface.

Sample *LP8* (Fig.98) is coarse-grained dolomite collected from the wall surface of the small-sized shaft in Stopnje. The sample's surface is very rough and sandy. Sheets of crystallised calcite protrude from it.

Figure 98: Completely weathered late diagenetic dolomite LP8 (4 cm) from Velika ledenica v Paradani.

Sample *LP9* (Fig.99) is recrystallised, dolomitised limestone from the same shaft as sample *LP8*. It is very weathered, both inside the rock and at its surface, which is covered by a thin layer of flowstone. Weathering is particularly intense along open fissures. Selective dissolution has removed the micrite component of the rock, leaving rhomboid dolomite crystals protruding from the sample's surface.

Figure 99: Recrystallised and dolomitised limestone LP9 (5 cm) from Velika ledenica v Paradani is completely weathered.

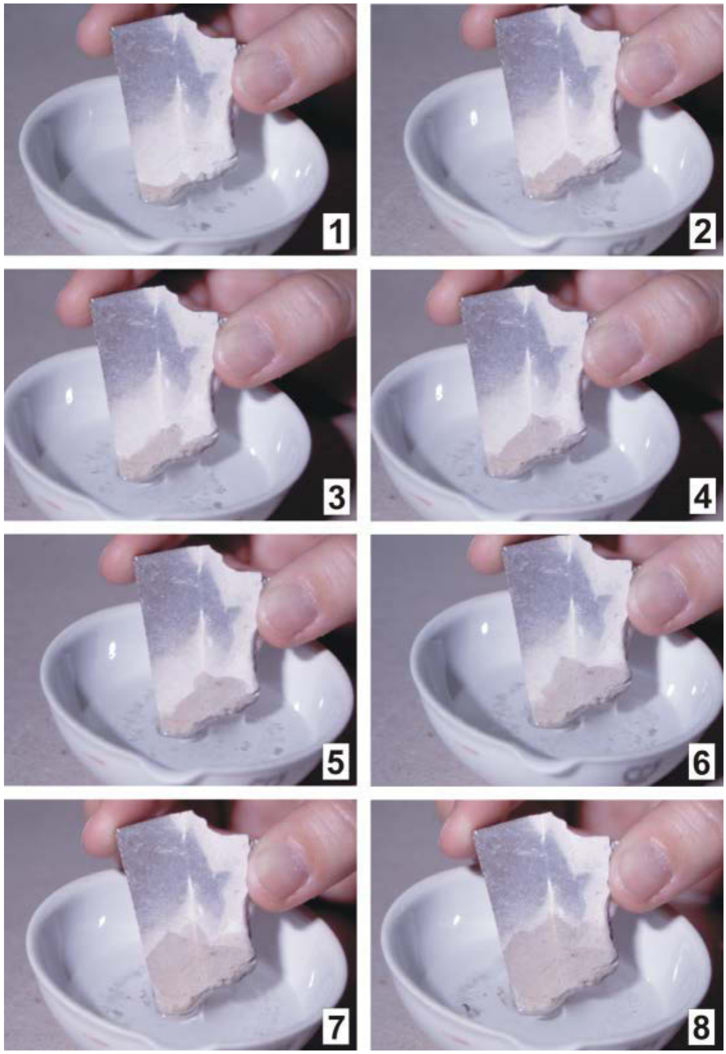
ABSORPTION OF MOISTURE INTO THE WEATHERED ZONE

Since the weathered zones of rock in the caves are exceptionally wet after rainfall, I attempted to find out how water was absorbed into the weathered rock. I selected a piece of sample *Ma2* (Fig.100), and placed its edge in contact with water in a test container. The experiment continued until the moment when water reached the end of the weathered zone. The data obtained by these measurements are given in Figure 101.

At the beginning of the experiment, the sample weighed 28.65 g. After 5 minutes of moistening its weight increased to 31.64 g. The difference in weight is equal to 2.99 g. In this difference also includes detached particles, which were floating on the surface of the water; their total weight was 0.1414 g (Fig.102).

This shows that in a mere 5 minutes, almost 3 g of moisture, which in a cave could be aggressive water, is absorbed into and could react with, the sample.

Figure 100: Part of a limestone sample Ma2 (2 cm), which was used in experiment of moisture penetrating into the weathered zone.



STAGE	TIME	PENETRATING OF MOISTURE
1.	10"	To first calcite vein; 0,4 cm from source.
2.	20"	To main fissure; 1,2 cm from source.
3.	29"	Towards second calcite vein; 2 cm from source.
4.	40"	To second calcite vein; 2,4 cm from source.
5.	56"	Along main fissure in the middle and across calcite veins.
6.	1' 25"	Along main fissure and along edges.
7.	3' 30"	Along edges to calcite veins.
8.	5' 07"	Almost to the top of weathered (discoloured) zone.

Figure 101: Description of the moistening experiment; there are eight significant steps in water progress in about 5 minutes long experiment.

Sample Ma2	Sample weight (g)
Dry	28.65
Wet (5 minutes)	31.64
Difference	2.99

Figure 102: Moisture rate in the sample Ma2 after 5 minutes of moistening the sample weight increases for about 9.4%.

Penetrating of the water into limestone sample is shown in Fig. 103. A prominent open fissure runs along the middle of the sample. Beside this fissure the rock is the most intensely weathered. Two calcite veins are found in the sample's cross-section. These act as a barrier to the progress of moisture and thus also to weathering. Both calcite veins are not weathered, so moisture bypasses these obstructive veins in open fissures that intersect them, as well as along the sample's edges, where calcite veins are weathered and thus permeable to water.

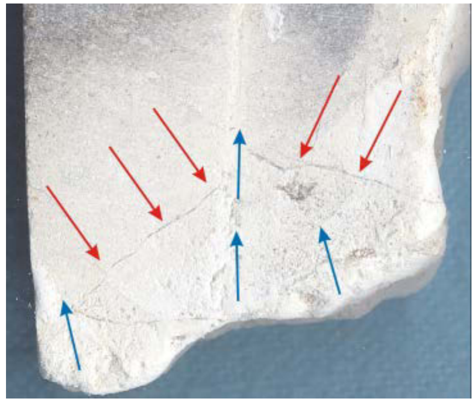


Figure 103: Main open conduits where water penetrates into weathered zone are marked blue and calcite veins functioning like barriers are marked red.

CONCLUSIONS CONCERNING CROSS-SECTIONS

The samples of weathered limestone and dolomite are weathered to different extents. In some cases only the sample's edge is weathered and the transition from fresh to weathered part is sharply delineated; while in others the transition may be gradual, continuing from a completely weathered edge across the discoloured zone and into the fresh part.

Only the edge is weathered in cases when the sample is homogeneous and the rock has not been influenced by selective dissolution for a longer period of time.

Figure 104: The most weathered layer is the surface part of the cave ceiling, deeper layers are less weathered; Krempljak cave.

Continued transition from the weathered zone into the fresh part of the sample is present, when the rock is homogeneous and dissolution advances into it in an even manner. A stepwise transition from the weathered zone to the fresh part is related to stratification in the sample, where individual layers are weathered to different extents (Fig.104).

SURFACE OF THE WEATHERED WALL – CHARACTERISTICS AND PECULIARITIES

Figure 105: The initial stages of boxwork on the cave wall may start to form by calcite veins and/or stylolite protruding from the surface.

Figure 106: Number of holes on the weathered wall in Jama II na Prevali.

During the weathering of carbonate rocks in the cave environment a process of incomplete dissolution is taking place. This dissolution is markedly selective and advances into the rock more easily and quickly along fissures and bedding planes. Small grains are dissolved first during the dissolution process.

These processes are subsequently reflected in the surface roughness of the carbonate rock. The surface texture of the weathered wall depends on textures (fossils, laminations, calcite veins, grain-size (sparite, micrite, etc.), present in the carbonate rock prior to weathering. As a result of weathering prominent calcite veins and/or stylolite may start to form the initial stages of boxwork on the surface of the wall (Fig.105), and fossils may protrude from the surface (Fig.44).

Tiny holes, with diameter of up to 1 cm and up to few cm deep, develop in the surface of the weathered wall. Holes appear in different stage of development: they are single or in number (Fig.106); they are developed in mud covering weathered rock; they are presented in total weathered rock, in soft material (Fig.107), or in still hard weathered rock; they are covered by flowstone crust (Fig.108) or they are cemented

(Fig.109). They are often arranged into a sort of a network, which displays a rhomboid form (Fig.110). According to the literature, these hollows could be a consequence of the action of microorganisms, but these explanations, have yet to be tested. I have presumed that the holes could also arise from the drying up of the damp weathered matter or from more intensive dissolution at certain places where pores are connected into small channels and are broadening due to dissolution (Fig.82).

The weathered wall may be soft when it is wet, also different in a colour, and solid when it is dry (Fig.111). Frequently it is covered with a thin crust of reddish-brown flowstone, which is so thin that the texture of the wall's surface may shimmer through it (Fig.112). Flowstone crust can be corroded after all (Fig.113) and weathered surface is exposed again. Porous weathered rock can be also cemented if inflowing water becomes saturated (Fig.24).

Special phenomena are tracks of dormice on the weathered cave walls (Fig.59). Thiny flutes, five of them in a package (Fig.114) are presented in many cave, specialy abundant are in cave Jama II na Prevali. Tracks of teeth and already biger holes are presented along

Figure 107: Holes in a soft weathered wall from Martinska jama (photo J. Žumer).

Figure 108: Holes in a soft weathered cave wall, covered by brown flowstone crust from Pečina v Borštu. Holes appear also through flowstone crust.

Figure 109: Cemented holes at the bottom of Pečina v Borštu cave. Wall is covered by mud also.

Figure 110: Holes arranged into a network, which displays a rhomboid form, Pečina v Borštu.

Figure 111: The weathered ceiling is different in colour and in hardness when wet, Krempljak cave (photo J. Žumer).

Figure 112: Weathered wall is covered with a thin crust of reddish-brown flowstone, which is so thin that the texture of the wall's surface may shimmer through it.

the weathered walls. They were gnawed out in many generations (Fig.115).

The weathered wall is not covered by a flowstone crust where is in direct contact with the clastic deposits. In such instances the wall surface is smooth, without boxwork or holes, while the boundary between the weathered wall and the sediment is sharply defined (Fig.52).

Figure 113: Flowstone crust can be corroded by aggressive water flow, cave wall in Pečina v Borštu (photo J. Hajna).

Figure 114: Tracks, teeth or claws, of dormice on the weathered cave wall, detail; Jama II na Prevali.

Figure 115: Single tracks and holes of different generations on the wall of Jama II na Prevali.

FORMATION OF AUTOCHTHONOUS CARBONATE CLASTS - CASE STUDIES

This chapter describes caves that have part of their passages developed in limestone and part developed in dolomite. Examples are the caves at Kaninsko pogorje. Upper parts of the caves are developed in Dachstein Limestone, while the lower parts are developed in Main dolomite. Another case is the cave Velika ledena jama in Paradana, the passages of this cave are developed in Jurassic limestone and dolomites.

GEOLOGICAL AND SPELEOLOGICAL CHARACTERISTICS OF KANINSKO POGORJE

The greatest number of deep caves in the Kaninsko pogorje region is found at Rombonski podi (Gabrovšek 1997). In the cave investigated there is a succession of a series of shafts with meanderening canyons in between and older, but now inactive horizontal passages (Audra 2000).

Collapse blocks and gravel occur in the vertical parts of the caves, while in the horizontal parts older stratified loam and sands, which are occasionally covered by recent sands and clay, are currently being washed away by trickles of water. Recent fine-grained sediments are mostly accumulating under active shafts in the deeper parts of the caves (Manca 1998).

X -ray analysis of selected loams from caves Črnelsko brezno, Čehi 2 and Renejevo brezno, was undertaken as a part of this carbonate autochthonous clastic sediments research. The entrances of these caves are located in the Goričica under Hudi vršič area north of Rombon and Renejevo brezno at Kaninski podi (Fig.116).

The basic data for the caves is taken from Cave Register of Speleological Association of Slovenia and Karst Research Institute ZRC SAZU.

The Basic Geological Map, 1 : 100 000, Sheet Beljak and Ponteba (Jurkovšek 1986) shows that the Kaninsko pogorje region is composed of Upper Triassic Dachstein Limestone. The Limestone layers dip generally SW direction at an angle of 15^0 to 40^0. At the base of the Dachstein Limestone there is the Norian-Rhaetian "Main dolomite", which

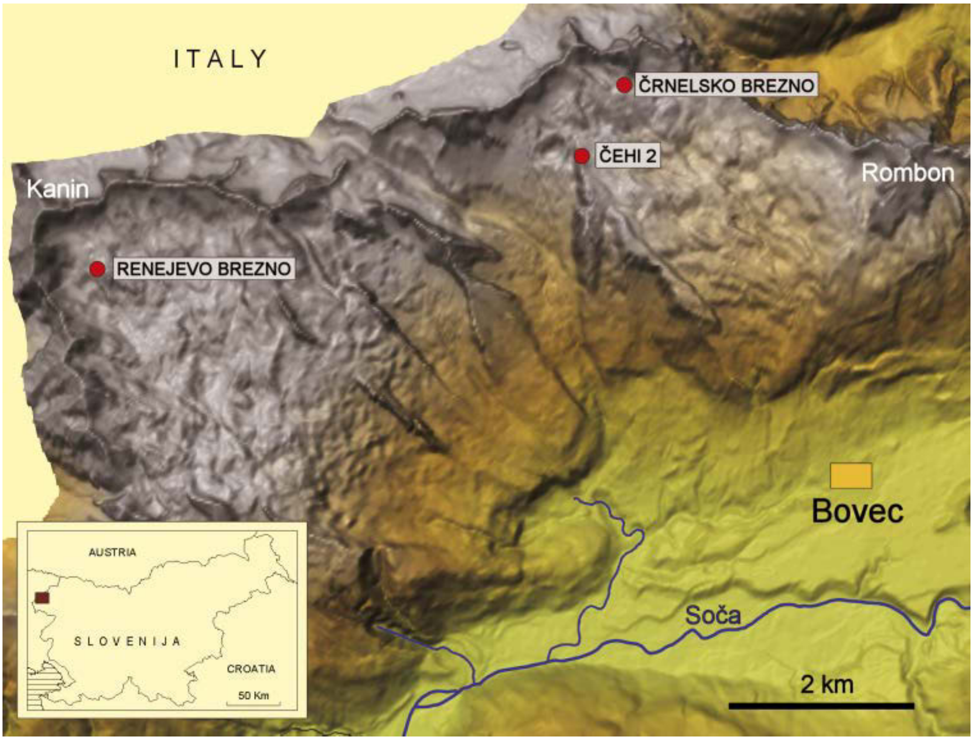


Figure 116: Position of the caves Čehi 2, Črnelsko brezno and Renejevo brezno on Kanin mountain.

is clearly visible in the Možnica and Krnica valleys, as well as in deeper parts of certain caves. The Dolomite dips to the SW at angles of 25^0 to 50^0. In Led Zeppelin Cave on the Italian side of mountain Kanin, cavers came across dolomitised limestone at a depth of 800m (1330 m asl.). Dolomite layers occur at a depth of approx. 850m and continue down to the cave's bottom at a depth of 960m (Manca 1998, Audra 2000). In Vandima cave, dolomitised limestone was not detected until the very bottom of the cave (-1042 m), yet it was found in two neighbouring caves Čehi 2 and Črnelsko brezno (Gabrovšek & Pintar 1993). Gabrovšek & Pintar (1993) concluded that the predominantly horizontal and easily passable cave galleries with numerous chambers and gorges with lakes developed along the contact zone between the limestone and the strongly dolomitised limestone - almost dolomite.

Gabrovšek (2000b) recorded that at a depth exceeding 700 m in Renejevo brezno there are heavily weathered meander walls where the weathered zone extended for several cm into its interior. Water had washed the weathered fragments away from the wall and these grains were accumulated as white mud at the bottom of the cave. Some of this mud was carried further along the passages by water where it was cementing the breakdown blocks together.

Clastic sediment samples were obtained for me from Čehi 2 cave, Črnelsko brezno and Renejevo brezno. These caves are deep shafts at Kaninsko pogorje between Veliki Kanin and Rombon mountains. The piles of carbonate sand are presented also at the bottom of shafts in Skalarjevo brezno on mountain Kanin, but unfortunately I did not sample them.

CAVE ČEHI 2. REG. NO. 6200

The entrance into Čehi II cave lies on the mountain-ridge south of Hudi vršič at an altitude of 2034 m (y = 53855 735, x = 5136 950). Deep shafts succeed one another, crossed by horizontal galleries, to a depth of 900 m after which the cave continues in the form of sloping passages intersected by some smaller shafts. With a total depth of 1533 m, this cave is currently is the deepest cave in Slovenia.

Clastic sediment samples

The passage walls at the bottom of the cave, 1485 m below the surface, are extensively weathered (Marinšek 2002). Glažar S. collected samples of clastic sediments from the cave. The location of samples is indicated in the extended profile (Fig.117).

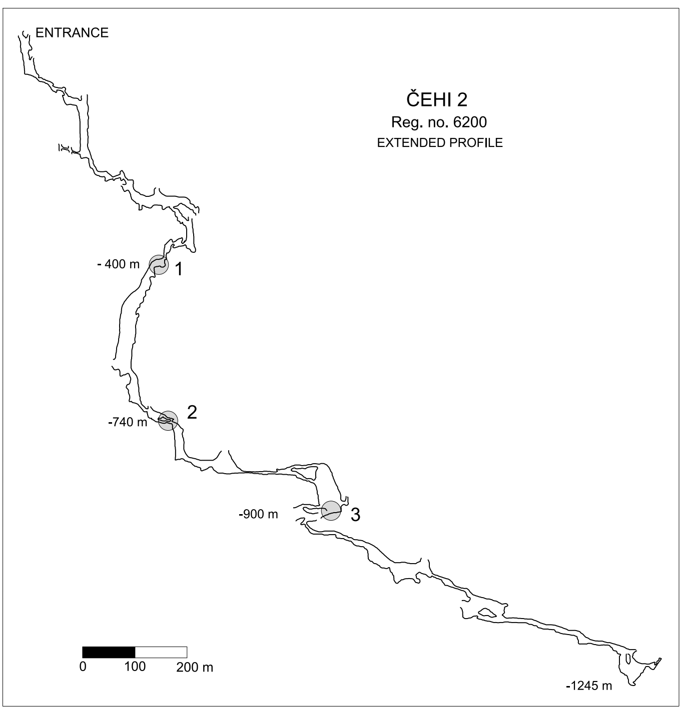
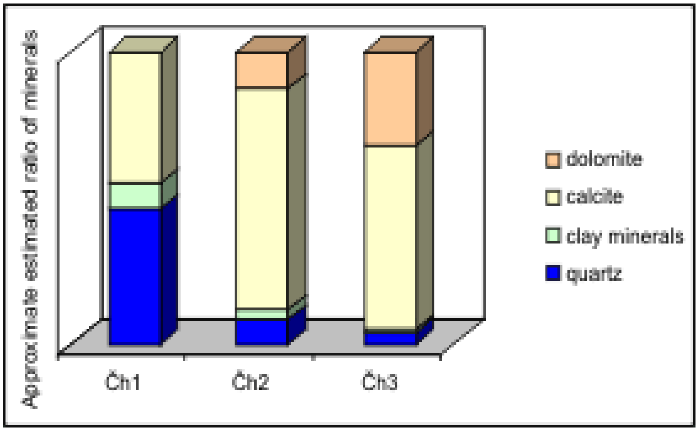


Figure 117: The location of samples is indicated in the extended profile of cave Čehi 2 (Cave Register of IZRK ZRC SAZU). Samples: 1 – Čh1, 2 – Čh2, 3 – Čh3.

Sample *Čh1* was collected from the bottom of the smallest shaft at a depth of 400 m in front of the other shaft called “Grosso e Stanco”. It is milky brown clay (7,5 YR 5/4) containing weathered fragments of limestone. Sample *Čh2*, was collected from the gallery “Veccio Tribola” at a depth of 740 m. It is white clay (10 YR 8/2(8/3)) with a touch of yellowish brown shade. Sample *Čh3*, was collected from a depth of 900 m beside Bivak. It is white clay (10 YR 8/2). The mineral composition of samples taken from cave is on Fig.118.

Figure 118: The mineral composition of clastic deposits from Čehi 2 cave.



The clay from a depth of 400m (sample *Čh1*) contains predominantly quartz and calcite, as well as some clay minerals. Some illite/muscovite group minerals are also present, with hematite only in traces. The sample does not contain dolomite.

The white clay from a depth of 740m (sample *Čh2*) contains mostly calcite. The amount of dolomite is greater than that of quartz, and the amount of both is relatively insignificant. The sample contains very small amounts of clay minerals (illite/muscovite and chlorite).

The white clay from a depth of 900m (sample *Čh3*) consists mostly of calcite; while the amount of dolomite has significantly risen; there is little of quartz, while clay minerals occur only in traces.

There is a distinct increase in the amount of carbonate grains in the clastic sediments with depth and as a simultaneous decrease in the amount quartz and clay minerals.

ČRNELSKO BREZNO, REG. NO. 6040

The entrance into Črnelsko brezno is situated south of Črnelski Vršič below Velika Črnelska špica. The cave entrance lies at 2080 m asl. (y = 5386 170, x = 5137 707). The maximum depth of the cave is 1198 m. In its entrance area and down to a depth of 520 there is a succession of larger and smaller shafts. Beyond that depth the cave extends in the form of narrow, horizontal galleries. Other smaller shafts intersect these.

Clastic sediment samples

P. Audra collected the samples from Črnelsko brezno primarily for paleomagnetic dating (Audra 2000). Two of these samples were provided to me for analysis. The collection locations of the samples in the cave are indicated in the extended profile (Fig.119). The mineral composition of samples from cave is on Fig.120.

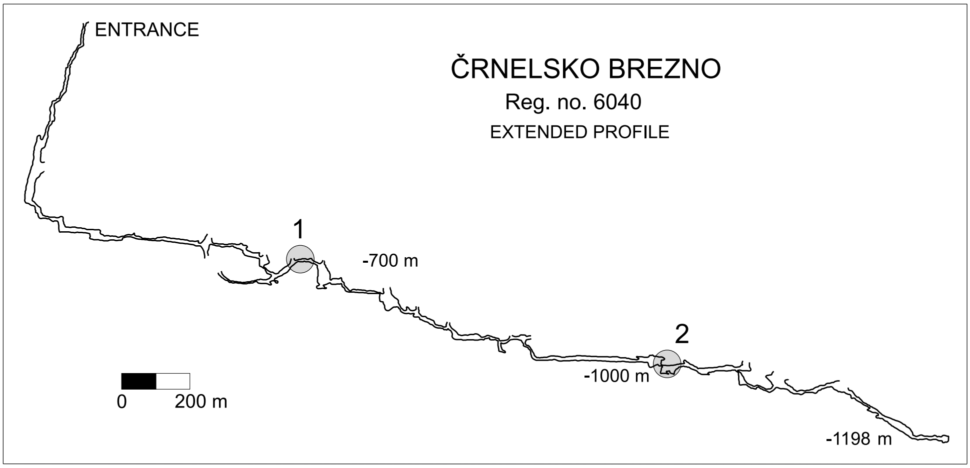


Figure 119: The location of samples is indicated in the extended profile of Čehi 2 cave (Cave Register of IZRK ZRC SAZU). Samples: 1 – Čr1, 2 – Čr2.

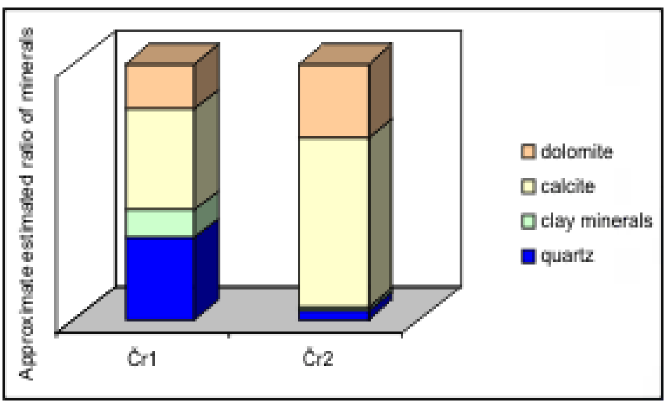


Figure 120: The mineral composition of clastic deposits from Črnelsko brezno cave.

Sample *Čr1* is clay gathered from the Ho-Chi-Minh Gallery at a depth of 700 m. Audra (2000) found that this sample was magnetically reversed, indicating that these clays are more than 780,000 years old, i.e. they date back to the last magnetic field reversal (Brunhes/Matuyama). The sample is mostly calcite with abundant quartz, while the amount of dolomite is slightly lower. The sample contains very small amounts of clay minerals (illite/muscovite and chlorite).

Sample *Čr2* was collected from glacial-karstic stratified clays ("varvas") at a depth of 1000 m. Audra (2000) found that this sample was also magnetically reversed. The sample consists mostly of calcite, the amount of dolomite has increased, and there is a small amount of quartz, while clay minerals are present only in traces. The amount of carbonate grains in samples from this cave, when compared to the amount of quartz and clay, minerals considerably increases with the cave's depth similar to the situation in Čehi II cave.

RENEJEVO BREZNO, REG. NO. 7090

The entrance into Renejevo brezno is located at the crossing between Kaninski podi and southern slope of Kanin mountain at 2260 m above sea level (y = 5380 710, x = 5135 760). The cave consists of a series of interconnected vertical shafts and horizontal meanders extending to a depth of 1071 m.

Weathered dolomite sample

F. Gabrovšek provided me with some samples from this cave, which were collected on the expedition of the Ljubljana caving club (DZRLJ). The locations of the samples are indicated on the extended profile (Fig.121) made by the same club (Gabrovšek 2000b). The mineral composition of samples from the cave is given in Fig.122.

Sample *Re1c* was collected from the wall of a cave passage called Mokavec at a depth of 650 m and is an extensively weathered dolomite. Sample consists of very fine heavily weathered carbonate grains. When dry it is white10 YR 8/2 in colour. The sample is almost entirely composed of dolomite, which contains quite a lot of iron, and only traces of calcite. The position of the main dolomite x-ray peak is deflected towards ankerite, suggesting that some of the magnesium in the dolomite was replaced by iron.

Figure 121: The location of samples is indicated in the extended profile of Renejevo brezno cave (after Gabrovšek 2000b). Samples: 1 – Re1c, 2 – Re2.

Clastic sediment samples

Sample *Re2* is brownish silt collected from the sandbank on the floor of the chamber above Tomovina, located at a depth of 750 m. The sample is finely grained silt with individual grains of quartz and clay minerals (chlorite), together with individual and larger rhomboid dolomite crystals. When dry, the sample is very light brown 10YR 8/3 in colour. The sample predominantly consists of dolomite with a high iron concentration. There is an insignificant clay mineral component and calcite exists only in traces. X-ray diffraction could not detect any quartz, although individual quartz grains are visible under the microscope. The mineral composition of samples from cave is given in Fig.122.

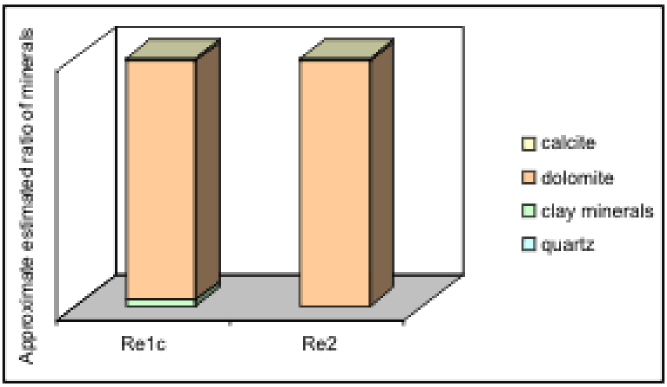


Figure 122: The mineral composition of samples from Renejevo brezno cave.

The crystal lattice organisation (Goldsmith & Graf 1958) of the dolomite containing a large amount of iron was calculated to clarify what is happening to the dolomite during weathering. In the weathered dolomite sample *Re1c*, the level of organisation was 0.78 while in the dolomite silt sediment *Re2*, the crystal lattice organisation is only 0.54.

DISCUSSION AND CONCLUSIONS

The mineral composition of the stratified clastic sediments differs from that of the fine-grained clastic sediments that are presently accumulating at the bottom of the shafts at Kaninsko pogorje. Recent autochthonous clastic sediments are piled up at the bottom of the active shafts in the form of mud, clay, and sand.

The young active shafts intersect older horizontal galleries. These galleries are not genetically related to contemporary speleogenetic processes, they formed under completely different conditions (phreatic) and were filled with non-carbonate sediments.

Stratified allochthonous sands and clays occur in the galleries (Manca 1998). These differ in composition from those being deposited at present. They are composed predominantly of quartz and clay minerals, indicating an allochthonous origin. In some places the older sediments were eroded by water and became mixed with recent carbonate clastic sediments. This produces clastic sediments with mixed mineral composition. Occasionally it is possible to recognise different generations of carbonate clasts mixed with the older clastics.

The concentration of carbonate clasts in the clastic sediments increases with depth below the surface, because the amount of weathered material washed away from the walls increases with depth (Fig.123).

Depth	CAVE ČEHI 2				ČRNELSKO BREZNO				RENEJEVO BREZNO		
(m)	calcite %	dolomite %	quartz %	clay min. %	calcite %	dolomite %	quartz %	clay min. %	calcite %	dolomite %	clay min. %
400	45	0	46	9							
650									1	97	2
700					40	18	32	10			
740	76	12	9	3							
750									1	99	
900	62	32	4	2							
1000					66	29	3	2			

Figure 123: The mineral composition of clastic deposit samples from different depths in caves Čehi 2, Črnelsko brezno and Renejevo brezno. Percents (%) are approximately estimated ratios of the minerals.

Dolomite only appears in sediments deeper in the caves because the dolomite strata underlie the Dachstein Limestone. As the strata predominantly dip of strata to the SW (Čar & Janež 1992), it is possible that water draining from the mountains might carry dolomite particles from cave passages and fissures in the dolomite or dolomitised limestone located at higher altitudes into passages at a lower level.

The amount of dolomite clasts in the sediment is always greatest in the deepest parts of the cave, where passages are developed in dolomite, and water washes dolomite particles from the passage walls.

Samples from the cave vividly illustrate that the proportion of carbonate grains in the sediment increases while the proportion of quartz grains decreases.

The mineral composition of recent sediments and older loams indicates that erosion of carbonate grains from the cave walls is occurring today in the same way that it did in the past. Washing grains form the cave walls and intensified mechanical erosion of the surface may have been accelerated in the past when ice covered the surface of the ground.

Samples of weathered dolomite and clastic sediment from Renjevo brezno have almost identical mineral compositions. This shows that dolomite silt can directly form by weathering of cave passage walls. The amount of dolomite silt created by this process is considerable. It is currently being washed away from the cave walls and is piling up in veritable sandbanks on the floor of the chamber above Tomovina.

VELIKA LEDENA JAMA V PARADANI, REG. NO. 742

Velika ledena jama was selected to investigate the ratio between autochthonous chemical and mechanical erosion in the cave formation processes. In the cave accumulations of carbonate clastic sediments occur at the bottom of the stepped shafts and passage walls are corroded to various degrees depending on the lithological properties of the rock.

The research described so far shows that two processes, solution of limestone and mechanical removal of grains from weathered limestone can both be responsible for the excavation and/or widening of cave passages in carbonate rock. It should be possible then to determine the relative importance of each process at particular localities, that is to find the ratio between the amount of chemical solution and the amount of mechanical erosion involved in the formation of karst passages.

MAIN CHARACTERISTIC OF THE CAVE

Cave location and geological setting

Velika ledena jama v Paradani is also called Velika ledenica, or in short Paradana. Its entrance is situated at the bottom of a large depression at an elevation of 1135 m (y = 5410 830, x = 5094 490) north of the Trnovski gozd's main mountain ridge and northwest of Veliki Golak. Ice is present in the entrance area throughout the year, its amount and height fluctuates with the seasons.

Trnovski gozd is a karst plateau composed of Triassic, Jurassic, and Cretaceous rocks that are overthrust over the Eocene flysch. This mountainous mass was later fractured by faults in the Dinaric direction (Placer & Čar 1974) and secondary fissures, which form fissured zones. These zones are made of parallel fissures a few centimetres to several metres apart that mostly have a common north-south orientation.

The Basic Geological Map 1: 100 000, Sheet Gorica (Buser *et al.* 1968) shows that the cave entrance lies in Lower Jurassic limestones containing some dolomite. The beds dip generally towards the southwest. The rock around the cave is light to dark grey in colour. Where it outcrops in a depression in front of the cave entrance the limestone contains some dolomite beds (Mihevc & Gams 1979).

Speleomorphological characteristics and the significant geological elements

Members of the local Logatec Cavers Association first systematically investigated the cave (Mihevc & Gams 1979). In 1996 the cave's depth was reported as 385m, more recently it has been penetrated to a depth of 600 m (Nagode 2002). This makes it by far the deepest cave in the Trnovski gozd region. The cave drains runoff from its surrounding area.

The entrance is located at the bottom of a large karst depression. Following the entrance there are three great chambers after which there is a succession of shafts. The shafts are interconnected with short sections of active and fossil passage (Mihevc & Gams 1979). Mihevc (1995) classified the shafts into three groups on the basis of their genesis: - stepped shafts, shafts in fissured zones and independent shafts.

The cave passages are guided by various geological structures, the strike and dip of beds and also by faults and fissured zones. The general geological description of the cave given here follows that of Mihevc and Gams (1979).

In the entrance section passages are formed along bedding planes in the limestone and dolomitised limestone, which dip at 50 degrees to 218. In the upper parts of the cave interbeds of thinly bedded limestone and dolomite occur in the limestone. These have a variety of colours and grainsizes. In Stari rov, in the upper part of the cave before Stometrca and below Glista in Stopnje, stratification is apparent in the limestone and dolomitised limestone. Occasionally thinly stratified dark grey and greenish schisty rocks are interbedded with the carbonates. In Nova dvorana there is an alternating succession of dolomite and dolomitised limestone.

In Stometrca, in Mačji kraj and in the lower part of Stari rov the rock is tectonically fractured to such a degree that stratification cannot be detected. Various tectonic zones can be seen in the cave, some of which influence the formation of passages, while others just cross them. Velika ledena jama for example is crossed by a NE trending fault at an angle of 45^0.

The ceiling of Mala ledena dvorana follows a fault, while its floor follows the dip of the bedding. Below Krožni rov the passage follows both the bedding plane and a fault. There are also several faults in the cave oriented in the Dinaric direction and in an E –W direction. In central part of the cave there is a pronounced fissured zone with N – S orientation (Mihevc 1995).

ANALYSED SAMPLES

Limestone and dolomite

The cave was lithologically and tectonically mapped for the purpose of this study. The main lithological units were plotted on extended profile produced by the Logatec Caving Club (Mihevc & Gams 1979) as a base. The locations of the sampling sites are marked on the same extended profile (Fig.124). The mineral composition of the samples is given in Fig.125.

Sample *LP1* is dolomitised limestone collected from Mala ledena dvorana. Due to selective corrosion, calcite fills of open fissures and cavities protrude from its surface, giving the rock a wafer-like appearance. More than a half of sample *LP1* consists of calcite. The rest is dolomite, with a very insignificant amount of clay minerals. The crystal lattice organisation of the dolomite is very low, only 0.24, which suggests early diagenetic dolomitisation. The dolomitised limestone is micritic with a pronounced fenestral and fissured porosity. Hollows in the rock have geopetal fills; the lower part contains micrite, while in the upper part is filled with large calcite crystals. Fissures are filled with calcite crystals and their orientation is not explicitly directed. The surface of the dolomitised limestone is evenly weathered and slightly coarse.

Three samples -*LP2*, *LP3* and *LP4* were collected from the wall below Ladijski

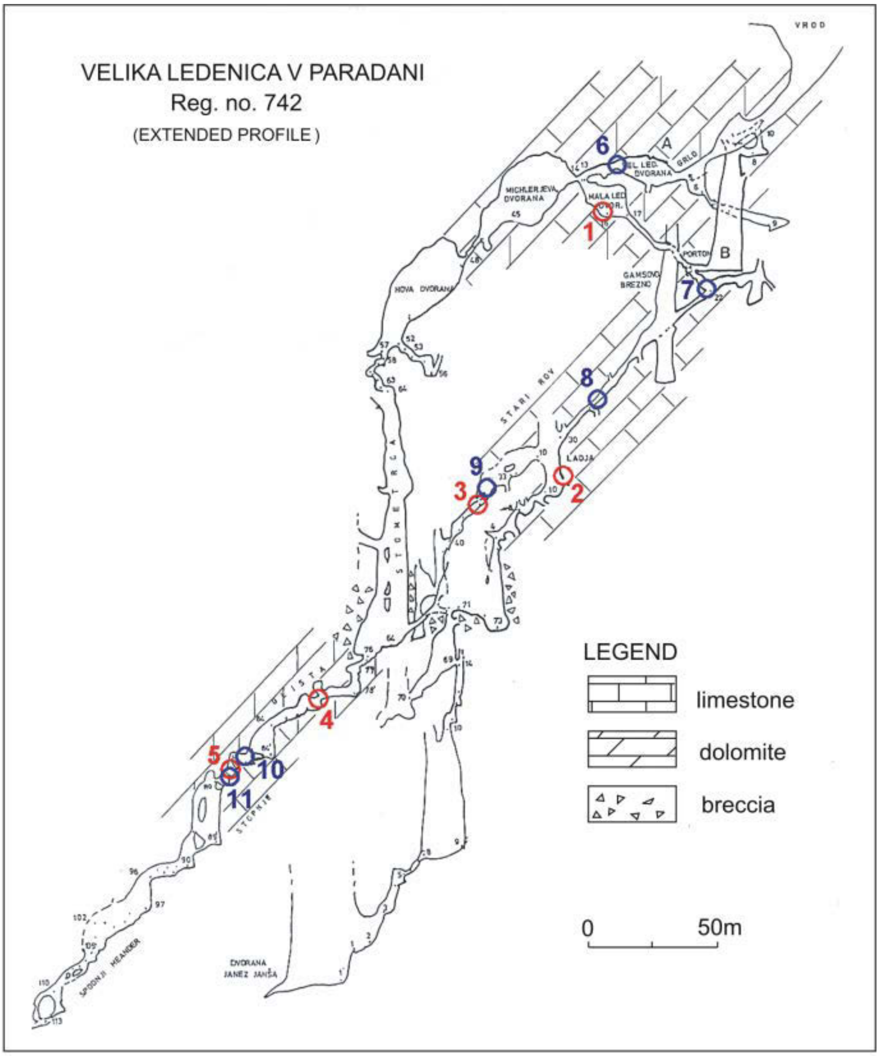
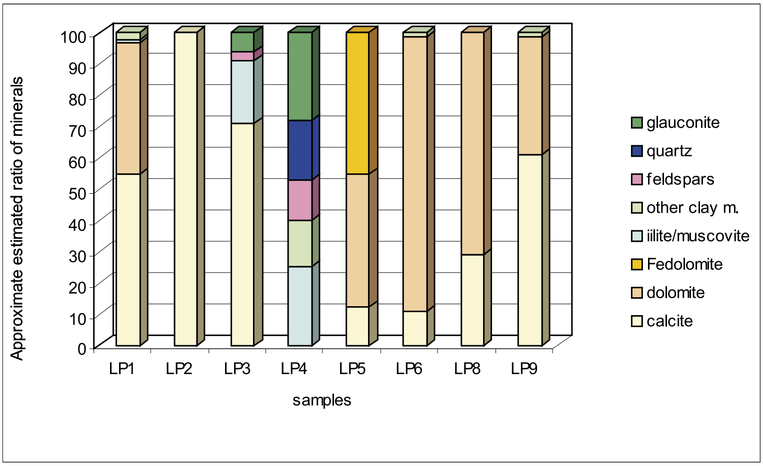


Figure 124: Main lithological units and the location of samples are indicated in the extended profile of Velika ledena jama v Paradani cave (Cave Register of IZRK ZRC SAZU). Limestone and dolomite samples: 1 – LP1, 2 – LP2, LP3, LP4, 3 – LP5, 4 – LP6, LP7, 5 – LP8,LP9. Clastic sediment samples: 6 – LPs1, 7 – LPs2, 8 – LPs3, 9 – LPs4, 10 – LPs5, LPs6, 11 – LPs7.

Figure 125: The mineral composition of the limestone and dolomite samples from Velika ledena jama v Paradani cave.



kljun. Sample *LP2* is a light brown, micritic limestone with calcite crystal clusters and light green clasts. The sample's surface has been selectively corroded with white calcite crystals and green clasts (maiority made of glauconite) protruding from it. Sample *LP2* is composed entirely of calcite. It is a biomicrite with large hollows of palaeokarstic origin, which are filled with radial, fibrous, mosaic cement. The surface of the sample is evenly weathered to the depth of approximately 1 mm. Solution of the micritic part of the limestone occurred evenly, so no individual grains protrude from its surface.

Sample *LP3* is a light green layer surrounding the micritic limestone. The main constituent of the light green clasts in sample *LP3* is calcite; there is a small amount of illite/muscovite group mineral; a small amount of glauconite, and a smaller amount of feldspars. Sample *LP4* is dark green claystone shale collected from a bedding plane between limestone layers within the same passage wall. In this sample, glauconite and the illite/muscovite group mineral are approximately equally represented and constitute more than a half of the sample. The remainder is composed of quartz, some other clay minerals and feldspars.

The wall at the bottom at Stari rov is covered with a thin layer of flowstone, below which the rock is weathered to a depth of several centimetres. In this part of the cave there is no flowing water, so that the weathered zone remains attached to the wall. The rock in the cave wall is most weathered where it is in contact with the brown sediment (Fig.126). Brown sediment occurs on the floor of Stari rov, and used to fill it up in the past. The wall at the bottom at Stari rov is covered with a thin layer of flowstone, under which the rock proves to be weathered several centimetres deep. Sample *LP5* is white material collected from the weathered zone. It is predominantly composed of Fe-dolomite and dolomite with a small amount of calcite. The ankerite peak is clear in the X-ray diffractogram, however it is more possible that there is some replacement of magnesium by iron in the dolomite, so that there is Fe-dolomite presented.

Sample *LP6* is grey dolomite from Glista. The outer part of the dolomite is intensely weathered and porous. Its surface is very coarse and completely decolourised, with indi-

Figure 126: Weathered walls in bottom of Stari rov from where sample LP5 was collected, Velika ledena jama v Paradani (photo A. Mihevc).

vidual rhomboid shaped grains protruding from the surface. The sample consists mostly of dolomite; there is a little calcite, and very small quantities of clay minerals. The degree of crystal lattice organisation is 0.58. The dolomite is a dolosparite. It is composed of large dolomite crystals, which are considerably weathered. There are hollows with geopetal fillings and fissures filled with calcite. There is considerable intragranular porosity.

Sample *LP7,* heavily weathered coarse dolomite, was collected from under the first shaft after Glista; it also has a very coarse surface.

Two samples (*LP8* and *LP9*), taken from the wall of the smaller shaft in Stopnja, were also analysed. Sample *LP8* is coarse dolomite with sheets of crystal calcite that protrude out of the wall. The sample's surface is exceedingly coarse and sandy, with grains falling freely off; these are being carried away where water is flowing across the wall. Sample *LP8* contains mostly dolomite, while calcite constitutes one third of the sample.

Sample *LP9* was collected from the lateral wall where there no water flows across it. This sample is recrystallised, dolomitised limestone, which does not contain any large crystals. The rock is considerably weathered; its surface is covered with a thin flowstone layer. Sample *LP9* consists mostly of calcite, with a smaller amount of dolomite; clay minerals are present in very small quantities. The degree of crystal lattice organisation is 0.65. Large rhomboid dolomite crystals are growing in the micritic matrix. Cavities and some fissures are filled with mosaic calcite cement.

Clastic sediments

In this cave, clastic sediments vary in their age, shape and mineral composition. Remnants of previous, older fillings include- porous sandstone in the wall of Velika ledena dvorana, dark red clay in Krožni rov, and older brown clay mud in Stari rov (Mihevc & Gams 1979). Recent and slightly older carbonate sands occur at the bottom of Stopnje's shafts (Zupan & Mihevc 1988). Locations of the samples are given in Fig.124.

The mineral composition of the following clastic sediment samples: *LPs1*, *LPs2*, *LPs3*, *LPs4*, *LPs5*, *LPs6* and *LPs7***,** was determined by X-ray diffraction (Fig.127).

Sample *LPs1* is sandstone, the remnants of which are stuck to the wall of Velika ledena dvorana. It consists mostly of quartz and calcite. There is calcite cement binding the sandstone grains. The heavy fraction is predominantly goethite, with a large amount of ilmenite and zircon, and little rutile and anatase.

The red clay (sample *LPs2*), which is mixed with carbonate gravel from Krožni rov, contains gibbsite, quartz, clay minerals, goethite, calcite and feldspars in approximately same proportion, with a small amount of hematite and hornblende also present.

Sample *LPs3* is brown loam from Stari rov between Gamsovo brezno Ladijski kljun. Slightly more than a half of it is goethite, a significant proportion of illite/muscovite group mineral and hornblende, few feldspars, and only a trace of quartz.

Sample *LPs4*. is brown loam from the passageway at the bottom of Stari rov'. Almost half of it is quartz; there is a lot of calcite and just a little illite/muscovite group mineral, goethite, other clay minerals, and gibbsite.

Some loosely –cemented sand lies across the lateral parts of the passage at the beginning of Stopnje. It was collected and divided into a light fraction (sample *LPs5*) and heavy fraction (sample *LPs6*). Sample *LPs5* consists mostly of dolomite; there is little calcite, very small quantities of quartz and illite/muscovite group mineral. Goethite

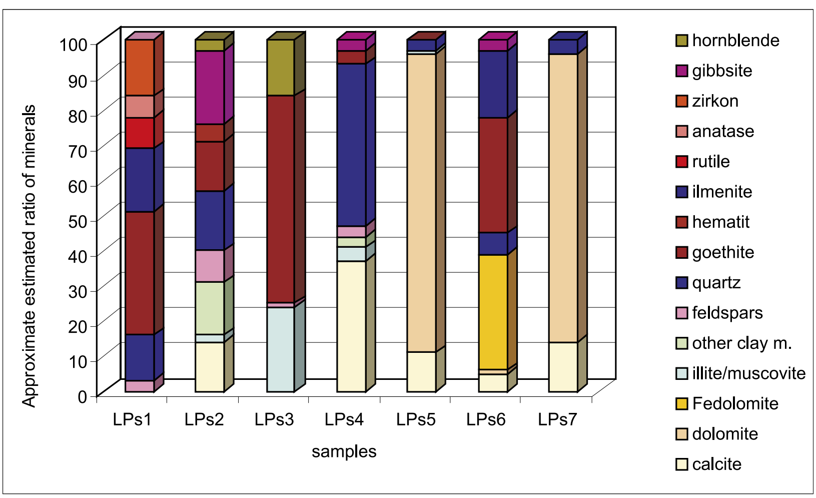


Figure 127: The mineral composition of clasic deposits from Velika ledena jama v Paradani.

and feldspars are present only in traces. Sample *LPs6*, however is approximately 1/3 goethite and dolomite with a large amount of iron; there is also a lot of ilmenite and a small amount of gibbsite.

This sandstone consists of grains eroded from cave passage walls. The grains include - dolomite with a large amount of iron, dolomite, calcite and mineral grains from more aged clastic sediments, which were transported around the cave by water. The high proportion of dolomite with a large amount of iron is not unusual, similar dolomite rich in iron with an almost ankerite peak, also occurs in the weathered rock in the lower part of Stari rov.

Sample *LPs7* is recent sand from Stopnje. It is mostly dolomite, with only a little quartz and calcite. Its composition suggests that it originated from protruding dolomite grains that were washed away from the surfaces of dolomite cave passage walls. That carbonate grains are accumulating as clastic sediments is confirmed by the mineral composition of the sand and silt that has collected at the base of the shafts in of Stopnje.

CONCLUSIONS

Several different types of limestone and dolomite that weather in a variety of ways occur in this cave. The style of weathering depends on lithological differences in the rock and, more importantly, is closely related to the rock texture. The texture determines the surface roughness of the weathered rock.

Rock surface roughness results from rock particles jutting out from the rock. These jutting particles are in turn the source of autochthonous carbonate silt and sand. Zogović (1966) explained the origin of dolomite silt in the following way: - the surface of the rock gets roughened to a certain extend, the water is able to tear away the exposed particles.

Consequentially, mineral grains, whose adhesion is already loosened by dissolution or that have been exposed to selective dissolution, are torn away more easily than grains in fresh unweathered rock. Water carries these grains away and they accumulate when the velocity of the water, and of the sediment, falls bellow a critical value. This process is occurring under the steps in Velika ledena jama where washed away carbonate particles are accumulating on the levelled riverbed beside the wall. It is important to emphasise that this process is not the mechanical erosion of the allochthonous material, but the transport of exposed particles that have detached from the cave wall.

In this cave it is possible to distinguish between several rock types, which are affected differently by corrosion and which may also differ in surface roughness: -

- Micritic limestone with a smooth surface.
- Partly crystallised micrite limestone, containing calcite crystals and green clay intraclasts with a slightly roughened surface on its uncrystallised parts. (But larger crystals and intraclasts jut out from its surface)
- Dolomitised limestone with slightly roughened surface.
- Coarse-grained dolomite with calcite crystals, with a very coarse surface, from which even bigger calcite crystals jut out.

- Coarse grained dolomite with an evenly roughened surface.

All of these a rocks are a suitable source rocks for the formation of autochthonous silt and sand, with the exception of micritic limestone, which has an evenly dissolving surface.

The ratio between autochthonous chemical and mechanical erosion during the formation of karst passages is largely determined by rock texture, and on whether the water flows fast enough over the exposed grains to tear them from the surface of the rock.

Washing away is a conspicuous and dominant process during times of high rainfall, when water plunges into potholes as waterfalls and mechanically erodes the wall surfaces. When water flows more slowly over steps and in smaller quantities, it is in contact with the rock for a longer time and begins to dissolve it until equilibrium is reached.

How the rock dissolves depends on its mineral composition and the texture. Different types of dissolution may be observed in Stopnje, where the same water corrodes different types of carbonate rock and their surfaces are indented to different degrees, due to their different mineral composition and texture. The micritic limestone's surface is smooth, while the granular dolomite is very coarse.

The rock surface on the cave passage walls is primarily formed by corrosion, which selectively dissolves the rock. In Velika ledena jama in Paradana, calcite clusters protrude from the micritic limestone, just as they do from the granular dolomite. The individual dolomite grains stand out from the surface, because the intergrain contacts and smaller grains dissolve first. The rock surface is finally shaped by flowing water, which mechanically tears off the particles that were exposed by corrosion and washes them away.

THE ORIGIN OF CARBONATE CLASTS

X-ray analyses of clastic sediments in selected caves showed an increased amount of carbonate minerals (carbonate clasts) in cave sediments that originated in non-carbonate environments; particularly in sediments that accumulated at the bottom of active shafts.

The carbonate minerals in clastic cave sediments are calcite and dolomite grains, i.e. lithoclasts and crystals of limestone and dolomite that were torn away from cave passage walls.

These tiny grains were mechanically eroded from walls by water and accumulated in the form of autochthonous carbonate silt and clay. Despite their minuteness, these tiny grains do not dissolve, but are transported by flowing water.

The formation of carbonate lithoclasts and their removal from the cave walls depends on the corrosion and abrasion potential of the flowing water and on the rock's texture. The effectiveness of dissolution of the rock depends on: -

- The rate of the reaction taking place on the rock surface,
- The transport of reactive substances,
- The removal of the products of dissolution,
- The reaction between CO_2 with water- $CO_2 + H_2O = H^+ + HCO_3^-$ (Dreybrodt 1988), and

- The lithological properties of the rock.

The mechanical action exerted by the flowing water on the rock results from is the force of the water and the abrasive effects of the material carried by the water. In the cases described here the process of knocking or driving out rock particles by the suspended load, for example by quartz grains (Gams 1959a, Newson 1971a) does not occur. Rather but much particles are torn from the rock surface by adhesion. Due to adhesion between the water and the rock wall (Trudgill 1985), fast and eddying turbulent water may wash away smaller particles that were previously isolated by corrosion. The velocity of water flow and processes of chemical and mechanical erosion are also efected by rocky features (Slabe 1994, 1995) as well as by differences in the coarseness of rock surface in cave passage walls. These, however, have not been investigated here.

The ides that carbonate particles in clastic sediments should be considered autochthonous lithoclasts is well illustrated by the mineral composition of the recent sediments of Renejevo brezno and Velika ledenica v Paradani. These clastic sediments contain mostly dolomite, which is not, as a rule, precipitated in caves. The presence of dolomite in these sediments also makes it improbable that the carbonate silt has a glacial origin, because there is no dolomite in the surface catchment of the caves.

The enrichment of the cave allochthonous sediment with carbonate minerals is also illustrated where water in caves flows fast or is flowing through narrow channels and siphons, and is able to mechanically erode passages walls in a more pronounced and effective manner. Some of the enrichment of the cave clastic sediments with autochthonous carbonate clasts could be also ascribed to the washing away of weathered carbonate rock particles from the earth's surface by percolating water through the cave ceiling.

The autochthonous origin of carbonate clasts may also be confirmed also by stable isotope analyses of carbon in the grains. Compared with limestones of marine origin, chemical cave sediments are enriched with the light carbon isotope (Pezdič 1999). A lower concentration of the light isotope would confirm that the clasts originated from limestone.

An increased amount of carbonate clasts was not observed in cave sediments where they were carried by water flowing through large channels with a free water surface, nor where water was flowing slowly through large submerged channels. Water flowing through small open channels and smaller submerged channels, where the flow of water is faster effectively washes the cave walls, so the amount of carbonate clasts in the cave sediment significantly increases.

The largest quantity of carbonate clasts occurs where water in form of cascades or trickles flushes the passage walls. This is most apparent in stepped shafts, where water during and after rainfall high velocity flows effectively flushes the cave walls.

The autochthonous carbonate clastic sediments described above consist of fragments of bedrock, i.e. lithoclasts, which originate from weathered cave passage walls, from which they were torn away by water. As it continues on its way, the water deposits them where its flow slows down. Autochthonous carbonate clastic sediments may occur on theirown or be mixed with the material that the fluvial, gravitational or aeolian processes have brought into the cave from a non-karst environment.

CONCLUSION

ANALYSIS RESULTS

A variety of methods were used to investigate the process of limestone and dolomite weathering in the cave environment. Initial field work involved mapping the cave passages where the cave walls are weathered, collecting specimens, measuring temperature and in one case the *in situ* pH of weathered limestone (in Pečina v Borštu cave).

Samples were analysed by chemical methods including the complexometric method, EDS analysis on the SEM and Ion Beam Analysis. Mineralogy and petrology were studied using X-ray powder diffraction, thin-sections and cross sections were examined by microscopy, computer scanner and under the SEM. The number of analyses undertaken was not sufficient, however, for a statistical evaluation of the results.

FIELD WORK RESULTS

A weathered layer a few millimetres thick is frequently developed on the walls of cave passages. It occurs in fissures, as well as on the rock surface. Thicker zones of the weathered bedrock, however, are much rare, especially in larger spaces. The rock may be weathered wherever it is in contact with rainwater or air, that is, where it is exposed to conditions that differ from those in which it was deposited. The dissolution is usually occurs perpendicular to the rock surface, while the depth of dissolution depends on the surface's roughness (Ford & Williams 1989).

In the cases described here the dissolution advances deep into the rock. It is, however, an incomplete dissolution and leaves behind a porous sponge-like weathered zone.

Dissolution not only advances along open fissures but also along the various textures in the rock; it dissolves smaller grains, the borders between the larger grains, and particular zone in micritic and biomicritic limestones.

Šušteršič (1991) claimed that rocks differ in the way they change from the solid state to solution; in the first case the dissolution front is smooth and transversely cuts into mineral grains and the matrix/cement, while in the second the rock behaves as a mosaic, mineral grains in the matrix/cement dissolve at a slower rate than the surrounding grains and are extracted from the bed in the form of a silt-like material. He quoted as an example dolomite, which may, due to its petrographic properties and tectonic fracturing, dissolve in both ways (Zogović 1966).

Incomplete dissolution occurs both in cave passages and at the Earth's surface. It can be seen most dramatically in cave passage walls. The most weathered were those walls that were either moistened by percolating water, in contact with the fine-grained non-carbonate sediments, or were wetted by condensed water.

If carbonate rock is covered with clastic sediments or soil it will usually weather under them. Sub-sediment rocky features (Gams 1971 and 1997, Slabe 1992, 1994, 1995, 1999) may form on the surface of rock covered by alluvium or soil, due to water flowing along the sediment-rock contact. The development and form of sub-sediment rocky features is a consequence of the manner of water flow; the composition, stratification and texture of the bedrock; and the degree to which the bedrock is fractured or crushed (Slabe 1999).

Renault (1968) described the chemical reaction between carbonate rock and sediments. He claimed that acidic clay in contact with dolomite absorbs Ca^{2+} from the dolomite so that dolomite becomes soft.

In the cases described carbonate rock was in contact with non-carbonate alluvium. No chemical reactions (in the sense of Pezdič *et al.* 1998) of any kind were recognised between them, either by field research observation on from an examination of their mineral composition.

Sometimes carbonate rock in contact with clastic sediments does not display visible signs of being weathered (Mihevc 1996a). Mihevc described cave passage walls that are completely unweathered, despite being in direct contact with the clastic cave sediments very long time.

All the cases described here are examples of *in situ* weathering of limestone and dolomite. "Phantom rocks" with the altered chemical composition, as described by Vergari & Quinif (1997) and Kaufmann *et al.* (1999), were not formed. What remained was porous and discoloured skeleton of the primary rock.

When the dissolution processes stops, for whatever reason, thick zones of weathered limestone or dolomite remain on the passage walls of numerous caves. This occurs when aggressive water ceases to flow, and when the weathered rock is not washed away by flowing water.

OPTICAL ANALYSIS RESULTS

Macroscopic descriptions and the scanning of samples cross sections

Samples were examined in hand specimen and in sawn cross-sections and their colours were observed (Goddard *et al.* 1970). The following colours were recorded: N4 - medium dark grey, N5 - medium grey, N6 - medium light grey, N7 - light grey, N8 - very light grey, N9 - white and 5YR8/1 - reddish grey.

In cross sections of weathered limestones and dolomites the transition from fresh rock into weathered rock one is clearly visible. Different stages of weathering, the textures and textures along which the weathering is advancing into the rock and the thickness of the weathered zones can be observed.

Dissolution progresses into the rock along open fissures and along micro-porosity that cannot be resolved by the naked eye or by microscopy. During weathering, the rock first loses some of its colour. Fading gradually increases, leading to the state of complete discoloration, when the residual rock becomes white.

By selective dissolution of individual components of the rock, the previously solid compact rock becomes increasingly porous. This does not occur only along fissures as might have been expected, but also in what appears to be completely compact, solid rock. Solution acts selectively on individual parts of the rock, particularly tiny grains, joints and cement between the grains. This is very apparent in recrystallised limestones and late-diagenetic dolomites.

Zones of micrite, which apparently do not differ from neighbouring parts, may also dissolve. It is possible that rock micritisation has masked more soluble primary textures, or that some soluble primary structures are unable to be resolved by the techniques used in this study.

As dissolution advances into the rock's interior along soluble pathways, it leaves in its wake larger and more interconnected pores, which may unite to form small cave pockets. After dissolution, a sponge-like, porous rock skeleton, whose particles are heavily weathered, without any colour or shape, is left behind. The skeleton is composed of silt or clay sized particles. If dissolution continues, the sponge-like texture may fall apart and the outer part of what was once solid rock becomes clay-like and completely soft.

Filled fissures may impede further advance of dissolution, as may less soluble parts of the rock. Less soluble rock may have larger crystals, but may also be composed of less soluble micrite fields. Dissolution may, however, bypass these hindrances and stage a "lateral" or "rear attack". When the less soluble obstacles eventually weather away, they become conduits for a new advance of aggressive moisture and dissolution progresses in a "mosaic" manner.

Experiments showed that water advances rapidly into the weathered part of the rock, being pulled up by capillary forces. Calcite veins take more time to bypass or break through. They will impede progress until they weather themselves and become permeable.

Transmitted Light Microscopy

The main problem with microscopic thin sections is insufficient resolution, due to the small size of the grains. Since dissolution attacks all grains with an equal intensity, the smaller ones get dissolved, while larger ones remain present. Those that are not completely dissolved are left in the form of tiny carbonate particles, whose texture is no more detectable; the rock's porosity is so insignificant that it remains even under the microscope invisible.

All that can be seen under the microscope is that dissolution of the rock has taken place, leaving in its wake an undissolved residue. At some places there is simultaneous deposition of calcite spar cement with dissolution of the rock. In cases when the secondary crystallisation does not occur, the porosity remains the same.

During sample preparation some difficulties arose due to grains dropping off. For this reason the transition from the fresh rock to the weathered zone were not seen distinctly.

SEM observations of cross-sections

In cross-sections, the transition from the fresh limestone into the weathered one is particularly well expressed, for example in sample *Pr2*. The arrangement of pores in a pattern is also distinctly visible. It is also clear that the process taking place, is not precipitation of secondary calcite crystals on the surface of the dissolving limestone, but an increase in porosity due to weathering. Dissolution advances into the rock primarily along grains contacts. Preparation of the cross -sections thin sections presented the same difficulties as occurred with the thin sections, individual grains broke off due to the excessive porosity.

CHEMICAL ANALYSIS RESULTS

Complete Chemical Analysis

Qualitative chemical analysis was undertaken on four samples from two caves, Martinska jama and Jama II na Prevali. The results are in the Fig.128, with those quantities, the values of which were below the detection limit of research methods, marked negatively. The results indicate that in limestone samples *Ma1* and *Pr2* the concentration of three elements and one oxide decreased, while that of four other elements actually increased. MgO, Sr, Au and U concentrations decreased while Y, Sc, La and Sm increased.

The quantities of other elements and oxides were in some cases lower in the weathered part of one sample, while in the second sample they were greater and vice versa. The concentration of some oxides and elements remained unaltered in both cases. The loss on ignition (LOI) in *Ma1* is higher in the fresh part of the sample, while in *Pr2* it was higher in the weathered part.

According to the research literature, the concentration of Mg, Sr and U decrease during limestone weathering. In the case of dolomite weathering, along counted elements, Na also decrease (Gascoyne *et al.* 1978, Kogovšek & Habič 1981, Gautlier *et al.* 1999, Al- Aasm & Packard 2000, Panahi *et al.* 2000). This is confirmed by analyses undertaken in this project.

SAMPLE	SiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI	TOTAL
	%	%	%	%	%	%	%	%	%	%	%	%
Ma1a	0,15	0,06	0,05	0,002	0,48	55,76	0,20	-0,01	-0,001	0,02	43,09	99,81
Ma1c	0,08	0,04	0,05	0,002	0,30	55,93	0,15	0,10	-0,001	0,02	42,90	99,56
Pr2a	0,07	0,03	0,02	0,006	0,46	56,25	0,15	0,04	-0,001	0,02	41,47	98,50
Pr2c	0,20	0,08	0,05	0,006	0,26	55,82	0,20	0,04	-0,001	0,02	42,47	99,14

SAMPLE	Ba	Sr	Y	Zr	Be	V	Ag	Cd	Cu	Ni	Pb	Zn	Bi
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Ma1a	2	229	2	20	-1	13	0,4	-0,3	2	-1	-3	-1	-2
Ma1c	2	176	3	17	-1	10	0,6	-0,3	2	-1	-3	-1	-2
Pr2a	2	607	4	15	-1	13	0,6	0,4	2	-1	-3	-1	-2
Pr2c	4	427	7	18	-1	16	0,4	0,9	3	2	-3	-1	-2

SAMPLE	Au	As	Br	Co	Cr	Cs	Hf	Ir	Mo	Rb	Sb	Sc	Se
	ppb	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm	ppm	ppm	ppm	ppm
Ma1a	92	-2	1	-1	-2	-0,5	-0,5	-5	-5	-20	0,8	-0,1	-3
Ma1c	24	-2	1	-1	3	-0,5	-0,5	-5	-5	-20	0,4	0,3	-3
Pr2a	123	-2	-1	-1	13	-0,5	-0,5	-5	-5	-20	0,4	0,1	-3
Pr2c	49	-2	1	-1	12	-0,5	-0,5	-5	-5	-20	0,4	0,2	-3

SAMPLE	Ta	Th	U	W	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Ma1a	-1	-0,5	1,4	-0,3	0,3	-3	-5	-0,1	-0,1	-0,5	-0,1	-0,05
Ma1c	-1	-0,5	0,7	-0,3	1,1	-3	-5	0,3	-0,1	-0,5	-0,1	-0,05
Pr2a	-1	-0,5	1,4	-0,3	1,1	-3	-5	0,1	-0,1	-0,5	0,1	-0,05
Pr2c	-1	-0,5	1,3	-0,3	2,1	-3	-5	0,3	-0,1	-0,5	0,2	-0,05

Figure 128: Results of complete lithochemical analysis Package 4E (exploration grade; methods: ICP, INAA, ICP/MS; Actlab 2000). Negative values are under the methods limits.

The general conclusion from complete chemical analysis is that the amount of insoluble residue in the weathered part of limestone *Pr2* decreased when compared with the unweathered part, while limestone sample *Ma1* there was more insoluble residue in the weathered part than in the unweathered. This shows that during dissolution the quantity of insoluble residue does not always necessarily increase. An explanation has yet to be found for how, and in what form, the missing insoluble residue is removed.

Complexometric Analysis

	CaO %	MgO %	kalcit %	dolomit %	sk.karb.%	net.ost.%	CaO/MgO
BJ1a	55,24	0,69	96,86	3,14	100	0	80,06
BJ1c	55,69	0,28	98,7	1,29	99,9	0,1	198,89
BJ2c	55,29	0,44	97,47	2,03	99,5	0,5	125,66
BJ3c	52,32	0,2	92,98	0,92	93,8	6,2	261,6
Ma1a	55,13	0,8	96,31	3,69	100	0	68,91
Ma1c	55,24	0,6	97,07	2,77	99,84	0,16	92,07
Ma2a	55,12	0,8	96,31	3,69	100	0	68,9
Ma2c	55,18	0,73	96,68	3,32	100	0	75,59
Ma3c	54,12	0,61	94,1	2,77	97,87	2,13	88,72
Pr2a	55,29	0,68	96,68	3,32	100	0	81,31
Pr2c	55,35	0,28	98,46	0,92	99,38	0,62	197,68
Kr1a	51,87	0,93	89,29	4,24	94,53	5,47	55,77
Kr1c	52,77	0,48	92,97	2,21	95,18	4,82	109,94
TJ2b	30,45	19,6	5,71	89,63	95,34	4,66	1,55
TJ2c	29,89	17,9	8,91	81,88	90,79	9,21	1,67
Žd1b	54,29	0,19	93,6	3,5	97,1	2,9	285,74
Žd2c	50,75	0,69	88,88	3,14	92,02	7,98	73,55
Rmab	29,97	20,86	1,68	95,44	97,12	2,88	1,44

Figure 129: Results of Complexometric analyses from the samples:
Pečina v Borštu – BJ, Martinska jama – Ma, Jama II na Prevali – Pr, Krempljak – Kr , Turkova jama – TJ, Spodmol na Ždroclah – Žd and Remergrund II – Rm;
a – fresh rock, b – discoloured rock, c – weathered rock.

18 samples were analysed using the complexometric method. The results are presented in the Fig.129. The concentration of common carbonate changes from one cave location to another. Limestone from Krempljak cave has the lowest average carbonate component of 94.85 %. The lowest carbonate concentration in dolomite was found in Turkova jama, where the average value was 93.69 %. Limestone in Jama II na Prevali had the highest average carbonate concentration of 99.69 %, the second highest of 99.54% was in limestone from Martinska jama.

Comparing the carbonate concentration between individual samples showed that weathered limestones and dolomites have lower carbonate concentrations than their unweathered equivalents. This implies that the insoluble residue concentration increases in the weathered part. The only exceptions are two samples from Krempljak cave, where there is more insoluble residue in the fresh unweathered limestone.

The lowest carbonate concentration in limestone samples was 88.9 % $CaCO_3$, and the highest was 98.7 % $CaCO_3$. The only samples outside this range were those containing dolomite. The lowest calcite concentration in dolomite was 1.68 % CaCO3 and lowest dolomite concentration was 81.88% $CaMg(CO_3)_2$. The highest $CaCO_3$ concentration in dolomite was 8.91 % and the highest dolomite concentration was 95.44% $CaMg(CO_3)_2$. The CaO and MgO concentrations differ from sample within these ranges, and this is also reflected in the CaO/MgO ratio.

The most important conclusion from complexometric analysis is that there is a lower concentration of MgO in the weathered part of the rocks than in the fresh part. This indicates that MgO is being removed during weathering. As a consequence ever-purer calcite is left on the walls, although the interior texture of the calcite is increasingly weathering. Mg is removed from the crystal lattice of both calcite and dolomite.

A decrease of the Mg ion ratio in weathered parts of limestones and dolomites has been previously documented. Kogovšek & Habič (1981), who measured magnesium hardness, found that Mg is removed from limestone during weathering. In trickles of water in Planinska jama the magnesium hardness was 35 %, but only the calcite was precipitated from the water.

This is due to the greater solubility product of $MgCO_3$ when compared with $CaCO_3$. Burger (1989) also reported the loss of Mg during dolomite weathering, but he did not explain it. Slabe (1988) interpreted the lower concentration of Mg in the surface of a corroded cave wall, in Komarjev rov in Dimnice as due to the complete dissolution of impure limestone, which contains Mg and the repeated precipitation of pure calcite crystals from condensed moisture. In all the cases described here, however, calcite crystal precipitation is not occurring, only the weathering of limestones and dolomites.

EDS Analysis using SEM

Samples from Martinska jama and Jama II na Prevali caves were analysed by EDS on the SEM. Carbon, oxygen, calcium, magnesium and strontium were determined for both samples. In the fresh part of sample *Ma2* some sulphur, iron and nickel were detected, and in sample *Pr2* molybdenum was also present. In the weathered part of sample *Ma2* silicon, aluminium and chlorine were detected.

The elemental composition indicates that both samples consist primarily of calcite with a few impurities. In both samples the concentrations of Mg and Sr are lower, and the Fe and Ni that were present in the fresh part of the sample *Ma2* are absent in the weathered part. This shows that ions with a lower ion potential are being removed during the weathering processes.

Ion Beam Analysis

Ion ban analysis showed that at the boundary between fresh and weathered rock there is an increase in the concentration of iron, zinc and manganese and a slight fall in the concentration of strontium and chromium. The Fe and Zn concentration is highest at the boundary between fresh rock and the weathered zone.

X-ray diffraction did not detect any minerals that would contain these elements; perhaps they are lodged directly in the calcite crystal lattice. During weathering they might migrate out of it, or incorporate themselves into it.

Organic Carbon Analysis

The elementary chemical analyses did not explain a why weathered rock loses its colour. Only the concentration of MgO, Sr, Au and U were reduced in the weathered part, while other oxides and elements has the same concentration in both the fresh and the weathered parts.

Organic carbon analysis was used to see if changes in the rock colour were due to changes in organic carbon concentration. Organic matter in the marine sediment stems from different environments and organisms and can be distinguished by its stable iso-

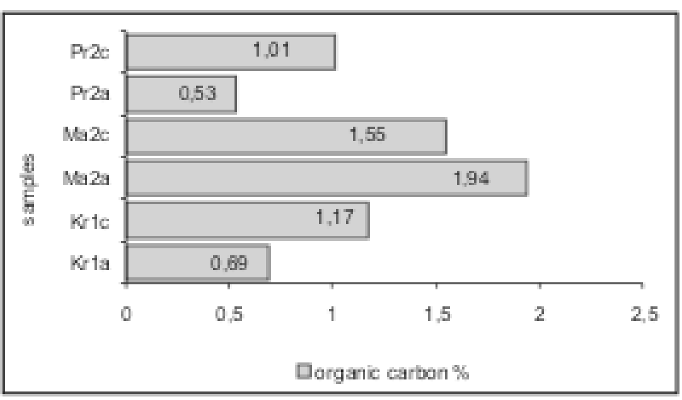


Figure 130: Results of organic carbon analyses. Samples from caves: Kr – Krempljak, Ma – Martinska jama, Pr – Jama II na Prevali; a – fresh limestone, c – completely weathered limestone.

tope composition. If organic carbon does cause colouring in limestones, then it may be oxidised during weathering. Resultes of the analysis are in Fig.130.

The organic carbon concentration in the weathered part was of a lower only in limestone from Martinska jama. In the limestone taken from Krempljak and Jama II na Prevali, however, its concentration increased in weathered part. This is probably due to the presence of microorganisms in weathered parts.

If the colour of carbonate rock is due to organic carbon, it is not due to its absolute concentration in the rock, but to some other property of the carbon.

Conclusions from the chemical analyses

During limestone and dolomite weathering the concentrations of Mg, Sr and U fall. In all the analyses undertaken the concentration of Mg decreased in the weathered part of the sample. This can be explained because the ions lost during weathering are primarily those with a lower ion potential.

The amount of the insoluble residue in the weathered part is sometimes increased, which is to be expected; however, in some cases there is more insoluble residue in the unweathered rock, which is altogether unexpected. This unexpected result is probably due to the transport of accessory minerals in the form of the colloid and/or gel, and to the micro-environmental conditions of the individual sample in the cave.

MINERALOGICAL ANALYSIS RESULTS

Limestone and dolomite

The limestone and dolomite samples examined were, apart from some rare exceptions, very pure. They were predominantly composed of calcite or dolomite. Other minerals occurred in very insignificant quantities and were present in traces at the limit of detection.

In a few cases the amount of insoluble minerals (feldspars, clay minerals and quartz) was greater in the fresh part of the rock than in the weathered one. In some cases there was not even a trace of them in the weathered part, which indicates that they were removed during the weathering processes.

During weathering, limestone and dolomite become purer. One possible explanation is that the impurities are washed away in the form of a colloid, but evidence for this mechanism has no yet been found. Sometimes quartz remains in the weathered part, but in other instances it does not. The limestone purification may also be related to the loss of colour.

In some cases the main calcite x-ray peak rebound is higher in the weathered part, in but in other cases it is higher in the fresh. This suggests that there is no direct relationship between weathering and calcite crystal lattice order. The ordering of the dolomite crystal lattice is higher in fresh and colourless parts of the rock than in completely weathered parts.

In most cases, the mineral compositions of fresh and weathered parts of the samples do not differ significantly. The quantity of insoluble residue is sometimes higher in the weathered and sometimes higher in the fresh part. It is not necessarily the case that weathered parts contain a higher concentration of insoluble residue.

The principal conclusion from these investigations is that in the majority of cases carbonate rocks undergo a purification process during weathering.

Clastic Sediments

Sand, silt and clay sediments, in contact with the weathered cave passage wall are not the insoluble residues of the bedrock, because their mineral composition is distinctly different. The sediments contain minerals of the illite/muscovite group, which are not present in limestones and dolomites. This indicts that these sediments have an allochthonous origin. They are derived from flysch, and were transported into caves.

MICROBIOLOGICAL ANALYSIS

Caves are unusual environment for bacteria. In the caves studied in this project the temperature remains constant throughout the year at about ten degrees.

Aerobic bacteria were found in the weathered limestone, cave pools and luminescent water drops that adhere to cave ceilings. Cultures from the weathered rock differed from those grown from cave pools and from luminescent water drops.

The weathered limestone is not a suitable environment for the active growth of microorganisms. It is not clear if microorganisms accelerate or even cause dissolution of the limestone. They may just live on the dissolution products or shelter in the pores produced by dissolution. The significance and role of microorganisms on dissolution of carbonate rock in caves is an area with great potential for further investigation.

MAIN CONCLUSIONS FROM RESULTS

Field research showed that thin weathered zones are common on the walls of cave passages developed in carbonate rock. The surface roughness of these walls is greatly increased as a result of weathering. Thicker zones of the weathered bedrock are rare, especially on the large surfaces.

Weathered zones are the result of incomplete carbonate rock dissolution. At first sight, the most weathered passage walls appear to be those that are: -

- soaked by percolation water,
- in contact with alluvium, or are

- subjected to condensation corrosion.

In the course of weathering the rock's colour gradually fades away and becomes white, with a grey or yellowish hue.

During selective dissolution of individual components, the once compact carbonate rock becomes more and more porous, not only along fissures, but also along various textures. This, in turn, results in mosaic porosity and the loss mechanical strength.

From analysis of cross sections, thin sections and flaked off sections it is evident that the white zone on the surface of the rock is not produced by the precipitation of secondary minerals. Rather it is due to an increase of porosity within the rock.

Chemical analysis showed that the amount of Mg, Sr and U in the weathered zone of carbonate rocks consistently decreases. It became evident that these elements are being removed during weathering.

The quantity of organic carbon in the weathered part is sometimes higher and sometimes lower. Changes in colour between fresh and unweathered rocks are not simply due therefore to a change in the gross concentration of organic carbon.

The mineral composition of weathered carbonate rock does not differ significantly from of the fresh rock. The amount of insoluble residue is sometimes higher in the weathered part and sometimes higher in the fresh. Major calcite x-ray diffraction peaks are, with few exceptions, more numerous in the weathered part. During the weathering the crystal lattice order in dolomites is reduced.

The analysis shows that during weathering limestones and dolomites become purer, while they simultaneously lose their mechanical strength.

DISCUSSION

Weathering of carbonate rocks usually results from dissolution, its transformation from the solid state into solution (Carson & Kirkby 1972, Summerfield 1991). It may act unimpeded, provided there is a constant flow bringing in aggressive water and carrying away ions from the dissolved rock. The fact is that weathering of carbonates is usually limited by dissolution.

In the cases described in this work solution is not limited to the surface of the rock, and does not leave behind a smooth cave wall surface, as is the case with solution by with flowing water but it is penetrate into the rock. Field investigations, the analysis of cross sections and the moistening of the weathered limestone have led to the idea that in the case of existing weathered zones on cave walls, the water responsible for solution moves by molecular diffusion and capillary action, whichever is the faster, and carry dissolved ions away from the grain boundaries. When the inflow or outflow of water stops, the fluid present in the connected pores becomes saturated, or dries up, and the rock ceases to be dissolved.

In these cases dissolution advances into the rock, not only along large open fissures but also through tiny micro-fissures and pores. Dissolution acts quite selectively. Firstly smaller grains and the contacts between grains are dissolved. Progresse of the dissolution follows the irregularities on the surface of and within grains. It may also follow microtextures and obscured primary rock textures that cannot be resolved under the light microscope. A porous rock skeleton is left behind after dissolution.

During dissolution the pores become larger and increasingly interconnected, so that aggressive water advances more easily and deeper into the rock's interior.

With the lapse of time even the more resistant parts of carbonate rock weather as well. Calcite veins and the shell fragments that jut out from the weathered rock surface become porous and soft. With continuing dissolution the rock becomes more porous and fragile, until its texture completely collapses.

Advancing dissolution increasingly separates individual particles. Carbonate silt and clay may be produced, depending on the rock texture. Carbonate silt is formed from sparite and micro-micrite, while micrite becomes clay. Both the carbonate silt and clay of still remain attached to the passage walls.

At the same time the rock becomes less resistant to mechanical actions, such as mechanical erosion by water. Due to their small grainsize the smallest possible stream may carry the particles that were isolated by dissolution, down the wall. This may carve shapes in the weathered zone and deposit and silt and clay in forms, which resemble stalactites (Šušteršič & Mišič 1996, Gabrovšek 2000a).

Skabrne (1980) noted that when clastic sedimentary rocks chemically weather and they crumble according to their texture. A similar phenomenon was also observed in limestones and dolomites, especially where dissolution along the edges of mineral grains weakens the mechanical cohesion of the rock. Limestones with sparite and microsparite structure start dissolving along the edges of grains and along the deformities in the crystal surface. During chemical weathering of clastic sedimentary rocks, clay-sized grains are mostly produced in limestones and dolomites these tiny grains usually dissolve, except in those cases described above, where the dissolution process stops.

Porosity in the cases described does not increase due to the mobilisation of more soluble minerals out of the carbonate rock, as was claimed by Worthington (1991), Lowe & Gunn (1997). Nor is it related to the formation of sulphides or the oxidation of sulphides - pyrite, which in other situations accelerate carbonate dissolution.

Thicker weathered zones are found in the calm parts of the caves, where walls are in the contact with clastic sediments or they are wetted by trickling or condense water and where weathered material is protected against mechanical erosion (Fig. 131).

Thick weathered zones were neither found in contact with large quantities of water, nor were they found in contact with constantly flowing water. Thicker zones of weathered rock predominantly occur on walls that have been, or still are, in contact with fine-grained sediments. Mineralogical investigations showed that the clastic allochthonous alluvium does not chemically react with the weathered rock, however,

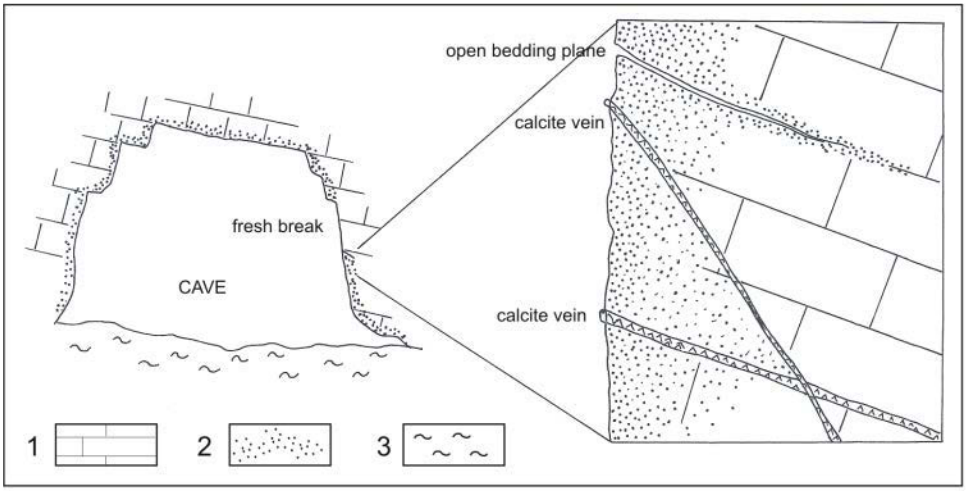


Figure 131: Presence of thick weathered zones of carbonate rocks in cave environment is connected: to calm place without flowing water, to contact with clastic sediments, to wetting by trickling or condensed water.

it does contribute the moisture required for dissolution. It is not known, however, if the alluvium once contained minerals, which chemically reacted with the rock on the passage wall and are no longer present. The mineral composition of the contact area, between the weathered zone and the alluvium, does not support such a supposition.

Thicker zones of weathered rock may also form where percolation water creeps along the passage wall and mosaically dissolves the rock. In both cases, under the alluvium and where water trickles along the wall, the water is drawn into the interior of the rock and along interconnected pores and fissures by capillary action. A similar situation occurs with condensed moisture. The flow of water in these cases is not large, the rock may be moist, rather than wet, but this moisture is sufficient to cause dissolution. So the main reason for limestone weathering in many cases is corrosive moisture. Davis & Mosch (1988) used the term corrosive moisture to describe the drenching of clay pebble surfaces in Colorado Cave. The corrosive moisture is in their cases is actually condensed or vadose (percolation) water. In the cases I have been dealing with, the main corrosive moisture was condense, percolating and moisture from clastic sediments.

The humidity of weathered walls changes significantly during the course of a year. Sometimes the walls were completely wet, at other times they were entirely dry. The fluctuation of humidity during the year is obvious; it is related both to rainfall and to the velocity of the water creeping along the walls. Moisture penetrates very quickly into the weathered part of the wall. It may stop only at the larger calcite veins, and it may also take some time to cross over open fissures or those partly filled with clay.

The explanation given here for the formation of mosaic porosity and the sponge-like rock "skeleton", is similar to that used by Trudgill (1986) to explain the formation of porosity in the limestone karst soil (rendzina). With He demonstrated how, with an inflow of fresh, aggressive water, the pH of the system drastically falls and solution occurs. As the wet phase continues the pH rises, the floor dries up and solution processes stop. With the arrival of the new rainfall the process is repeated. Occuring of the weathered zones may be explained by conceptual model of incomplete dissolution (Fig.132) repeted in cycles.

Similar fluctuations in pH were observed during measurements of wet rock. pH values were in most cases above 8. This indicates that at that moment solution in the rock had ceased and that water in the pores had become saturated. The next inflow of water or moisture after rainfall will, due to increased hydrostatic pressure, squeeze the remaining water out of the pores.

This suggests that when the wall dries up, new moisture penetrates quickly into the rock, because the pores have been emptied. Consequentially, dissolution should also go faster, so that water in pores loses its aggressiveness again, becomes saturated and the pH increases. At every new wetting event, the water will use the pores and channels, which were produced during the previous cycle. It may also widen them a little and the dissolution front will with move deeper into the rock. Through its contact with carbonate particles in the porous skeleton the aggressive water becomes quickly saturated, so that only a part of its former quantity is able to inter-react with the rock. This mechanism

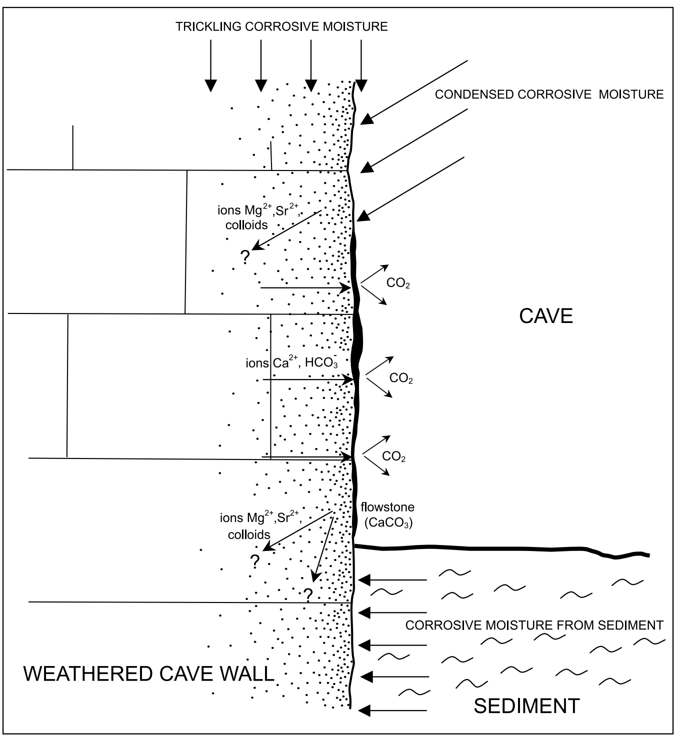


Figure 132: Conceptual model of cyclic incomplete dissolution on cave wall. Wall is dissolved by condense and percolating aggressive moisture or by moisture captured in clastic sediments. Diluted ions and colloids migrate out of weathered zone; on the weathered wall precipitation of flowstone crust is going on.

is repeated in cycles, so that the rock becomes ever more porous but does not entirely dissolve.

A similar process also takes place with trickles of percolating water (Kogovšek 1986) during the rise and fall of the flow in one pulse. When the flow increases the carbonate hardness of water substantially increases as well, because the incoming water firstly squeezes the remaining saturated water out of the pores and fissures. The saturated water in the pores is replaced by the aggressive water, which immediately starts to react with the rock and, after certain period of time becomes saturated as well.

The following explanation is offered for the development of the porous skeleton. Pores and connections between them, in the form of small channels, grow so water may flow through them so quickly that it does not interact with their walls (it does not dissolve them), but dissolves only at the weathering front, which has already moved further into the rock's interior. This mechanism is repeated in cycles, so that the interior of the rock becomes ever more porous and weathered. This may also be the reason why the rock does not dissolve entirely.

Water that slowly flows or creeps along the walls may come into contact with the rock more easily and may be able to dissolve the rock before they reach t mutual equilibrium. The water that arrives at the weathered rock dissolves all that remained from the previous cycle. The aggressive water causes dissolution and becomes quickly saturated as it penetrates into the rock. Only a small amount of aggressive water reaches the end of the open pores. What happens at the contact between carbonate grains and water is in the realm of crystal physics and remains a matter of speculation.

It remains unclear where the dissolved ions actually migrate. Particularly considering that weathered rock in contact with alluvium is not covered with a flowstone layer. The Incomplete limestone dissolution in this case is most likely taking place in the vadose zone. Flowing water in the phreatic zone would wash the particles from the wall - if not before, then during its retreat or the silt would crumble away from the wall of its own accord. The water flow may simultaneously carry away the ions, and dissolution progress into the rock more slowly. It is possible that incomplete dissolution is nevertheless taking place, yet because of the continuous washing away of the particles it is not possible to clarify this dilemma.

Limestone porosity increased in these cases, because less resistant calcite grains were dissolved. Small grains and those with a less well-ordered texture due to the presence of Mg ions in their crystal lattice, were primarily dissolved. Due to their lower ionic potential, Mg ions are more mobile and the first to leave their places in the crystal lattice, thus they weakening the interior texture and increase the propensity to dissolution. Theoretically water in porous media in contact with calcite reach equilibrium immediately; and the water becomes saturated or even supersaturated with $CaCO_3$, but it is not necessary saturated with Mg^{2+}, so the dissolution of the parts containing the Mg ion may continue (Bathurst 1975).

Where the weathered rock is in the direct contact with the cave environment, a thin calcite crust is almost always being precipitated on its surface. The partial pressure of CO_2 of the outgoing, saturated, water falls in contact with the cave air, and a thin flowstone layer is deposited. It is also possible the calcite may crystallise in the pores of the weathered rock. Secondary deposition of calcite crystals reduces the porosity of the weathered rock and partly restores the some of the rock's mechanical strength.

The flowstone layer that covers the weathered zone of carbonate rocks is predominantly a brownish red colour. Both insoluble residue from the weathered rock and clay particles brought into the cave from the surface by percolation water, or deposited on the passage walls by floods, accumulate in this layer. The larger calcite crystals in the flowstone frequently grow perpendicularly to the passage wall.

The thin flowstone layer, which is deposited all over the weathered rock may protect the loosened particles on the walls from being mechanically carried away. The flowstone layer may itself dissolve if aggressive water flows over its surface.

Weathered carbonate rock surfaces may result from dissolution by condensation corrosion. In most, but not all, examples of this process, a thin fine-grained calcite "coating" is deposited over the weathered surface

Wherever a crust or "coating" of secondary minerals is precipitated on the cave wall surface by condensed water, the border between the rock and the secondary mineral deposit is sharply and distinctly delineated and is not be necessarily related to the rock's increased porosity.

Often not only cave passage walls, but also flowstone, are deeply weathered. The weathered zone may have an appearance similar to that of moonmilk, nevertheless, we must not confuse this "moonmilk" on the walls and flowstone with genuine moonmilk, which is produced by the precipitation of aragonite and calcite, predominantly in presence of microorganisms.

Rock weathering due to the frost in the entrances to caves where ice is present, is seemingly very similar to the weathered rock described here, but the weathering mechanisms is entirely different. In the cases described here, the formation of the weathered zone does not result from frost action. The thick weathered zones of carbonate rocks mostly occur deep in the cave interior and have no connection whatsoever with the circulation of cold air.

How the weathered carbonate rock is transported from its place of origin depends on its own properties, as well as those of the eroding and transporting water. Water may erode rock mechanically or chemically. The ratio between the two types of erosion is determined by numerous local factors.

When rock is tectonically crushed, for instance, water will easily dissolve the rubble and mechanically wash it away faster. When rock is not tectonically broken down, the dissolution is most strongly influenced by its mineral composition and texture.

Dissolutional weathering, as described here, leaves the weathered part of the carbonate rock its primary place unless it is in contact with flowing water, which could tear the dissolved particles from the passage wall and carry them away.

Dissolution does not only leave a thick weathered zone in its wake, but also a coarsened wall surface.

In cases where the roughened surface comes into contact with flowing water, the water will wash the exposed particles from the wall, carry them away and finally accumulate them as cave sediment. Carbonate particles may be deposited either by themselves or they may be mixed with allochthonous alluvium. In such cases the non-carbonate alluvium becomes substantially enriched with carbonate particles (Newson 1971a, Zupan & Mihevc 1988, Zupan 1990).

The formation of autochthonous carbonate silt and clay depends on various local factors: -

- the suitability of the rock.
- the degree of the weathering of the wall surface,
- the inflow of water which washes shafts after rainfall, and/or
- on floods washing wall surfaces.

Where water flows through passages fast enough, it may tear particles that were already loosened by solution, off the walls. In the case of more weathered rocks, however, a weak flow of water may suffice, for example, the mere water trickling along the weathered wall. Abrasion by quartz pebbles, as proposed by Gams (1959a) or Newson (1971a); is not required but simply mechanical erosion by means of flowing water in the vadose or phreatic zones.

Water flowing rapidly along a cave passage, interacts with the rock exposed in the walls to a minimal degree, where there is one present, it reacts only with layer of adhesively bound coating. Using its force, rapidly flowing water breaks through the coating and is able to dissolve or tear exposed grains from the wall surface at a faster rate. How the grains are exposed and how many exposed grains there are, depends on the texture of the carbonate rock, how it has been altered by selective dissolution, and the resulting roughness of the rock surface.

Grains that jut out from the surface and whose ties are weakened by dissolution are more exposed and inclined to be washed away from the wall by water (Fig.133). The force of flowing water (Fw), which acts upon the exposed grains, must be greater than the forces (Fg) that tie the mineral granule to the rock. (Fw depends on the water's velocity and on the surface of the granule it acts upon; Fg, however, is proportional to the grain's adhesion, which in turn depends on the size and the surface of the grain's contact area with its base). It follows that mineral grains whose contacts have been already dissolved or exposed to selective dissolution are more easily torn off than grains from fresh unweathered rock.

For each particle there is a critical velocity, at which it is able to be moved. This is also called the critical erosion velocity (Briggs 1977). In the cases described here, the velocity of flowing water must exceed the critical velocity to be able to tear particles from the wall. As the water velocity and its transporting force decrise, the carbonate clasts are deposited independently as clastic carbonate sediments or they mix with allochthonous alluvium.

The ratio between chemical and mechanical erosion of carbonate rock in the cave passages is greatly influenced also by the rock's texture. It affects the initiation as well as

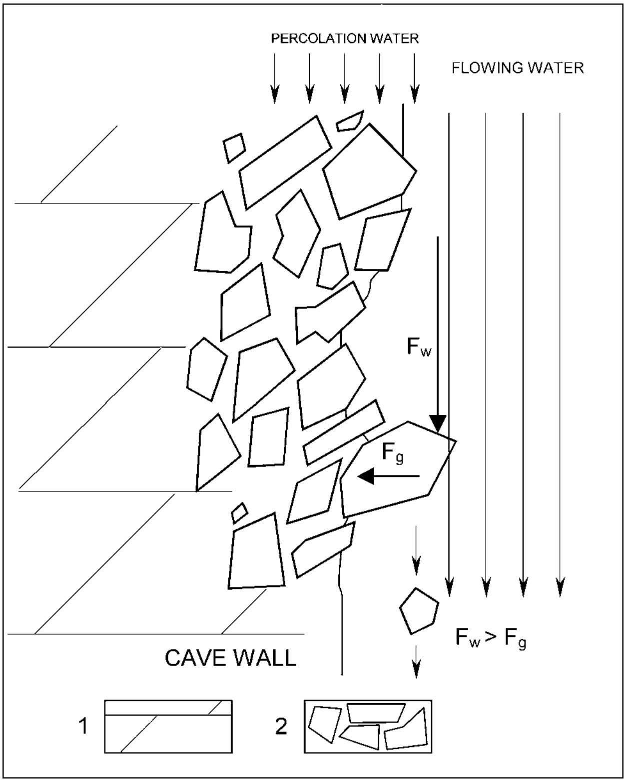


Figure 133: Conceptual model of mechanical erosion of weathered cave wall.
Legend: 1 – carbonate rock, 2 – carbonate clasts, Fg – strength of grain bond to the wall, Fw – water strength.

the course of the dissolution. Dolomite silt forms during the weathering of late-diagenetic dolomite (Zogović 1966). The wall surface of cave passages developed in dolomite is rough, with large grains jutting out from it. These grains eventually form autochthonous carbonate silts. Carbonate clay forms from finely grained micritic limestones. The grains in carbonate clay are so small that in most cases they dissolve rapidly.

Dissolution follows the internal texture of the rock and in particular cases leaves in its wake mosaic porosity – zones of strongly porous and weathered rock. Sufficiently fast-flowing water may also erode it mechanically. The more the rock is chemically weathered, the more easily water will tear off its particles.

The ratio between chemical and mechanical erosion is particularly important in the genesis of cave passages, through which water flows fast enough to tear grains, weakened and exposed by selective corrosion. However, where corrosion is strong enough to act frontally it polishes the wall to such an extent that it is no longer rough. In this instance water cannot wash away exposed particles, for they are absent. The water then just flows through the passages and may knock some particles out of the wall by its force.

One of the greatest remaining problems is to determine the ratio between corrosion and the transport erosion in excavating and shaping cave passages. In other words, to what extent does chemical weathering of the rock occur, so that it may enable the beginning of mechanical washing away of loosened particles?

The field observations demonstrated that this ratio depends on various conditions, such as: -

- the location in the cave,
- the composition, texture and structure of the rock,
- contact with cave sediment,
- the presence of flowstone coating,
- the manner of the inflow of water, its physical and chemical properties,and
- the manner and the time of contact with water.

With regard to the extent of carbonate rock weathering, the water velocity should be fast enough to tear the rock particles from the cave wall surfaces.

In addition to the rock grains, water tears away; crushed rock fragments from tectonic zones exposed in cave walls, and rock particles fallen from walls, which were previously fractured by tectonic and load releasing fissures. The flow of water carries the loosened particles away and deposits them as its transport force weakens. This is why the quantity of carbonate pebbles in the cave streamway may increase downstream.

Whether the formation of weathered zones in carbonate rocks on cave passage walls is a significant factor in the excavation and development of cave passages, or is simply a peculiarity occurring during the karst passage formation process is unclear at this stage. One difficulty is that in most instances where weathering zones are forming they are simultaneously being washed away by water.

The cases described here show that there are two types of weathered carbonate rocks in cave passage walls, thick weathered zones and thin weathered zones. These can be distinguished by the roughness of the wall surface. From observation it appears that which develops depends primarily on the texture of the carbonate rock in the wall and whether the rock is at least occasionally in contact with flowing water.

Silt and clay zones on cave walls result from weathering of the bedrock and not from precipitation of secondary minerals. The weathered zone in carbonate rocks may reach the depths from a few millimetres to several centimetres and may form in various types of limestone and dolomite.

This weathering occurs in limestones, dolomites and dolomitised limestones, irrespective of theirs: -

- geological setting,
- location,
- contact with sediment, or
- exposure to air circulation

Thick weathered zones are more common in calm parts of cave passages, where they are in contact with cave sediment. When the weathered rock is in contact with fast flowing water, the weathered zone is only a few millimetres thick, because water is rapidly washing away t particles loosened by dissolution.

THE MOST IMPORTANT FINDINGS AND THEIR SIGNIFICANCE FOR SPELEOGENESIS

The most important findings of this research are: -

- Zones of carbonate silt or clay and white porous rock on cave passage walls are a product of weathering and are not precipitated secondary minerals.
- Dissolution penetrates into the rock along various textural features, such as: -
- fissures,
- primary porosity,
- microtexture,
- crystal deformities, and
- primary textures covered by micritisation or neomorphism;

the latter may also hinder the expansion of dissolution.

- Selective dissolution roughens \the weathered rock surface and produces a spongework-like texture in the weathered rock, which may reach a depth of several centimetres.
- If the weathered rock comes in contact with flowing water, the water tears surface exposed particles from the rock surface and carries them away. If water does not flow over the exposed particles fast enough or they are somehow protected from being washed away, they remain attached to the wall rock.
- The ratio between corrosion and the mechanical erosion of carbonate rocks on cave passages walls is more significant for the formation of roughness and rocky relief on the wall than for the growth of the passage.
- Microorganisms are present in the processes, but it is not yet know if they contribute to the weathering process or not.
- Corrosive moisture is drawn into the porous rock by capillary action.
- Autochthonous clastic carbonate sediments are composed of grains that were once exposed on the selectively dissolved cave wall surface and have been washed away from it.

Water flows at such a rate through pores and the connections among them in the weathered zone it does not interact with grains near the wall surface, but dissolves only at a weathering front, which moves deeper into the rock. This mechanism operates in cycles and is probably related to fluctuations in the corrosive humidity. The relationship with corrosive humidity is yet to be tested experimentally.

Incomplete dissolution of carbonate rocks could play an important role in speleogenesis, particularly in the development of initial channels. During incomplete dissolution, carbonate rock porosity increases proportionally with the selective dissolution of calcite and dolomite by carbonic acid and not by the dissolution of more soluble fractions such as gypsum and anhydrite, etc.. During weathering, pores in limestone and dolomite enlarge and establish connections between them, which leads to an increased effective porosity. The enlargement of pores and the expansion of their interconnections consequentially can result in the formation of initial channels.

Incomplete dissolution, accompanied with the simultaneous washing away of weathered rock, also accelerates the growth of passages. The ties that bind grains together dissolve, and water mechanically erodes away the remaining grains. By this process the enlargement of passages increases, particularly during floods or high water splash through the cave channels.

Obstructions to passage growth occur mainly only at an early stage in the process when the passages are very small and may get filled up by newly formed carbonate silt or clay. Accelerated enlargement of passage dimensions results from occasional or exceptional washing away of thicker weathered zones of limestone or dolomite following high or flooding.

The recognition that incomplete dissolution occurs, and is responsible for the formation of autochthonous carbonate clastic sediments raises many new questions about the origin and evolution of limestone caves including: -

- How common is incomplete dissolution?
- Is it only a vadose process, or does it occur in contemporary phreatic environments?
- What proportion of the limestone mass is removed by complete solution and what proportion by incomplete dissolution and solid-state transport?
- Is incomplete dissolution a significant factor in the early stages of speleogenesis, or it restricted to passages that are large enough for humans to enter?
- What is the role of microorganisms in incomplete dissolution?

These, and related questions offer considerable scope for further research into the process, products and significance of incomplete dissolution.

I am concluding with the fact that the removal of the limestone from its primary place is not always conditioned merely by dissolution, but is in case, when water washes the exposed carbonate particles from the cave walls and mechanically carries them away, limited also by the transportation.

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POVZETEK

Kras je samosvoj del zemeljske skorje, katerega značilnosti pogojuje kemično delovanje vode na relativno dobro topne kamnine. Kras je prisoten povsod tam, kjer se vzpostavi značilno podzemno pretakanje vode. Najpomembnejši proces pri oblikovanju krasa je raztapljanje karbonatnih kamnin z ogljikovo kislino ali tako imenovana kraška korozija. O nastanku in nato razvoju krasa odločajo tako litološke lastnosti karbonatnih kamnin kot njihova efektivna poroznost in zadostna količina padavin.

Preperevanje karbonatnih kamnin na stenah jamskih rovov je osnovna tema tega dela. Preperevanje je v splošnem odvisno od razkroja kamnine in odnašanja nastalih produktov. Za karbonatne kamnine velja, da je preperevanje razpadno omejeno, to pomeni, da je hitrost preperevanja edino odvisna od hitrosti raztapljanja. Moje raziskave pa kažejo, da je delno omejeno tudi s transportom.

Ugotovila sem namreč, da se vsa karbonatna kamnina ne raztopi že takoj, to pomeni, da s primarnega mesta ni odnesena v ionski obliki, ampak prepereli delci ostanejo na stenah jamskega rova. Nepopolno raztapljanje lahko karbonatno kamnino samo pripravi na mehansko odnašanje njenih preperelih delcev z vodnim tokom. Koliko se karbonatna kamnina raztopi na sekundarnem mestu, oziroma jo odnese kako drugače, še ne vemo. Odneseni karbonatni delci, velikostnega reda melja in gline, se lahko nato akumulirajo v jamskih rovih kot klastični jamski sedimenti.

Ali je nepopolno raztapljanje karbonatnih kamnin pomemben dejavnik ali pa je samo ena od posebnosti pri oblikovanju kraških rovov ne morem opredeliti, ker voda lahko načeto kamnino sproti odnaša. Na stenah jamskih rovov najdemo močno preperel apnenec ali dolomit samo, če je ta zaščiten pred nadaljnjim raztapljanjem in tudi pred mehansko erozijo. Že mineraloške analize jamskih klastičnih sedimentov so dokazale tezo, da se vse karbonatne kamnine ne raztopijo takoj, temveč jih voda odnaša v obliki delcev. Nekateri jamski sedimenti vsebujejo velik delež karbonatnih klastov, o čemer je pisal že Newson, ki izvirajo iz sten jamskih rovov. Karbonati v jamskih klastičnih sedimentih niso prisotni le kot posamezne plasti sige med naplavinami ali pa kot vezivo, to so drobni delci matične karbonatne kamnine, litoklasti, velikostnega reda melja in gline.

Pogosto uporabljena metoda, da se iz jamskih sedimentov že pred resnejšimi analizami z raztapljanjem izloči ves karbonat, je že v osnovi zgrešena. Obide namreč pomembno dejstvo, da se vsa karbonatna kamnina ne raztopi vedno do konca že na stenah jamskih rovov.

Način, kako je karbonatna kamnina na krasu odnesena s primarnega mesta, zavisi predvsem od njene kemične in mineralne sestave ter kemičnih in hidro-mehanskih lastnosti vode, ki je na krasu glavno naravno topilo, erozivno in transportno sredstvo. Kamnina je lahko odnesena s primarnega mesta v obliki ionov ali mehanskih delcev, to je s kemično ali mehansko erozijo; lahko pa tudi s prepletanjem obeh. Na razmerje med prvo in drugo vrsto vplivata vodni tok z vsemi svojimi značilnostmi ter sestava in mehanske lastnosti kamnine. V raztapljanje se pa največkrat vmeša še biogena korozija.

Izbor vzorčnih jam sem prilagodila cilju, da ugotovim ali prihaja do enakega načina preperevanja v karbonatnih kamninah, ki so si različne po sestavi, strukturi in starosti. Na osnovi obravnavanih primerov sem skušala razložiti, kje in zakaj se nepopolno raztapljanje pojavlja in to glede na lego v jami, na prisotno vlago, na stik s sedimentom, in tip kamnine.

Obdelala sem dele jamskih rovov in vzorce iz Pečine v Borštu, Martinske jame, Krempljaka, Jame II na Prevali ter posamezne vzorce iz Turkove jame, Remergrunda II in Spodmola na Ždroclah. Preperele kamnine in klastične naplavine pa sem preučevala še iz Velike ledene jame v Paradani, Črnelskega brezna, jame Čehi II in Renejevega brezna.

Položaj preučevanih jam je različen glede na geografsko lego, tip krasa, speleogenezo in apnence ter dolomite, ki so različne starosti in geneze. Apnenci in dolomiti so triasni do paleocenski. Največ obravnavanih primerov je iz jam v krednih apnencih, v katerih je v Sloveniji tudi največ jam (Gospodarič 1986).

Načrte jam, merske podatke ter lege jam sem povzela po Jamskem katastru JZS in IZRK ZRC SAZU, dele posameznih jam pa smo za namen raziskav ponovno izmerili.

Iz vsake izbrane jame poleg njenih speleomorfoloških značilnosti in osnovne geologije, podajam pregled ostankov nepopolnega raztapljanja karbonatnih kamnin, ki sem jih zabeležila pri terenskem delu ter rezultate analiz vzorcev iz teh jam.

Proces raztapljanja se je ustavil, preden se je kamnina popolnoma raztopila. Ostanek raztapljanja v obravnavanih primerih tako niso netopne primesi, ki jih vsebujejo apnenci in dolomiti, ampak močno preperela matična kamnina.

Z izrazom nepopolno raztapljanje tako opredeljujem pojav, ko se karbonatna kamnina ne raztopi popolnoma, ampak ostane na stenah rovov močno preperel del matične kamnine, zelo porozen in razbarvan ter izgleda kot kreda ali karbonatni melj.

Med terenskimi raziskavami sem spoznala, da so tanjše preperele cone matične kamnine na stenah jamskih rovov pogost pojav, se odraža kot hrapavost skalne površine. Debelejše cone preperele matične kamnine so redkejše, zlasti na večjih površinah.

Preperele cone so rezultat nepopolnega raztapljanja karbonatne kamnine. Že na pogled so najbolj preperele stene rovov:

- ki jih zamaka prenikajoča voda,
- ki so v stiku z naplavinami,
- ki so izpostavljene kondenzni koroziji.

Najpomembnejši dejavnik, ki oblikuje preperele cone kamnin, je raztapljanje. Nemoteno se lahko odvija, če imamo na razpolago stalen vodni tok, ki dovaja agresivno vodo in odnaša ione raztopljene kamnine.

Med preperevanjem se kamnina najprej rahlo razbarva, z nadaljevanjem preperevanja se razbarvanost stopnjuje, kar vodi do popolne razbarvanosti.
Iz analiz prerezov, zbruskov in obrusov je tudi razvidno, da ne gre za izločanje sekundarnih mineralov na površini raztapljajoče se karbonatne kamnine, ampak za povečanje poroznosti.
Mineralna sestava svežega in preperelega dela karbonatne kamnine se ne razlikuje bistveno, netopnega ostanka je včasih več v preperelem delu, drugič v svežem delu. V preperelem delu so, z nekaj izjemami, glavni kalcitovi in dolomitovi odboji višji in s preperevanjem se dolomitu zniža stopnja urejenosti kristalne rešetke.
Iz rezultatov kemičnih analiz je razvidno, da se v prepereli coni karbonatne kamnine količina Mg, Sr, Au in U (ostalih elementov v posameznih primerih) dosledno zmanjša. Torej se med preperevanjem izgubljajo.
V preperelem delu je organskega ogljika enkrat več, drugič manj, tako da svežim delom karbonatne kamnine barve očitno ne daje.
Mikroorganizmi so prisotni v preperelem apnencu, ne poznamo pa še njihove vloge ali raztapljanje pospešujejo ali celo pogojujejo.
S selektivnim raztapljanjem posameznih delov postaja kompaktna karbonatna kamnina vse bolj porozna in to ne samo ob razpokah, ampak tudi ob različnih strukturah, kar povzroča mozaično poroznost.
Poroznost v apnencih se v danih primerih povečuje, saj se raztapljajo zrna kalcita, ki so manj odporna na raztapljanje. Raztopijo se zrna, ki so manjša in tista, ki vsebujejo večje število napak na kristalnih ploskvah. Nestabilna so tudi zrna, katerih notranja struktura je manj urejena zaradi prisotnosti Mg ionov v njihovi kristalni mreži. Mg ioni so zaradi manjšega ionskega potenciala (manjši radij) bolj mobilni in med raztapljanjem najprej zapustijo svoja mesta v kristalni mreži, s tem pa še oslabijo notranjo strukturo in povečajo nagnjenost do raztapljanja.
Debele preperele cone v tu opisanih primerih niso v stiku z večjo količino vode, niti s stalnim vodnim tokom. Značilno je, da debelejše plasti preperele kamnine najdemo največkrat na stenah, ki so bile v preteklosti, ali pa so še sedaj v stiku z drobnozrnatimi naplavinami. Z mineraloškimi raziskavami klastičnih alohtonih naplavin pa sem ugotovila, da le te s preperelo kamnino kemično ne reagirajo, prispevajo pa vlago, potrebno za raztapljanje. Ne vemo pa, ali so naplavljeni sedimenti morda vsebovali minerale, ki bi kemično reagirali s kamnino v steni rova in jih zato sedaj ni več. Vendar mineralna sestava preperele cone in naplavine na stiku med njima na to ne kaže.
Debelejše plasti preperele kamnine lahko nastanejo tudi v primeru, ko prenikajoča voda mezi po steni rova in kamnino mozaično raztaplja. V obeh primerih, pod naplavino in kadar voda mezi po steni, vlečejo v globino vodo kapilarne sile po povezanih porah in razpokah. Enako se dogaja, kadar imamo opravka s kondenzno vlago. Pretok vode v vseh teh primerih ni velik, v resnici gre bolj za vlago. Ta vlaga pa je sposobna raztapljati. Zato se mi je zdel izraz korozivna vlaga, ki ga uporabljata Davis & Mosch (1988) pri opisovanju natapljanja (jedkanja) površine glinastih prodnikov v Colorado Cave s korozivno vlago zelo primeren. Korozivna vlaga je v njunih primerih kondenzna ali vadozna

(mezeča voda).
Obe vrsti vlage sta pogojeni s klimatskimi dejavniki v jami in na površju. V primerih, ki sem jih podrobneje obdelovala, kondenzne vlage in tudi pogojev za njen nastanek nisem zaznala (debele cone preperele kamnine so največkrat v zatišnih delih jam). Vlažnost preperelih sten se je med letom močno spreminjala. Včasih so bile stene popolnoma mokre (izmerila sem do 39.7 % vode v porah), naslednjič pa so bile popolnoma suhe (ob vrtanju se je prašilo iz stene). Nihanje vlage je čez leto očitno, tako v povezavi s padavinami kot s hitrostjo prenikanja po steni navzdol. Prodiranje vlage v prepereli del stene je zelo hitro (preizkus navlaženja). Zaustavi se samo ob večjih kalcitnih žilah, nekaj časa pa potrebuje tudi za prehod čez odprte in delno zaglinjene (velikost delcev) razpoke. Nastanek mozaične poroznosti (spužvaste kamninske strukture) skušam razložiti s podobnim modelom, kot ga je za nastajanje poroznosti v rendzini na apnencu uporabil Trudgill (1985). Nihanje vrednosti pH sem zasledila med meritvami v vlažni kamnini. Vrednosti pH, izmerjene v vlažni kamnini, so bile v večini primerov nad 8. To pomeni, da se kamnina v tistem trenutku ni več raztapljala, ampak je bila voda v porah nasičena. V primeru, da ostane nasičena voda v porah, jo naslednji pritok vode ali vlage (po padavinah zaradi povečanega hidrostatičnega tlaka) iztisne iz por.
Nekaj podobnega se dogaja tudi v prenikajočih vodnih curkih (Kogovšek, 1986) med naraščanjem in upadanjem pretoka v vodnem valu. Pri naraščanju pretoka karbonatna trdota močno naraste, saj dotekajoča voda najprej iz razpok in por iztisne zastalo nasičeno vodo. Nasičeno vodo v porah zamenja agresivna voda, ki takoj začne reagirati s kamnino in se po določenem času spet nasiti.
Iz opazovanj sklepam, da v primerih, ko se stena posuši, prodira nova vlaga v kamnino še hitreje, ker so pore prazne. Nadalje predvidevam, da se hitro odvija tudi raztapljanje in vodi v porah se spet zniža agresivnost, raztopina se nasiti in pH naraste. Ob vsakem ponovnem vodnem valu voda uporabi za pretakanje pore nastale ob prejšnjem dogodku. Morda jih še malo razširi, glavna fronta raztapljanja pa se z vsakim novim vodnim valom pomakne globlje v kamnino. Agresivna voda se tako ob stiku s karbonatnimi delci v poroznem skeletu zelo hitro nasiti, ostane je samo del, ki je še sposoben reagirati z kamnino. Nepopolno raztapljanje apnenca se najverjetneje dogaja v vadozni coni. V freatični coni (stalno zaliti) bi vodni tok zrna odnesel s stene - če ne prej, ko bi se umikal, ali pa bi se melj s stene kar razpustil. Vodni tok bi tudi sproti odnašal ione in raztapljanje bi šlo v globino počasi, ker bi delovalo frontalno. Obstaja pa možnost, da se nepopolno raztapljanje dogaja, vendar zaradi sprotnega odnašanja delcev tega ne opazimo.
Mehanizem nastanka poroznega skeleta skušam razložiti z naslednjo hipotezo. Pore in povezave med njimi (manjši kanali) se večajo in voda se skoznje pretaka hitro, z njihovimi stenami niti ne reagira (ne raztaplja več), ampak raztaplja v »čelu«, ki je že globlje v kamnini. Predvideni mehanizem se ciklično ponavlja in kamnina je vedno bolj porozna in preperela v globino. To je tudi možen odgovor na vprašanje, zakaj se kamnina ne raztopi do konca.
Raztapljanje je v tu opisanih primerih izrazito selektivno. Raztopijo se manjša zrna in stiki med zrni. Selektivna korozija pa ne odvija samo na površini kamnine, kot je običajno,

ampak prodira tudi v kamnino samo. Večje kristale ter posamezna območja v mikritu pa pušča neraztopljene. Ti neraztopljeni ostanki gradijo porozni kamninski skelet. Pore se med raztapljanjem večajo in so vse bolj medsebojno povezane, tako da agresivna voda prodira vse lažje in vse dlje v notranjost kamnine.
Kamninski skelet postaja vedno bolj porozen, prodirajoča agresivna raztopina pa pušča za sabo vedno bolj preperele ostanke matične kamnine. Kamninski skelet se ne raztopi, bodisi zato, ker se proces raztapljanja odvija globlje v kamnini, bodisi, ker je bil ustavljen (ni dotoka nove agresivne vode ali pa se raztopina prenasiti). S časom preperijo tudi bolj odporni deli karbonatne kamnine. Kalcitne žile in odlomki školjk, ki štrlijo iz površine preperele kamnine postanejo porozni in mehki.
Z nadaljnjim raztapljanjem postaja kamnina poroznejša in krhkejša, dokler se njena struktura popolnoma ne sesuje. Napredujoče raztapljanje namreč vse bolj ločuje posamezne delce. Nastaneta karbonatni melj in glina (odvisno od strukture kamnine: sparit in mikrosparit – melj, mikrit – glina), ki pa ostajata še vedno na steni rova. Kamnina obenem postane tudi manj odporna na mehanske dejavnike, na primer proti mehanski eroziji vode. Že najmanjši vodni tok lahko prenaša z raztapljanjem osamele delce po steni navzdol in oblikuje kapnikom podobne oblike iz melja (Šušteršič & Mišič 1996, Gabrovšek 2000a).
Nastajanje karbonatnih litoklastov in njihovo izpadanje iz jamskih sten je pogojeno s korozijsko in abrazijsko sposobnostjo vodnega toka ter strukturo kamnine. Učinkovitost raztapljanja kamnine je odvisna od hitrosti reakcije na površini kamnine, prenosa reaktantov in proizvodov raztapljanja, konverzije CO_2 z vodo: $CO_2 + H_2O = H^+ + HCO_3^-$ (Dreybrodt 1988) ter litoloških lastnosti kamnine.
Mehansko delovanje vodnega toka na kamnino delimo na delovanje sile vode in na dolbenje z materialom, ki ga voda prenaša. V primerih, ki jih opisujem, ne gre za izbijanje delcev kamnine z lebdečim tovorom, na primer s kremenovimi zrni (Gams 1959). Newson 1971a), ampak za trganje delcev s površine kamnine zaradi adhezije. Zaradi adhezije med vodo in steno (Trudgill 1985) trga hiter, vrtinčast vodni tok s stene manjše delce, ki jih osami korozija.
Kako karbonatno kamnino odnese z mesta njenega nastanka je, odvisno od njenih lastnosti, kot tudi od lastnosti vode, ki je v stiku z njo. Voda lahko erodira kamnino mehansko in kemično. Razmerje med obema vrstama erozije je odvisno od mnogih lokalnih dejavnikov. Kadar je na primer kamnina tektonsko porušena, voda drobir lažje topi in ga tudi hitreje mehansko odplakne, kadar pa kamnina tektonsko ni porušena, na raztapljanje močneje vpliva njena mineralna sestava ter struktura.
Preperevanje, v obravnavanih primerih raztapljanje, kamnine se v jamskem rovu lahko ustavi, prepereli del karbonatne kamnine pa ostane na primarnem mestu zato, ker ni v stiku s tekočo vodo, ki bi natopljene delce trgala s stene rova in jih odnašala.
Raztapljanje za seboj ne pušča le debele preperele cone, ampak tudi hrapavo površino stene. Močno izražena hrapava skalna površina je značilna za prekristaljene apnence, dolomitizirane apnence in poznodiagenetske dolomite. V primeru, da hrapava površina pride v stik z vodnim tokom, ta izpostavljene delce spira s stene, jih odnaša in akumulira v jamskih naplavinah. Karbonatni delci se odlagajo kot samostojen sediment ali pa se

mešajo z alohtonimi naplavinami. Naplavina nekarbonatnega izvora se v takih primerih močno obogati s karbonatnimi delci.

Nastajanje avtohtonega karbonatnega melja in gline je seveda odvisno od različnih lokalnih dejavnikov, od primernosti kamnine in s tem načetosti površine stene, do dotoka vode, ki po nalivih spira brezna ali po izjemnih poplavah, ki spirajo stene. Tam, kjer se voda skozi rove pretaka dovolj hitro, z raztapljanjem načete dele kamnine odtrga od stene. Pri bolj preperelih kamninah pa je zadosten že šibek vodni tok, na primer samo mezenje po prepereli steni. Naj poudarim, da to ni abrazija s kremenovimi prodniki v smislu Gamsa (1959) ali Newsona (1971a), ampak za mehansko erozijo s tekočo vodo v vadozni ali freatični coni.

Voda, ki hitro teče mimo sten jamskih rovov, z izpostavljeno kamnino minimalno kemično reagira, reagira samo njen laminarno adhezivno vezani film. Hitro tekoča voda s svojo silo razbije laminarno plast in zato lahko tudi hitreje raztaplja ali pa trga iz površine stene izpostavljena zrna. Kako so zrna izpostavljena in koliko jih je, je odvisno od karbonatne kamnine, ki s svojo strukturo pogojuje selektivno raztapljanje in s tem nastanek bolj ali manj hrapave površine.

Iz okolja štrleča zrna, katerih vezi so oslabljene z raztapljanjem, so izpostavljena in primerna, da jih voda odplakne s stene. Sile tekoče vode (Fw), ki delujejo na izpostavljena zrna, morajo biti večje od sil (Fg), ki vežejo mineralno zrno v kamnino. Fw je odvisna od hitrosti vode in površine zrna na katero deluje; Fg pa je sorazmerna z adhezijo zrna, ki je odvisna od velikosti in površine stika zrna z osnovo. Sledi, da se mineralna zrna, katerih kontakti so bili načeti z raztapljanjem ali izpostavljeni s selektivnim raztapljanjem lažje odtrgajo, kot pa zrna iz sveže, nepreperele kamnine.

Za vsak delec obstaja kritična hitrost, ko je še zmožen gibanja, to je kritična hitrost erozije (Briggs 1977). V tu opisanih primerih mora bi hitrost vode večja od kritične hitrosti, da delce lahko odtrga s stene. Ko vodi pade hitrost in transportna moč, se karbonatni klasti usedajo kot samostojni klastični sedimenti ali pa pomešani z alohtonimi naplavinami.

Na razmerje med avtohtono kemijsko in mehansko erozijo karbonatne kamnine v jamskih rovih poleg hitrosti tekoče vode odločilno vpliva tudi njena struktura. Struktura vpliva na začetek in potek raztapljanja. Iz poznodiagenetskega dolomita med preperevanjem nastaja dolomitni melj (Zogović 1966). Površina stene rova izoblikovanega v dolomitu je hrapava in iz nje štrlijo velika zrna, ki so primerna za nastanek avtohtonih karbonatnih meljev. Iz mikritnih apnencev nastaja karbonatna glina, katere zrna pa so tako majhna, da se v večini primerov zelo hitro raztopijo. Raztapljanje sledi notranjim strukturam v kamnini, za sabo v posebnih pogojih pušča močno porozno in preperelo kamnino, ki jo zadosti hitro tekoča voda tudi mehansko erodira. Bolj ko je kamnina kemično preperela, lažje voda trga njene delce.

Razmerje med kemijsko in mehansko erozijo ima vpliv predvsem na genezo jamskih rovov, skozi katere se voda pretaka dovolj hitro, da lahko trga z selektivno korozijo izpostavljena zrna. Kjer je korozija dovolj močna, da deluje ploskovno, steno tako zgladi, da ni hrapava. Takrat voda ne more spirati delcev, ker ji ni, ampak se skozi rove samo pretaka ali pa izbija iz stene delce s svojim tovorom.

Največji problem je ovrednotiti razmerje med korozijo in transportno erozijo pri oblikovanju jamskih rovov. Z drugimi besedami, do katere stopnje deluje kemijska razgradnja kamnine, da potem lahko nastopi mehansko odplavljanje razrahljanih delcev. Iz terenski opazovanj se je pokazalo, da razmerje zavisi od različnih pogojev, od položaja v rovu, sestave in strukture kamnine, stika z jamskimi naplavinami, prekritostjo s sigo, načinom dotoka vode, fizikalnimi in kemičnimi lastnostmi vode in načinom ter časa stika z vodo (Zupan Hajna 2002). Vsekakor mora biti glede na stopnjo preperelosti karbonatne kamnine hitrost vode zadosti velika, da delce kamnine odtrga s površine jamskih sten.
Voda poleg zrn kamnine trga z jamskih sten tudi porušene dele kamnine iz tektonskih con in odnaša izpadle kose iz sten, ki so predhodno pretrte s tektonskimi in razbremenitvenimi razpokami. Vodni tok razrahljane dele kamnin odnaša, jih preoblikuje in odlaga, ko vodi transportna moč pade. Zato se lahko vzdolž vodnega toka v jamskih rovov delež karbonatnih prodnikov celo poviša (Kranjc 1989).
Mislim, da je v speleogenezi pojav nepopolnega raztapljanja karbonatnih kamnin lahko pomemben dejavnik pri nastajanju prvih kanalov, ker se poroznost karbonatne kamnine povečuje s selektivnim raztapljanjem kalcita in dolomita (Zupan Hajna 2002). Med preperevanjem se pore v apnencu in dolomitu večajo, vzpostavlja se povezava med njimi in s tem povečuje efektivna poroznost. Večanje por in širjenje povezav med njimi vodi v nastanek prvih kanalov. Za nastanek por in povezav med njimi pa v obravnavanih primerih zadostuje raztapljanje z ogljikovo kislino.
Nepopolno raztapljanje pri sprotnem odnašanju preperele kamnine pospešuje tudi rast rovov. Vezi med zrni se raztopijo in voda mehansko odnaša (erodira) preostala zrna. S tem je večanje rova hitrejše in intenzivnejše. Ovira pri rasti rovov se lahko pojavi samo dokler so rovi še zelo majhni in jih nastal karbonatni melj ali glina zamašita. Hitro povečanje dimenzij rova je pogojeno z občasnim ali izjemnim spiranjem debelejših preperelih con apnenca ali dolomita po ekstremnih nalivih ali poplavah.
Da so karbonatni delčki v klastičnih sedimentih res avtohtoni litoklasti nakazuje tudi mineralna sestava recentne naplavine v Renejevem breznu. V naplavini je v glavnem dolomit, ki se praviloma ne izloča kot jamski kemični sediment, dovolj ga je pa preperelega v stenah brezen pred dvorano z akumulirano naplavino. Hkrati s pojavom dolomita v jamski naplavini ovržem tudi možnost, da so karbonatni melji ledeniškega nastanka, ker na površju nad jamo ni dolomita.
Povečanega deleža karbonatnih klastov v jamskih sedimentih ni opaziti v primeru, če jih vodni tok prenaša skozi velike kanale s prosto gladino (Zupan Hajna 1998) in velike zalite kanale, kjer je pretakanje vode počasnejše. Pri transportu sedimentov skozi rove manjših dimenzij in v manjših zalitih rovih, kjer je vodni tok hitrejši in ta spira jamske stene, se delež karbonatov v jamskih naplavinah močno poveča. Največji pa je delež karbonatnih klastov, ko voda v slapovih ali curkih spira stene rovov (Mihevc & Zupan 1988). Najbolj je to izraženo v stopnjastih breznih, kjer voda po nalivih teče z veliko hitrostjo spira jamske stene.
Avtohtone karbonatne klastične sedimente v tu opisanih primerih tako sestavljajo delci matične kamnine, to je litoklasti, ki izvirajo iz preperelih sten jamskih rovov, od koder

jih je voda odtrgala. V nadaljevanju jih voda odloži v zatišnih delih. Lahko same, lahko pa pomešane z materialom, ki ga voda prinaša v jamo iz nekraškega zaledja.

Karbonatni klasti se pojavljajo kot sestavni del klastičnih sedimentov predvsem v dnu aktivnih brezen, kjer stene spirajo vodni hitri vodni tokovi in v občasno zalitih jamskih rovih, kjer se voda pretaka dovolj hitro. Najmočnejše pa je mehansko spiranje sten po nalivih in času taljenja snega, ko se hitrost vode v breznih poveča.

S poznavanjem sestave preperelih con karbonatnih kamnin in dogajanja v kamnini med raztapljanjem ter načinom nastajanja avtohtonih karbonatnih klastičnih sedimentov opozarjam na še eno od številnih posebnosti krasa, na katero moramo biti pozorni pri razlaganju speleogenetskih procesov in oblikovanja kraških rovov.

IZVLEČEK

Raziskave predstavljene v tem delu posegajo v malo raziskano področje nepopolnega raztapljanja apnencev in dolomitov. Zato sem morala najprej izbrati primerne raziskovalne metode in s kvantitativnimi analizami čimbolj spoznati procese preperevanja karbonatnih kamnin v jamskem okolju.

Presenetil me je velik delež karbonatnih klastov v jamskih naplavinah, pa tudi pojavljanje debelih, mehkih con neznanega minerala na stenah jamskih rovov.

S svojim delom sem s pomočjo speleoloških, geoloških in kemičnih raziskovalnih metod skušala spoznati sestavo bele meljaste ali glinaste snovi na stenah rovov.

Po ugotovitvi, da gre za »topne« ostanke raztapljanja apnencev in dolomitov, sem skušala spoznati, kaj se dogaja v karbonatnih kamninah med raztapljanjem in zakaj se ne raztopijo do konca.

Preperela cona karbonatne kamnine je po mineralni in kemični sestavi skoraj enaka kot je sestava matične kamnine, močno pa ji naraste poroznost.

Topni ostanek nepopolnega raztapljanja apnenca je v nasprotju s teorijami o nastanku krasa, ki so namreč sprejele mnenje, da se apnenec, če nanj deluje agresivna raztopina, raztopi. V primerih klasičnega kraškega raztapljanja po končanem raztapljanju karbonatne kamnine ostane samo njen netopni ostanek.

Iz rezultatov opravljenih analiz sem skušala določiti še razmerje med avtohtono kemijsko in mehansko erozijo pri nastajanju jamskih rovov, želeč spoznati, do katere stopnje se karbonatna kamnina raztopi, da je pripravljena na mehansko erozijo, v smislu mehanskega spiranja hrapavih sten s tekočo vodo.

S sten jamskih rovov, katerih delci so bili izpostavljeni selektivni koroziji, zadosti hitro tekoča voda lahko trga delce in jih odnaša naprej po jami. Ko vodi transportna moč pade, se delci akumulirajo kot drobnozrnata avtohtona karbonatna usedlina.

Na stenah rovov se nahajajo debele cone preperelega apnenca ali dolomita, kadar se proces raztapljanja iz kakršnega koli vzroka ustavi. To je v primerih, kadar ni več dotoka agresivne vode in če nastajajoče karbonatne preperine tekoča voda sproti ne odnaša.

ABSTRACT

The studies, reported in this book, investigated the little explored subject of incomplete solution of limestones and dolomites. I first had to choose suitable research methods and, qualitative analyses to understand the process of carbonate rock weathering in the cave environment.

I was surprised by the presence of significant quantities of carbonate clasts in cave sediments and also by the occurrence of thick, soft zones of an unknown mineral on the walls of cave passages.

Aided by speleological, geological and chemical methods I endeavoured to establish the composition of this white, silt- or clay-like substance on the cave walls.

When it became clear that it was a »soluble« residue of limestone and dolomite solution, I tried to find out what happens in carbonate rocks during the dissolution process and why the rocks do not dissolve completely.

The weathered zone of a carbonate rock is almost identical to the parent rock in its mineral and chemical composition, yet it is much more porous.

The presence of a soluble residue of incomplete limestone solution is in disagreement with classical theories of karst origin, which predicts that limestone, when affected by an aggressive solution, will dissolve completely. According to these theories, only insoluble residues will remain after carbonate rock has been dissolved.

From the results of analyses I tried to determine the relationship between autochthonous chemical and mechanical erosion occurring during the formation of cave passages, seeking to understand to what extent the carbonate rock dissolves in preparation for mechanical erosion; i.e. the mechanical rinsing of walls by flowing water.

Water that is flowing fast enough may tear off the particles produced by selective corrosion of the cave walls. When its transporting power decreases, particles accumulate in the form of a fine-grained autochthonous carbonate deposit.

On the cave walls thick zones of weathered limestone or dolomite remain when the solution process ends for whatever reason. This usually happens when there is no more inflow of aggressive water or when flowing water no longer transports the carbonate weathering products.