Weathering of Cave Walls in Martinska Jama, SW Slovenia

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Abstract

Martinska Jama is a cave situated in karst area of Matarsko Podolje in the south-west part of Slovenia. The cave was formed in transition between Lower and Upper Cretaceous carbonate beds. In some parts of the cave limestone walls are extremely weathered specially in side passage Boeganov Rov. Limestone beds are weathered from few millimetres to some centimetres in depth, depend on freshness of breakdowns and presence of fissures. The weathered zone of carbonate rock is almost identical to parent rock in its mineral and chemical composition yet it is much more porous. It is very unusual that the weathered remain is not insoluble rest but purified calcite. Weathered zone of limestone bedrock has “spongy” like texture. The main reason of limestone weathering in this part of the cave is probably corrosive moisture which has it origin in percolation water from the surface above the cave.

Introduction

Weathering of the cave walls is characteristic in the caves formed in different karst type, different geographical position and in carbonate rocks of different origin and age. In Slovenia weathered zones of carbonate rocks were found in the caves of Alpine and Dinaric Karst areas, at different altitudes and in caves which have been formed in limestones and dolomites from Upper Triassic to Paleocene.

In article the weathering of limestone bedrock in Martinska Jama cave is represent. Cave Martinska Jama is located in karst area of Matarsko Podolje in SW Slovenia (Fig.1) at 565 m above sea level (y = 5425 555, x = 5045 305).

Fig. 1: Map of Slovenia showing the location of cave Martinska Jama.

Cave was formed in Cretaceous limestone – $K_{1,2}$ (ŠIKIĆ et al., 1972). Limestone beds dip toward NE with dip angle 20 – 30^0. The main tectonic structures in the area are in “Dinaric” NW-SE direction, well expressed are also N - S and in E -W directions.

Speleomorphology of the Cave

Cave lies on N slope of Veliki Mavrovec hill at foothills of Slavnik mountain. Entrance to the cave is open on SE slope of small collapse doline. The length of cave passages is 1004 m and the depth is 120 m. From the collapse doline cave is elongated in two directions (Fig. 2). Main part of the cave follows the geological structural elements, specially the main tectonic directions. First part of the cave follows N-S direction but the main part of the cave lies in NW-SE direction, only the last part of the cave follows the E-W direction. Freatic forms of cave channels are removed by breakdowns and weathering processes. Weathering of limestone is significant specially for small side passage Boeganov Rov, in smaller quantity was noticed was also in side passage Stranski Rov.

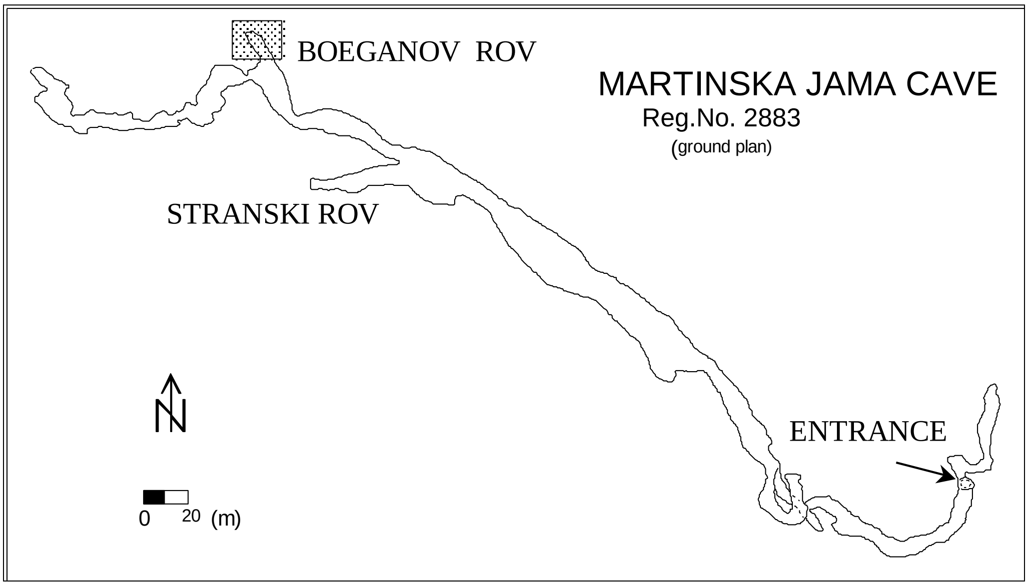

Fig. 2: Ground plan of Martinska Jama cave with marked passage Boeganov Rov.

Passage Boeganov Rov

Boeganov rov passage (Fig. 3) is interesting because its walls are completely weathered. At firs side it looks like they are covered by moon-milk precipitated from saturated water.

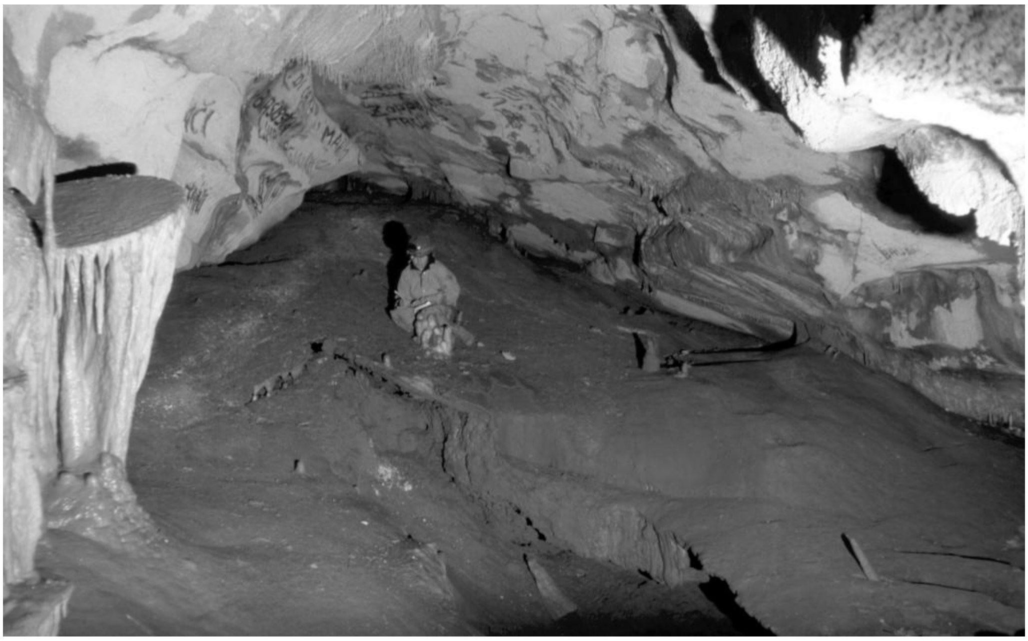

Fig. 3: Weathered walls of cave passage Boeganov Rov.

The passage is risen from the level of the main channel towards NW. Length of the passage is about 25 m. The entrance is almost closed by flowstone, inside the passage the small chamber is formed. The detailed ground plan is on Fig. 4. The walls of the chamber are not covered by flowstone, except of dripping water bound on the stronger fissures or bedding planes.

Temperature is almost constant during whole-year, it varies between 8,7 to 9,0^0C. The air current was not perceived in the passage. In the passage there is no permanent water flow, wetness of the walls depends directly on atmospheric precipitation and intense percolation through fissures.

In Boeganov Rov passage limestone beds dip toward NE with dip angle 20^0 (dip 30/20). For water percolating is significant specially in one distinctive bedding plane which projects lower limestone bed into the cave at the W passage wall. The bedding plane was also tectonised the red clay is presented in it.

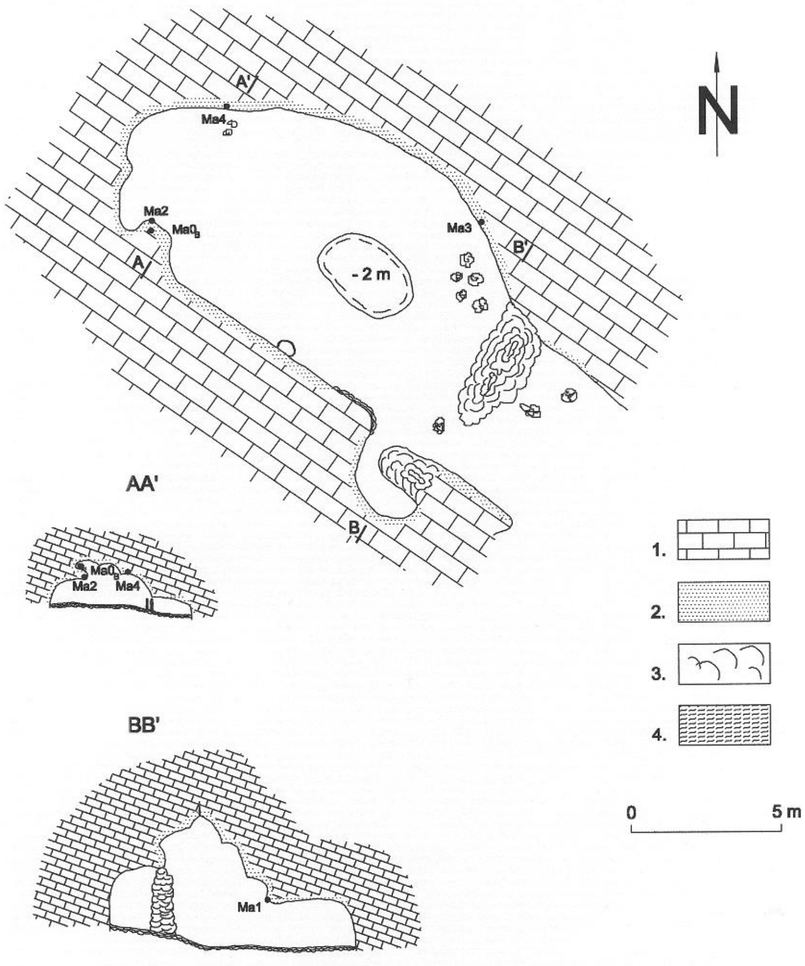

Fig. 4: Detailed ground plan of Boeganov Rov passage with two profiles: AA' and BB'. Legend: 1.- limestone, 2. - weathered zone, 3. - flowstone, 4. - fluvial deposits and marked locations of the samples, Ma0 – Ma4 - samples.

Along and under that particular bedding plane flowstone is precipitated because strong percolating of the water is presented. This water is also source for the wetness of the walls, specially were they are weathered. Porous weathered limestone acts like sponge, it sips the moisture. The moisture is aggressive at first, at each new cycle when new aggressive water reach the cave after rain at the surface. Aggressive moisture penetrates into limestone and at first dissolves contacts between the grains and small grains.

Sandyclay deposits are found on the passage floor and at rocky shelves on cave walls. Deposits have fluvial origin from non-carbonate Eocene flysch rocks. All cave walls are not in the contact with sediments now, but my be they were in the past.

Weathered Walls

Walls and the ceiling of Boeganov Rov passage are wholly weathered. Weathered limestone is white in colour and porous. It pass over to fresh one through some steps. Surface of limestone in the cave is soft and porous, separated grains of limestone are exposed and they create micro-roughness of the wall. Roughness of weathered limestone surface depends on its texture.

Fig. 5: Outstanding of calcite veins was formed by selective corrosion. Weathered limestone is porous and wet.

In some places the beginnings of “boxwork” (PALMER, 1981) is formed with outstanding of calcite veins (Fig. 5) and in the other places small rounded holes (Fig. 6) are presented. Surface of the limestone is weathered. Weathering penetrates into carbonate rock along open bedding planes, fissures, irregularities etc.. The weathered zone of limestone is from few millimetres to some centimetres thick. Thickness varies regarding to fresh breaks on the walls and to open fissures.

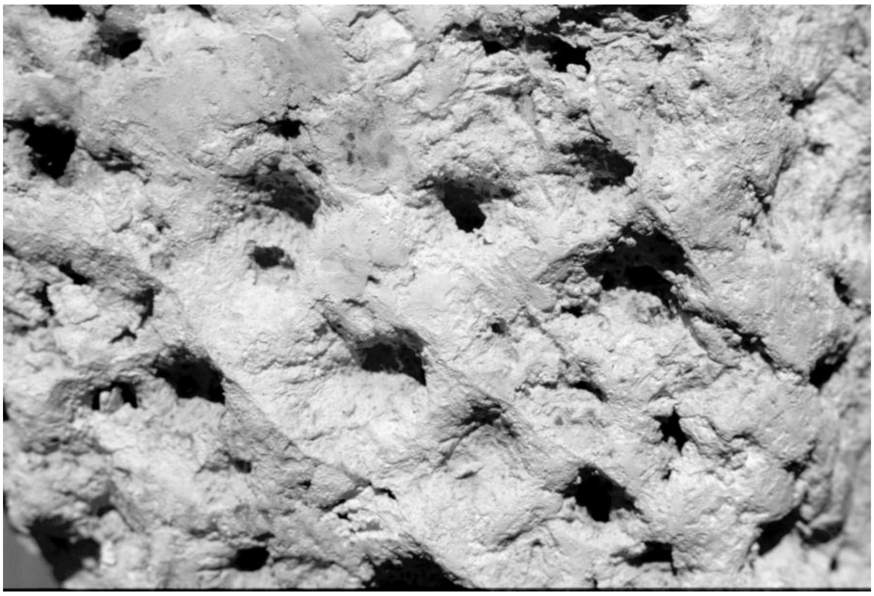

Fig. 6: Rounded holes on the weathered cave wall, diameters of lagers holes are about 1 cm.

Measurement of weathered limestone thickness was done by drilling (Fig. 7). The thicker measured weathered zone was 10 cm deep. Weathered limestone is porous and soft when is wet. When is wet is grey in colour, when is dry is white.

Percolating water also flows through open pores of weathered limestone, in the case when it becomes saturated calcite cement may be precipitated. In places where weathered limestone is cemented with fresh white or grey coloured cement, also sodastraw stalactites are formed. They are characteristic in places with stronger percolation of water through the open pores. Sodastrows are not bound on open fissures but they are dispersed on wider area of cave ceiling due to big porosity of weathered limestone.

Fig. 7: Measurement of weathered zone thickness was done by drilling.

Methods and Results

Samples were analysed by chemical, mineralogical and sedimentological methods.

Optically the thin sections, cross-sections, and SEM analyses of the samples were done. Chemical composition was defined by ACTALEB – Activation Laboratories LTD (Canada) with Total identification package of analyses (code 4E). Complexometry of samples were done on our Institute. EDS analyse under SEM was realised on J. Stefan Institute, Ljubljana. Mineralogical composition was determined by X-ray powder diffraction method on Department of Geology at Faculty of Natural Sciences and Engineering in Ljubljana. For the analyses samples were divided into: a. fresh part, b. discoloured part and c. wholly weathered part (Fig. 8).

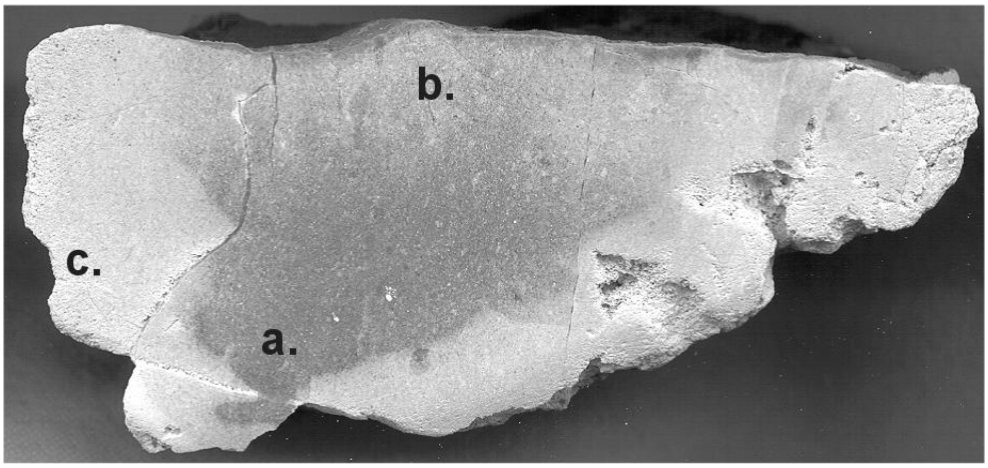

Fig. 8: Degrees of weathering in the sample Ma2. Legend: a.- fresh limestone, b.- discoloured limestone, c.- wholly weathered limestone.

Transition from fresh to weathered carbonate rock is seen in cross-sections of the samples which were scanned by computer scanner and also under SEM. Weathering is forced along the open fissures and interfered with calcite veins. The penetrating of weathering, that means dissolution, is not frontal but very much selective. Aggressive solution at first dissolves the contacts between the grains, small grains, defect grains etc..

Results of chemical analyses of sample Ma1 are presented in Fig. 9. Negative values indicate values under the detection limit.

	unit	Ma1a	Ma1c		unit	Ma1a	Ma1c
SiO_2	%	0,15	0,08	**Au**	ppb	92	24
Al_2O_3	%	0,06	0,04	**As**	ppm	-2	-2
Fe_2O_3	%	0,05	0,05	**Br**	ppm	1	1
MnO	%	0,002	0,002	**Co**	ppm	-1	-1
MgO	%	0,48	0,30	**Cr**	ppm	-2	3
CaO	%	55,76	55,93	**Cs**	ppm	-0,5	-0,5
Na_2O	%	0,20	0,15	**Hf**	ppm	-0,5	-0,5
K_2O	%	-0,01	0,10	**Ir**	ppb	-5	-5
TiO_2	%	-0,001	-0,001	**Mo**	ppm	-5	-5
P_2O_5	%	0,02	0,02	**Rb**	ppm	-20	-20
LOI	%	43,09	42,90	**Sb**	ppm	0,8	0,4
TOTAL	%	99,81	99,56	**Sc**	ppm	-0,1	0,3
Ba	ppm	2	2	**Se**	ppm	-3	-3
Sr	ppm	229	176	**Ta**	ppm	-1	-1
Y	ppm	2	3	**Th**	ppm	-0,5	-0,5
Zr	ppm	20	17	**U**	ppm	1,4	0,7
Be	ppm	-1	-1	**W**	ppm	-3	-3
V	ppm	13	10	**La**	ppm	0,3	1,1
Ag	ppm	0,4	0,6	**Ce**	ppm	-3	-3
Cd	ppm	-0,3	-0,3	**Nd**	ppm	-5	-5
Cu	ppm	2	2	**Sm**	ppm	-0,1	0,3
Ni	ppm	-1	-1	**Eu**	ppm	-0,1	-0,1
Pb	ppm	-3	-3	**Tb**	ppm	-0,5	-0,5
Zn	ppm	-1	-1	**Yb**	ppm	-0,1	-0,1
Bi	ppm	-2	-2	**Lu**	ppm	-0,5	-0,5

Fig. 9: Chemical composition of fresh and weathered part of the limestone sample Ma1. Ma1a - fresh part, Ma1c – weathered part.

In the weathered part of limestone the values of MgO, SiO_2, Al_2O_3 and Na_2O are lower, lower are also values of Sr, Zr, V, Au, Sb and U. The values of CaO, K_2O, Y, Ag, Cr, Sc, La and Sm are higher. In the fresh part of limestone sample Ma1 oxides present 99,81 % in weathered part they present 99,56 %.

Complexometry was done from samples Ma1, Ma2 and Ma3. Results are presented on Fig. 10.

Percent of CaO is higher in weathered parts than in fresh parts of limestone samples. It is also seen that content of MgO is lower in weathered part than in fresh part. In two weathered limestone samples the insoluble residue is higher, but in Ma2c there is no insoluble residue at all.

sample	CaO %	MgO %	calcite %	dolomite %	carbonate %	insoluble residue %	CaO/ MgO
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

Fig. 10: Complexometry results of limestone samples, a. - fresh part, c. – weathered part.

Qualitative EDS analyse on SEM was done two times in fresh part and two times in weathered part of limestone sample Ma2. At first out of windows 50 x 50 µm and the second time out of windows 100 x 100 µm. Typical measured spectra are presented on Fig. 11 and Fig. 12. The most characteristic result is that in weathered parts of limestone the amount of MgO is lower than in fresh part and that also the amount of Sr is lower in weathered part.

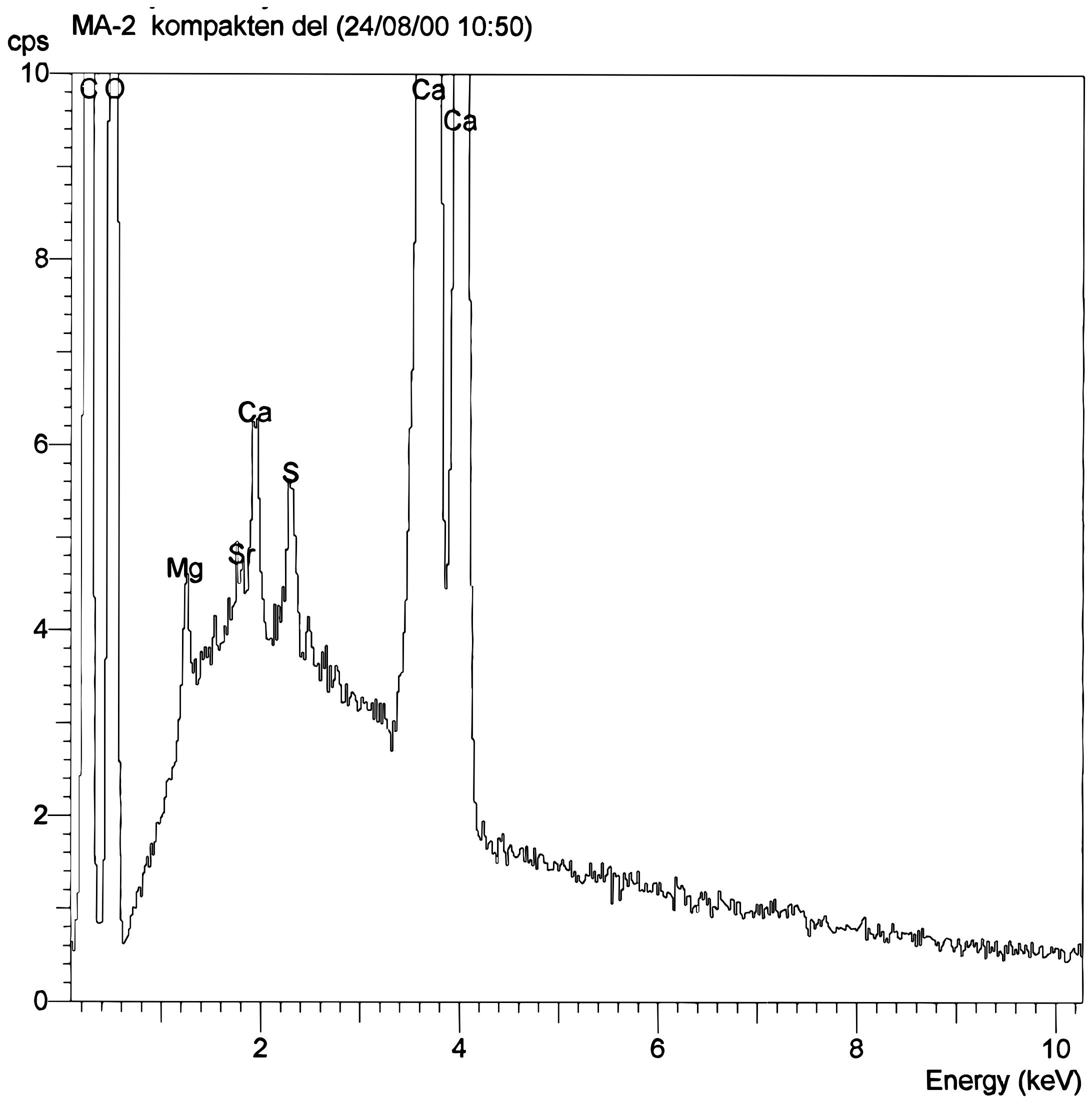

Fig. 11: Qualitative EDS analyse on SEM, measured spectrum of fresh part of limestone sample Ma2. Legend: Ca – calcium, C – carbon, O- oxygen, S – sulphur, Sr – strontium, Mg – magnesium.

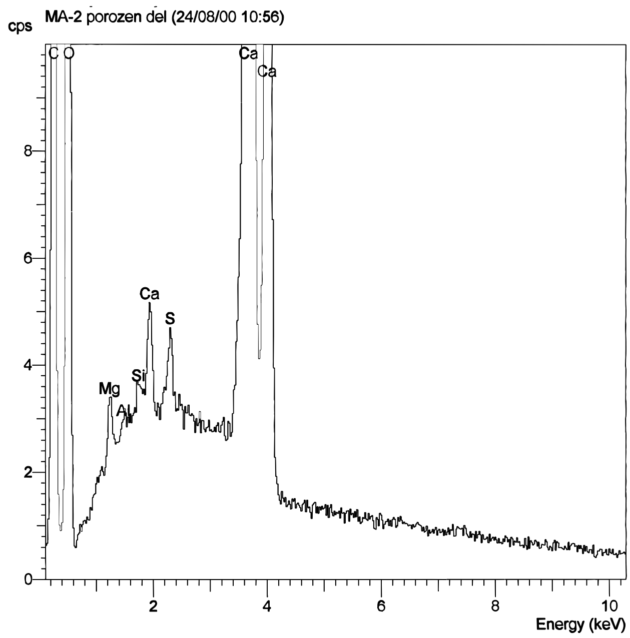

Fig. 12: Qualitative EDS analyse on SEM, measured spectrum of weathered part of limestone sample Ma2. Legend: Ca – calcium, C – carbon, O- oxygen, S – sulphur, Sr – strontium, Mg – magnesium.

Mineral composition of fresh and weathered samples of limestone is seen on Fig. 13. Fresh limestone, sample Ma2a, is composed 97 % of calcite, small amount of clay minerals and quartz. Weathered parts are even cleaner – 98 % of calcite, see Ma1b, Ma1c, Ma2b, Ma2c. But the difference is so small that from results we can't make any conclusions. Mineral composition of sandy deposit from the Boegan passage was also defined. It is composed 70 % of quartz, 15 % of mineral from illite/muscovite group and 15 % of goethite. It is clearly different in mineral composition like weathered limestone, so it can't be insoluble rest of limestone. Deposit has origin in weathered Eocene flysch of Brkini mountain, N of the cave.

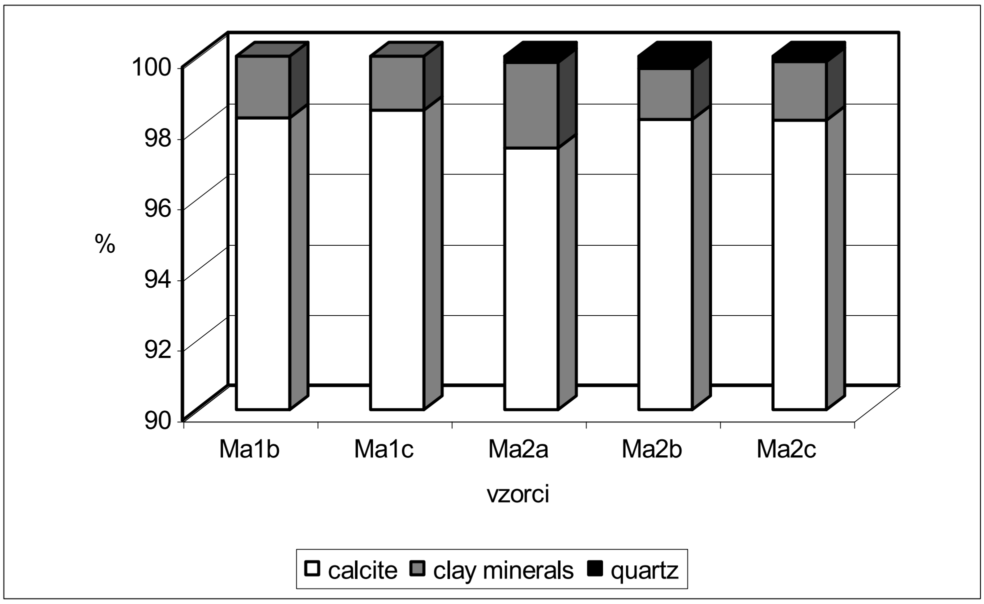

Fig. 13: Comparison between the mineral composition of fresh (a.), discoloured (b.) and wholly weathered (c.) limestone does not indicate any big difference.

Discussion

Weathering of limestone is part of limestone dissolution process, where dissolution is not complete and its rest is not non-soluble residue but very porous purified limestone.

The weathered part of limestone is almost identical to the parent rock in its mineral and chemical composition yet it is much more porous. In limestone different degree of weathering are seen. Weathered zones pass from wholly weathered limestone to fresh one through few steps of weathering. Fresh limestone at first becomes slightly discoloured and after weathering progresses becomes total discoloured (white) and porous. MgO and Sr are leached from calcite structure, so the calcite is purified during the weathering. In this case it is not going on the dissolution of the limestone and than precipitation of cleaner calcite crystals.

Weathered limestone is more and more porous and it has “spongy” like texture. Weathered limestone is wet the water is in it pores. If there is no source of the moisture the weathered wall of the cave becomes dry. The main reason of limestone weathering in this part of the cave is probably corrosive moisture (DAVIS & MOSCH, 1988) which has it origin in percolation water from the surface above the cave. Percolating water is strongly connected to the outside atmospheric precipitation so also the moistening is cyclic. Moisture is aggressive at first and it dissolves the limestone. Dissolution is selective and it stops when moisture becomes saturated or when its dry up. I have no evidence that the fluvial deposits in the passage have had any influence on the limestone weathering although the passage was once filled up by sediments. Probably the sediment was just one more agent to keep moisture on the cave walls.

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